



**Bismuth Oxy-halide ($\text{BiOBr}_m\text{I}_{(1-m)}$) Solid Solutions for the
Photodegradation of Methylene Blue Dye under Solar and
UV-Light Irradiation.**

Student Name: Robert Ouko Gembo

Student Reg No: 18100050

oukogembo@gmail.com, (+267) 75298867

Faculty of Science

Department of Chemical and Forensic Sciences

Botswana International University of Science and Technology

A Dissertation Submitted to the Faculty of Science in Fulfilment of the Requirement for the
Award of the Degree in Master of Science in Chemistry of Botswana International University
of Science and Technology

February 2021

DECLARATION

I, Robert Ouko Gembo declare that this dissertation is an original report of my research work. The work has not been presented and will not be presented to any institution for similar or any other degree award. The experimental work is entirely my work. Due references have been provided on all supporting literature and resources.

Signature:  5/2/2021

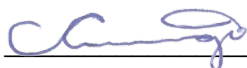
COPYRIGHT

This thesis/dissertation is copyright material protected under the Berne Convention, the Copyright Act of 1999, and other international and national enactments in that behalf on intellectual property. It must not be produced by any means in full or in part, except for short extracts in fair dealing; for researcher private study, critical scholarly review or discourse with an acknowledgment, without the written permission of the office of the Provost, on behalf of both the author and the BIUST.

CERTIFICATION

This dissertation entitled “**Bismuth Oxy-halide ($\text{BiOBr}_m\text{I}_{(1-m)}$) Solid Solutions for the Photodegradation of Methylene Blue Dye under Solar and UV-Light Irradiation**” was prepared by Robert Ouko Gembo and submitted as a fulfillment of the requirement for a degree of Master of Science in Chemistry at Botswana International University of Science and Technology.

Approved by:



(Prof. Cecil King'onde)

Date: 03/02/2021

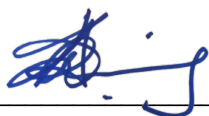
Supervisor

Department of Chemical and Forensic Sciences

Faculty of Science

Botswana International University of Science and Technology

kingonduc@biust.ac.bw (+267) 493 1880



(Prof. Ochieng' Aoyi)

Date: 4/02/2021

Co-supervisor

Department of Chemical, Materials, and Metallurgical Engineering

Faculty of Engineering and Technology

Botswana International University of Science and Technology

aoyio@biust.ac.bw (+267) 493 1222

ACKNOWLEDGEMENTS

The success of this research would have not been achieved without the contribution and assistance from these special people: firstly, I would like to sincerely and greatly thank my supervisors, Prof. Cecil K. King'onde and Prof. Ochieng' Aoyi for their consistent guidance, assistance, and patience throughout my study. They consistently steered me in the right direction whenever it was necessary. I am grateful to Botswana International University of Science and Technology, and the Department of Chemical and Forensic Sciences for funding and giving me the platform to display my ability.

I am deeply grateful to the members of the Department of Chemical and Forensic Sciences staff particularly Prof. Wellington Masamba (H.O.D), Dr. Stephen Majoni, Dr. Sebusi Odisitse, Dr. Foster Mbaiwa, and Dr. Melisew Tadele Alula. I thank all the technicians from the Faculty of Science, particularly the technicians from the Department of Chemical and Forensic Sciences, Mr. Madiba Mothusi, and Bokang Present from the Department of Physics and Astronomy. I thank all the postgraduate colleagues, especially El-Shalom Eigbe, and my entire research group members.

I thank my parents, Mr. and Mrs. Danis Mark Gembo Nam for investing in me since the onset of my schooling, for continuously inspiring me, loving, praying, and caring. Sincere gratitude to my siblings and Aunt Anne Ochieng for their prayers and moral support. I am greatly indebted to my friends in particular Naomi Amollo, Benton Otieno, Boniface Orero, Anthony Mabele, Joyce Elisadiki, and The Blossoms. Above all my enormous gratitude to God who made everything possible.

DEDICATION

I dedicate this research work to my parents Mr. and Mrs. Gembo, siblings, and younger sister Mildred Awino.

TABLE OF CONTENT

DECLARATION	i
COPYRIGHT	ii
CERTIFICATION	iii
ACKNOWLEDGEMENTS	iv
DEDICATION	v
TABLE OF CONTENT	vi
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF ABBREVIATIONS	xii
SYMBOLS AND GREEK NUMERALS	xiv
LIST OF CONFERENCE PRESENTATIONS	xv
ABSTRACT	xvi
FRAMEWORK OF THE DISSERTATION	xviii
CHAPTER 1	1
1. Introduction	1
1.1 Background of the study	1
1.2 Problem statement.....	3
1.3 Hypothesis	4
1.4 Aim and specific objective	4
1.5 Research questions.....	4
1.6 Justification of the study	5
1.7 Significance of the study.....	5
References	6
CHAPTER 2	8

2. Literature Review	8
2.1 Water pollution	8
2.2 Emerging contaminants	8
2.3 Organic dyes	9
2.4 Basis of color and classification of dyes.....	12
2.5 Organic dye removal technologies.	13
2.6 Conventional wastewater treatment methods	13
2.7 Advanced industrial textile wastewater treatment processes.....	16
2.8 Applications of BiOM Photocatalysts	30
2.9 Knowledge gaps.....	33
References	35
CHAPTER 3	48
3. Materials and Methods	48
3.1 Introduction.....	48
3.2 Chemicals and materials.	48
3.3 Experimental set up.	49
3.4 Experimental procedure.....	50
3.5 Photocatalysts characterization.....	51
3.6 Determination of point of zero charge (pH_{PZC}) by Salt Addition Procedure.....	53
3.7 Photodegradation studies	53
3.8 Estimation of chemical oxygen demand	54
3.9 Investigation of the catalyst stability/recyclability	54
References	55
CHAPTER 4	56
4 Results and Discussion.....	56

4.1 Structural Analysis of photocatalysts.	56
4.2 Morphological analysis.....	61
4.3 Brunauer-Emmett-Teller (BET)	63
4.4 Optical properties.....	66
4.5 Point of zero charge (pH_{PZC}) or isoelectric point (pH_{IEP})	68
4.6 Photocatalytic activity Evaluation	69
4.7 Estimation of chemical oxygen demand	80
4.8 Degradation parameters	81
4.9 Investigation of the catalyst stability/recyclability	86
References	89
CHAPTER 5	97
5 Conclusion and Recommendations.	97
5.1 Conclusion	97
5.2 Recommendations.....	99
Appendix A: Energy-dispersive X-ray spectroscopy.....	100
Appendix B: Yearly scientific publications showing the use of photocatalysis in purification and detoxification of wastewaters.....	101
Appendix C: Yearly publications on bismuth-based photocatalysts, BiOCl, BiOBr, and BiOI photocatalysts.....	102
Appendix D: Schematic illustration of the degradation of methyl orange over modified BiOI	104
Appendix E: The suggested oxidation mechanism for cyclohexane over TiO_2 and BiOM photocatalysts.....	105

LIST OF TABLES

Table 1. Health hazards of the commonly used azo dyes	11
Table 2. Classification of dyes	12
Table 3. Recent studies on solid solutions and their corresponding photocatalytic applications	29
Table 4. Lattice parameters (a, b, c), constants (c/a) and unit volume of $\text{BiOBr}_m\text{I}_{(1-m)}$ samples.	58
Table 5. The calculated FWHM and crystallite size from XRD measurements	58
Table 6. BET surface areas and pore volume of the BiOBr , $\text{BiOBr}_{0.6}\text{I}_{0.4}$, and BiOI	65
Table 7. The absorption edges and the calculated optical band gaps.	67
Table 8. Calculated band gaps (E_g) and electronegativity (χ) of $\text{BiOBr}_m\text{I}_{(1-m)}$ samples.....	68
Table 9. The adsorption capacity of $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions	70
Table 10. Degradation efficiencies of $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions under solar irradiation....	71
Table 11. Degradation efficiencies of $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions under UV light irradiation	72
Table 12. Change in temperature with irradiation time under solar	75
Table 13. Apparent constants rate for the photodegradation of MB	77
Table 14. Degradation efficiencies under different initial pH values.	82
Table 15. Comparison of the degradation of MB over TiO_2 , ZnO , and the present study.....	88

LIST OF FIGURES

Figure 1. Pie chart showing the world's consumption of organic dyes	10
Figure 2. Schematic diagram of conventional wastewater treatment processes	14
Figure 3. Typical section of the water treatment plant.....	15
Figure 4. Summary of advanced oxidation processes used in industrial textile wastewater (ITW).....	17
Figure 5. Yearly scientific publications showing the use of photocatalysis in purification and detoxification of wastewaters. (Reprinted with permission from ref. Copyright (2020) Elsevier.....	22
Figure 6. Mechanism of Photocatalysis, (a) photogeneration of electron/hole pair, (b) surface recombination, (c) energy bandgap of SC.....	23
Figure 7. Coupling photocatalysis with other AOPs.....	25
Figure 8. Yearly publications on (a) bismuth-based photocatalysts, (b) BiOCl, (c) BiOBr, and (d) BiOI photocatalysts. (Reprinted with permission from ref. Copyright (2018) Elsevier. ...	28
Figure 9. Schematic illustration of the degradation of methyl orange over modified BiOI. Reprinted (adapted) from, copyright (2011), with permission from the American Chemical Society.....	32
Figure 10. The suggested oxidation mechanism for cyclohexane over (a) TiO ₂ and (b) BiOM photocatalysts. (Reprinted with permission from ref. Copyright (2017) Elsevier.....	33
Figure 11. Experimental set up (a) UV-lamp and (b) solar.....	49
Figure 12. XRD patterns of BiOBr _m I _(1-m) samples	56
Figure 13. Raman shift spectra for BiOBr _m I _(1-m) samples.	59
Figure 14. FTIR spectra of BiOBr _m I _(1-m) samples	60
Figure 15. SEM micrographs of (a) BiOBr, (b) BiOBr _{0.8} I _{0.2} , (c) BiOBr _{0.8} I _{0.2} , (d) BiOBr _{0.6} I _{0.4} , (e) BiOBr _{0.4} I _{0.6} , (f) BiOI.....	61
Figure 16. TEM images of (a) BiOBr, (b) BiOBr _{0.6} I _{0.4} , and (c) BiOI	63
Figure 17. (a-c) N ₂ adsorption-desorption isotherms of M = 1.0, 0.6, and 0.0, respectively (d-f) BJH distribution of the pore sizes of M = 1.0, 0.6, and 0.0, respectively.	64
Figure 18. (a) Absorption spectra from UV- vis analysis (b) Optical images showing resultant colors of BiOBr _m I _(1-m)	66
Figure 19. ΔpH against initial pH of BiOBr _m I _(1-m) solid solutions at 298 K	68

Figure 20. Adsorption efficiencies of MB over $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions	69
Figure 21. Degradation efficiencies of MB over $\text{BiOBr}_m\text{I}_{(1-m)}$ materials under solar irradiation.	70
Figure 22. (a-g) UV-Vis MB absorption spectra over $\text{BiOBr}_m\text{I}_{(1-m)}$ photocatalysts (h) Photodegradation efficiencies of MB over $\text{BiOBr}_m\text{I}_{(1-m)}$ under UV light irradiation.	73
Figure 23. Photodegradation of MB over $\text{BiOBr}_{0.6}\text{I}_{0.4}$ under UV-light irradiation	74
Figure 24. (a) Photodegradation efficiency due to thermal contribution and (b) corresponding % removal of MB after 3 h of solar irradiation.....	76
Figure 25. (a) Zero (b) First (c) Second-order for the removal of MB under UV light and (d) corresponding pseudo kinetics rate constants K_{app} with different catalysts.	78
Figure 26. Effects of scavenger on degradation efficiencies of MB over $\text{BiOBr}_{0.6}\text{I}_{0.4}$ photocatalyst.	79
Figure 27. Percentage COD removal over $\text{BiOBr}_{0.6}\text{I}_{0.4}$ with irradiation time.	80
Figure 28. (a) Effects of pH on photodegradation efficiencies of MB over $\text{BiOBr}_{0.6}\text{I}_{0.4}$ and (b) Degradation rate constants of $\text{BiOBr}_{0.6}\text{I}_{0.4}$ at different initial pH.	81
Figure 29. (a) Effects of catalyst loading on photodegradation efficiencies of MB over $\text{BiOBr}_{0.6}\text{I}_{0.4}$ and (b) Degradation rate constants of $\text{BiOBr}_{0.6}\text{I}_{0.4}$ at different catalyst loading. .	82
Figure 30. (a) Effects of initial concentration on photodegradation efficiencies of MB over $\text{BiOBr}_{0.6}\text{I}_{0.4}$ and (b) Removal rate constants of $\text{BiOBr}_{0.6}\text{I}_{0.4}$ at various dye concentrations....	83
Figure 31. (a) Effects of temperature on photodegradation efficiencies of MB over $\text{BiOBr}_{0.6}\text{I}_{0.4}$ as and (b) Degradation rate constants of $\text{BiOBr}_{0.6}\text{I}_{0.4}$ at different temperatures. .	85
Figure 32. (a) Effects of oxidant on photodegradation efficiencies of MB over $\text{BiOBr}_{0.6}\text{I}_{0.4}$ and (b) Degradation rate constants of $\text{BiOBr}_{0.6}\text{I}_{0.4}$ at different amounts of oxidant.	86
Figure 33. Recyclability test for $\text{BiOBr}_{0.6}\text{I}_{0.4}$ for the removal of 10 mgL^{-1} MB after 3 h of UV-light irradiation at pH 7.0 with 50 mg catalyst dosage.	87

LIST OF ABBREVIATIONS

AC	Activated carbon
AOPs	Advanced oxidation processes
BET	Brunauer-Emmett-Teller (m^2g^{-1})
BOD	Biochemical oxygen demand (mg/L)
CB	Conduction band
CBM	Conduction band minim
CECs	Contaminants of emerging concerns
COD	Chemical oxygen demand (mg/L)
CRT	Cathode-ray tube
BDDT	Brunauer, Deming, Deming, and Teller
DNA	Deoxyribonucleic acid
EC	Electrocoagulation
ECs	Emerging contaminants
EDCs	Endocrine-disrupting chemicals
EDS	Energy-dispersive x-ray spectroscopy
FTIR	Fourier-transform infrared
FWHM	Full width at half maximum (Radians)
IEE	Internal electric field effect
IEF	Internal electric field
IUPA	International Union of Pure and Applied Chemistry
MB	Methylene blue
MOF	Metal-organic frameworks
PPCPs	Pharmaceutical and personal care products
PVP	Polyvinylpyrrolidone
PZC	Point of zero charge
SC	Semiconductor
SEM	Scanning electron microscopy
SS	Suspended solids
STPs	Sewage treatment plants

TEM	Transmission electron microscope
TOC	Total organic carbon (mg/L)
UV	Ultraviolet
VB	Valence band
VBM	Valence band maximum
WHO	World health organization
XRD	X-ray diffractometer

SYMBOLS AND GREEK NUMERALS

$(\text{Bi}_2\text{O}_2)^{2+}$	Bismuth oxide ion
A_0	Initial absorbance
A_t	Absorbance at time t
BiOM (M = Br, I)	Bismuth oxy-halide
D	The average crystallite size
e^-/h^+	Electron-hole pair
E_{gap}	Energy bandgap
eV	Electron Volt
K/ $^{\circ}\text{C}$	Temperature
kV	kilovolt
M	Molar
mM	Millimolar
rpm	Revolutions per minute
t	Time (min)
C_t	Concentration at time t
C_o	Initial concentration
k_{app}	Reaction rate constant
qe	Adsorbate uptake at equilibrium

Greek symbols

μL	Microliter
μSCm^{-1}	Conductivity
$\text{\AA}$	Angstrom
β	Full width at half maximum (FWHM)
$\ominus$	Degrees
κ	Shape factor constant.
λ	Wavelength (nm)

LIST OF CONFERENCE PRESENTATIONS

1. Robert O. Gembo, Cecil K. King'onde, Aoyi Ochieng, 2019. Photodegradation of Methylene Blue (MB) using Bismuth Oxyhalide ($\text{BiOBr}_{1-m}\text{I}_m$) Nanomaterials. Alliance of International Science Organizations (ANSO)-Maasai Mara University (MMU)-Sino-Africa Joint Research Centre (SAJOREC) International Conference 4th – 6th September 2019, Maasai Mara University, Narok-Kenya.
2. Robert O. Gembo, Cecil K. King'onde, Aoyi Ochieng, 2019. Fabrication of Bismuth Oxyhalide $\{\text{BiOM}, (\text{M} = \text{Br}, \text{Cl}, \text{I})\}$ for the Photodegradation of Rhodamine 6G under Solar Irradiation (Poster). 1st Chemical Society of Botswana (CSB), 7th Federation of African Societies of Chemistry (FASC), 7th Southern and Eastern Africa Network of Analytical Chemists (SEANAC) Chemistry Conference 25th – 27th September 2019, University of Botswana, Gaborone-Botswana.
3. Robert O. Gembo, Cecil K. King'onde, Aoyi Ochieng, 2019. Photodegradation of Methylene blue using Bismuth Oxyhalide ($\text{BiOBr}_{1-m}\text{I}_m$) Nanomaterials under Solar irradiation. 20th WaterNet/WARFSA/GWP-SA Symposium 30th October to 1st November 2019, Indaba Hotel, Spa & Conference Centre, Four ways, Johannesburg, South Africa.

ABSTRACT

Continuous discharge of textile wastes such as dyes into the water bodies deteriorates the quality of water. Therefore, the removal of these materials from the wastewater should be a priority due to their carcinogenic properties, which pose a health hazard to both human beings and aquatic life. The use of advanced oxidation processes (AOPs) for example heterogeneous photocatalysis has been broadly studied due to their efficacy in the removal of such organic contaminants. Engineering of the bandgap via doping is among the strategies for enhancing the photocatalytic performance of the nanomaterials and the fact that bismuth oxy-halide (BiOM , ($M = \text{Br}, \text{Cl}, \text{I}$)) can be modified to form solid solutions make them suitable candidates for this study. This dissertation describes the synthesis, characterization, and applicability of $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions materials. The materials were prepared through a simple hydrothermal method at 160°C . The applicability of the prepared materials was examined through the photocatalytic degradation of Methylene blue (MB) dye under solar and UV-light irradiation.

The particle size and morphology of the synthesized solid solutions were obtained by scanning electron microscopy (SEM) and transmission electron microscope (TEM), respectively. X-ray diffractometer (XRD) patterns revealed the structural features of the prepared materials. The optical properties such as absorption edge, energy bandgap, and photodegradation studies were obtained by the UV-Vis spectrophotometer. The Brunauer-Emmett-Teller (BET) was applied to determine the surface area and the pore size distribution of the materials. Vibrational modes of the materials were determined using Raman spectroscopy. From SEM analysis, BiOBr displayed ultrathin plates-like structures that are large and thick with variable dimensions. $\text{BiOBr}_{0.2}\text{I}_{0.8}$, $\text{BiOBr}_{0.4}\text{I}_{0.6}$, $\text{BiOBr}_{0.6}\text{I}_{0.4}$, and $\text{BiOBr}_{0.8}\text{I}_{0.2}$ showed flake-like structures as the morphology, whereas BiOI displayed flower-like structures as the morphology. The formation of flakes and flower-like structure is due to the microplates undergoing self-assembly to form 3-dimensional structures. Energy-dispersive X-ray spectroscopy (EDAX) study confirmed the existence of Bi, O, Br, and I. The XRD peaks corresponding to (102) planes shifted to the lower diffraction angle with an increase in the composition of iodide.

From the optical properties analysis, the bandgap was tailored from 2.59 to 1.96 eV via doping. The BET surface area of BiOBr , $\text{BiOBr}_{0.6}\text{I}_{0.4}$, and BiOI was found to be 0.517, 3.249, and 1.890

m^2/g , respectively. The photodegradation of MB was monitored through color and COD reduction. After 3 h of solar and UV irradiation, the degradation efficiencies over $\text{BiOBr}_{0.6}\text{I}_{0.4}$ were 99 and 88%, respectively. The stability of the $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solution was revealed by the reusability of $\text{BiOBr}_{0.6}\text{I}_{0.4}$ for 5 cycles with degradation percentage decreasing to 82% after the 5th cycle. From the scavenging experiment, it was confirmed that superoxide ($\text{O}_2^{\bullet-}$) and photogenerated holes (h^+) were liable for the degradation of MB. From the study, it can be established that bismuth oxyhalide solid solution is an effective material in the treatment of MB under irradiation from solar and UV-light and thus holds huge promise in environmental remediation.

FRAMEWORK OF THE DISSERTATION

This dissertation is divided into five main chapters.

- i. Chapter 1 contains an introduction that highlights a brief insight into the subject at hand. It also outlines the significance and motivation of this study as well as aims and objectives that will be tackled.
- ii. Chapter 2 contains background information on the emerging contaminants and textile industrial wastes. It also gives an overview of conventional treatment methods and advanced oxidation processes. Finally, this chapter provides a review of the work, which has already been reported by other researchers in this field, highlighting their findings.
- iii. Chapter 3 is a methodology section on the synthesis, characterization techniques, and assessment procedures.
- iv. Chapter 4 gives the results and discussions for all the findings. Results attained on the characterization, photocatalytic performance, and underlying discussions are underlined.
- v. Chapter 5 is a summary and conclusions from this study. The upcoming research directions are recommended in this chapter. The references are given at the end of every chapter of the dissertation.

CHAPTER 1

1. Introduction

1.1 Background of the study

The global environmental condition has immensely changed during the last few decades. Several national and international organizations have been holding campaigns on the control measures of environmental pollution that result from different industrial activities. Various governments have established different environmental departments that have made laws to safeguard the environment from contamination [1]. However, pollution of the environment remains one of the key problems faced by the modern world in the 21st century. Human beings, aquatic life, as well as other forms of life are relentlessly affected by global environmental pollution.

The problem of environmental pollution arises mainly due to the contamination of physical and biological components of the earth or atmosphere to an extent that the normal environmental functions are severely affected. Some environmental contaminants occur naturally as substances or energies. However, if they exceed natural levels, they are considered contaminants. When the use of natural resources is at a higher rate than nature's ability to repair itself, the result will be land, air, and water pollution [2]. Even though it has been known that pollution has been in existence since the beginning of life, the onset of the industrial revolution during the 19th century led to a proportionate increase in environmental pollution.

Urbanization, technological advancement, and population growth have resulted in a significant rise in demand for the use of natural resources leading to a great overstretching of these resources [2,3]. The human population is constantly increasing leading to a rise in demand for human essentials thus, resulting in the growth of medicine, agriculture chemical industries, and energy sources. This development has greatly led to a significant increase in land, water, and air pollution. Almost all methods applied in the production of human essentials results in environmental pollution. The intensive development in pharmaceutical and agricultural sectors have resulted in the production of compounds such as antibiotics, pesticides, and organic dyes that produce effluents that are discharged into the aquatic environment [4,5]. Organic dyes are extensively applied in several industries like pharmaceuticals, woven, distillers, cosmetics pulp

and paper, electroplating, fabric, and tanneries. Organic dyes are produced in large-scale hence they form an integral part of industrial wastewater [6]. These industrial wastewaters from organic dye manufacturing industries consist of excessive COD, resilient color, and different pH values. Some parameters such as suspended solids (SS), COD, TOC, and BOD that are used to indicate the quality of wastewater are usually prominent in industrial wastewater [7]. These parameters considerably lower the efficiency of conventional treatment methods

Due to the mutagenic and carcinogenic properties of organic dyes, eliminating them is considered as one of the main environmental remediation. In recent years, organic dyes from industrial wastewater have been removed by various novel technologies including physiochemical processes such as coagulation, reverse osmosis, flocculation, electrochemical oxidation, membrane bioreactor, Fenton process, and activated carbon adsorption oxidation had been used to eliminate organic dyes from industrial wastewater [8]. However, these treatment techniques still face several limitations such as excessive use of chemicals that lead to the generation of sludge with further treatment problems, long reaction time, convoluted technical requirements, high cost of installation and operation, sensitivity towards variability in wastewater input. These limitations severely restrict the applications of these methods [9,10]. In addition to physicochemical methods, the use of algae, bacteria, fungi, and yeast that are biological methods have been applied to eliminate certain types of organic of dyes.

Biological methods generate less sludge, environmentally friendly, and low cost compared to physiochemical methods. However, the use of biological methods requires a huge land area for operation, high sensitivity towards the toxic of certain chemicals, and the method requires longer treatment time [11]. Most of the organic dyes contain complex aromatic molecular structures, which are non-biodegradable [8]. Furthermore, the membrane technology that is an example of a physical process, cannot resolve this problem because it only transfers the dye to another phase hence no destruction of the dye. The use of the chemical process is fast, however, the process requires a huge amount of chemicals to be added into the effluents, this is not only costly but also results in secondary pollution as well as the production of harmful sludge that accumulates in final solutions [12,13]. Therefore, an alternative technique with high efficiency should be explored to remove organic dyes.

The reported AOPs such as electro-Fenton, electrochemical oxidation, catalytic ozonation, anodic oxidation, and photo-Fenton $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ are effective in the treatment of various types of wastewater since they use reactive radicals as the main oxidizing agents [14]. Heterogeneous photocatalysis is an example of AOP that is largely applied in environmental remediation. TiO_2 and ZnO photocatalysts have been traditionally used in transforming solar energy into chemical energy as well as decreasing the harmful contaminants into more useful and safe compounds [15]. Metal sulfides and oxides such as ZrO_2 , TiO_2 , CdS , WO_3 , ZnO , NiS , Fe_3O_4 , ZnS , and ZrO_2 [16] are usually applied in the field of photocatalysis owing to their chemical stability, less cost, strong ability to oxidize organic contaminants, low toxicity, and durability [15] but they also have some limitations like wider bandgap (ca 3.2 eV) and photo corrosion [17]. Hence, it is imperative to develop an alternative photocatalyst to improve or replenish the limitations of metal oxides and sulfides.

To overcome these limitations, it is important to develop alternative photocatalytic materials that are less costly and more stable. Bismuth oxy-halide (BiOM ($\text{M} = \text{Cl}, \text{Br}, \text{I}$)) materials are a novel class of photocatalyst due to their distinctive electrical and optical features, environmental-friendliness, crystal structure, unique layered, good chemical stability, high oxidation capacity, and internal electric field effect (IEE) [18,19]. These compounds are tetragonal matlockite (space group $p4/nmm$) consisting of a layer of $(\text{Bi}_2\text{O}_2)^{2+}$ interleaved by slabs of halogen ions $(\text{M}_2)^{2-}$ ($\text{M} = \text{Cl}, \text{Br}, \text{I}$) which crystallize into a layered structure, forming $[\text{M}-\text{Bi}-\text{O}-\text{O}-\text{Bi}-\text{M}]$ stacked slices, held together by non-bonding (van der Waals) interactions through the halogen ions along the c-axis. Due to these layered structures, bismuth oxyhalide compounds, display mechanical, unique optical, and electrical qualities and have found application in fields including photocatalysis, organic synthesis, nitrogen fixation, and solar-driven H_2 generation. Furthermore, separating the photoexcited e^- and h^+ is enhanced due to the built-in electric field that forms between the $(\text{Bi}_2\text{O}_2)^{2+}$ and 2M^- slabs, thus improving the photocatalytic activity [20,21].

1.2 Problem statement

Textile industrial wastewater is usually characterized by a high presence of dye and organic loading, which the conventional treatment methods cannot efficiently eliminate due to the presence of recalcitrant compounds such as flavones, anthocyananidins, and dihydropyrans.

According to the principles of green chemistry, the utilization of methods that minimizes the consumption of energy and the production of harmful materials is desirable. These objectives are not met by the use of conventional treatment methods, since the methods involve consumption of a high amount of energy, use hazardous chemicals like chlorine, ozone, and hydrogen peroxide, and they generate waste streams. The use of AOPs such as photocatalysis presents an opportunity to recover the environmental property of water treatment, especially for the treatment of chemical pollutants in water.

1.3 Hypothesis

The photocatalytic activity of individual BiOBr and BiOI materials, when doped to form $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions, are improved while the limitations associated with the individual photocatalysts is greatly reduced.

1.4 Aim and specific objectives

The main objective of this study is to develop and investigate the applicability of a bismuth oxyhalide ($\text{BiOBr}_m\text{I}_{(1-m)}$) solid solutions for the photodegradation of MB dye under irradiations of solar and UV light. The specific objectives include:

- (i). To synthesize and characterize $\text{BiOBr}_m\text{I}_{(1-m)}$ materials.
- (ii). To analyze the photocatalytic activity of $\text{BiOBr}_m\text{I}_{(1-m)}$ materials towards the removal of MB.
- (iii). To investigate the effect of degradation parameters on the performance of $\text{BiOBr}_m\text{I}_{(1-m)}$ materials
- (iv). To evaluate the catalyst stability/recyclability.

1.5 Research questions

1. What are the physical and chemical characteristics of $\text{BiOBr}_m\text{I}_{(1-m)}$ materials?
2. How is the performance of $\text{BiOBr}_m\text{I}_{(1-m)}$ materials towards the degradation of MB from wastewater?

3. What is the effect of degradation parameters on the activity of $\text{BiOBr}_m\text{I}_{(1-m)}$ materials?
4. What is the stability/recyclability of the $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions?

1.6 Justification of the study

An increase in demands for materials related to textile dyes, plastic, and fertilizers has led to a significant increase in industrialization, intake of nonrenewable sources, and technology. Therefore, developing green chemistry that includes moving away from these toxic non-biodegradable products is necessary. All wastes including industrial, municipal, and domestic wastes should be treated to make them safe before they are released to the environment. For this reason, the proposed solution is to develop a suitable method for waste treatment, to reduce the risk to human life. However, the use of photocatalysis has proved to be one of the effective methods to get rid of the recalcitrant products from these wastes.

The major purpose of this study is to develop an effective treatment method for MB dye from textile wastewaters. The efficiency of this method will be tested and is expected to be achieved through the color and the COD reduction from the wastewaters using bismuth oxyhalide ($\text{BiOBr}_m\text{I}_{(1-m)}$ $m = 1.0, 0.8, 0.6, 0.4, 0.2$, and 0) materials. The parameters involved during the photodegradation of the dye were also investigated.

1.7 Significance of the study

With the success of this study, there will be a provision of a breakthrough in the area of industrial wastewater treatment especially the treatment of organic dyes from textile wastewaters that remains one of the major global pollutants. The study will further expand the existing knowledge of photocatalysis by the use of bismuth oxyhalide ($\text{BiOBr}_m\text{I}_{(1-m)}$) solid solutions for the degradation of MB. The study seeks to show the importance of the use of nanotechnology in modern processes in wastewater treatment and water purification. This will contribute a lot by expanding the already existing knowledge on the application of nanotechnology in water and wastewater treatment.

References

1. S. Javaid, "Development and Optimisation of Treatment Technologies For Environmental Pollution Control," *Thesis*, no. September, pp. 89–240, 2006.
2. I. V. Muralikrishna and V. Manickam, "Introduction To Environmental Management," *Environ. Manage.*, pp. 1–4, 2017.
3. R. Ameta, M. S. Solanki, S. Benjamin, and S. C. Ameta, CHAPTER 6: *Photocatalysis*. Elsevier Inc., 135- 175, 2018.
4. A. Tkaczyk, K. Mitrowska, and A. Posyniak, "Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review," *Sci. Total Environ.*, vol. 717, p. 137-222, 2020.
5. K. Klaus, "Pharmaceuticals in the Environment," 57-75, 2010.
6. S. M. Lam, J. C. Sin, A. Z. Abdullah, and A. R. Mohamed, "Degradation of wastewaters containing organic dyes photocatalyzed by zinc oxide: A review," *Desalin. Water Treat.*, vol. 41, pp. 131–169, 2012.
7. W. J. Lau and A. F. Ismail, "Polymeric nanofiltration membranes for textile dye wastewater treatment: Preparation, performance evaluation, transport modeling, and fouling control - a review," *Desalination*, vol. 245, pp. 321–348, 2009.
8. S. Sarkar, A. Banerjee, U. Halder, and R. Biswas, "Degradation of Synthetic Azo Dyes of Textile Industry : a Sustainable Approach Using Microbial Enzymes," *Water Conserv Sci Eng*, vol. 2, pp. 121–131, 2017.
9. H. Ali, "Biodegradation of Synthetic Dyes — A Review," *Water Air Soil Pollution*. September 2009, pp. 251–273, 2010.
10. K. Balapure, N. Bhatt, and D. Madamwar, "Mineralization of reactive azo dyes present in simulated textile wastewater using downflow microaerophilic fixed-film bioreactor," *Bioresour. Technol.*, vol. 175, pp. 1–7, 2015.
11. E. Brillas and C. A. Martínez-Huitle, "Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review," *Appl. Catal. B Environ.*, vol. 166–167, pp. 603–643, 2015.
12. M. D. Chengalroyen and E. R. Dabbs, "The microbial degradation of azo dyes: Minireview," *World J. Microbiol. Biotechnol.*, vol. 29, no. 3, pp. 389–399, 2013.

13. S. Popli and U. D. Patel, "Destruction of azo dyes by anaerobic-aerobic sequential biological treatment: a review," *Int. J. Environ. Sci. Technol.*, vol. 12, no. 1, pp. 405–420, 2015.
14. Y. Deng and R. Zhao, "Advanced Oxidation Processes (AOPs) in Wastewater Treatment," *Curr. Pollut. Reports*, vol. 1, no. 3, pp. 167–176, 2015.
15. K. Nakata and A. Fujishima, "TiO₂ photocatalysis: Design and applications," *J. Photochem. Photobiol. C Photochem. Rev.*, vol. 13, no. 3, pp. 169–189, 2012.
16. V. Hasijaa, P. Raizadaa, A. Sudhaika, K. Sharmaa, A. Kumara, P. Singha, S. B. Jonnalagadd, V. K. Thakur, "Recent advances in noble metal-free doped graphitic carbon nitride-based nanohybrids for photocatalysis of organic contaminants in water: A review," *Appl. Mater. Today*, vol. 15, pp. 494–524, 2019.
17. H. Dong, G. Zeng, L. Tang, and C. Fan, "An overview on limitations of TiO₂ -based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures," *Water Res.*, vol. 79, pp. 128–146, 2015.
18. A. M. Ganose, M. Cuff, K. T. Butler, A. Walsh, and D. O. Scanlon, "Interplay of Orbital and Relativistic Effects in Bismuth Oxyhalides: BiOF, BiOCl, BiOBr, and BiOI," *Chem. Mater.*, vol. 28, no. 7, pp. 1980–1984, 2016.
19. W. Zhang, J. Fu, Y. Wang, X. Zhang, and J. Li, "A facile solvothermal method synthesis of nitrogen-doped graphene quantum dots/BiOX (X = Br, Cl) hybrid material for enhanced visible-light photoactivity," *Opt. - Int. J. Light Electron Opt.*, vol. 176, no. June, pp. 448–456, 2019.
20. C. C. Chen, J. Y. Fu, J. L. Chang, S. T. Huang, T. W. Yeh, J. T. Hung, P. H. Huang, F. Y. Liu, L. W. Chen. "Bismuth oxyfluoride/bismuth oxyiodide nanocomposites enhance the visible-light-driven photocatalytic activity," *J. Colloid Interface Sci.*, vol. 532, no. August, pp. 375–386, 2018.
21. L. Qiang, G. Li, X. Hu, and W. Tian, "One-pot preparation of Bi₆O₆(OH)₃(NO₃)₃·1.5H₂O (BBN)/Bi_{0.5}O_{0.5}Cl_xBr_{0.5-x} heterostructure with improved photocatalytic activity," *J. Photochem. Photobiol. A Chem.*, vol. 367, no. 3, pp. 375–383, 2018.

CHAPTER 2

2. Literature Review

2.1 Water pollution

The existence of living organisms depends on the availability of clean and reliable water sources. These water sources should be free from physical, biological, and chemical contamination. Besides cooking, drinking, washing, and recreation, water is also used for agricultural purposes and industrial purposes in generation of electrical power [1]. However, the seawater covers more than 97% [2] of the world's water and it is unfit for human consumption, three-quarters of freshwater is trapped in ice caps and glaciers, whereas only 0.01% is safe for human consumption [2]. Therefore, it is important to keep these sources safe from contamination. Apart from pollution caused by human activities, natural phenomena such as volcanic eruptions, storms, and earthquakes have also resulted in pollution of the water sources [3]. Freshwater resources, for example, lakes and rivers, are called surface waters, and groundwater (1.7%) makes a significant contribution to freshwater (0.6% of the world's total water supply) [2]. These clean sources of water are constantly polluted by various contaminants making them unsafe for human consumption.

2.2 Emerging contaminants

Emerging contaminants (ECs) are artificial organic chemicals, which are a threat to ecosystems and human health when released into the environment. These ECs are mainly generated because of continuous development in industries and the consumption of pharmaceuticals and other products. ECs are majorly categorized into flame retardants, endocrine-disrupting chemicals (EDCs), pharmaceutical, and personal care products (PPCPs) [4]. Natural water bodies have been discovered to contain traces of antibiotics, hormones, and painkillers [5]. Additionally, the daily usage of ECs with high solubility leads to the accumulation of EC-containing substances in the aquatic surroundings. The short-term removal of ECs is usually difficult due to their structural stability [6]. The potential risks and effects of ECs on ecosystems and human health have received attention [7]. Moreover, other inorganic and organic substances that commonly contaminate water include herbicides, textile dyes, and heavy metals (cadmium, mercury, silver, lead) [8,9]. These inorganic and organic chemicals have been traced in the

surface waters, wells, and ground. However, for this study, the major focus is on organic dyes that form the major environmental contaminants.

2.3 Organic dyes

A dye is a colored matter which upon application on fabrics imparts a permanent color that is not removable by washing with water, detergents, or light exposure [10]. In 1865, William Perkin discovered Mauveine as the first organic dye, thereby describing the dyestuff industry as mature. Since the discovery of Mauveine, people have generated more than 100,000 kinds of synthetic dyes through the industrial processes [11-13]. At the onset of the 20th century, Europe was the largest producer of the dyestuff. However, the current largest global producers and the main fabric suppliers of dyes are India and China. [Figure 1](#) is a pie chart adapted from the Chemical Economics Handbook showing the world's consumption of organic dyes.

Organic dyes are widely applied in food industries, paper, leather, rubber, paint, textile, cosmetics, plastic, printing, and pharmaceuticals. Presently, more than 100,000 tons of dyes are available for commercial purposes with azo dyes forming about 70% on a weight basis. Out of 1×10^6 tons of dyes produced annually, 50% is from the textile industry. Textile and paper industries form the primary and the largest consumer of dyes [14,15]. The reported global consumption of dyes by the textile industry is more than 10^7 kg/annual whereby 90% of this ends up on fabrics. The textile industry releases an approximate amount of 1×10^6 kg of organic dyes into the waste streams [15].

Over the past 25 years, Western Europe, Japan, and the United States have significantly reduced the number of dyes they produce annually whereas China, South Korea, and India have increased production. The consumption of textile dyes is directly influenced by human population growth. When discharged into the water bodies, they are not only undesirable due to their color but also carcinogenic or mutagenic and noxious to all forms of life. The carcinogens in some dyes include naphthalene, benzidine, and other aromatic compounds. They also affect aquatic plants as they reduce the transmission of sunlight through the water. Therefore, removing these dyes from the waste stream becomes important for the environmental remediation, as even small quantities of dyes in water can be highly detectable

and toxic. Thus dye-based toxicity has been investigated over the years to identify hazardous dyes and, consequently, to protect human health and the environment [15-17].

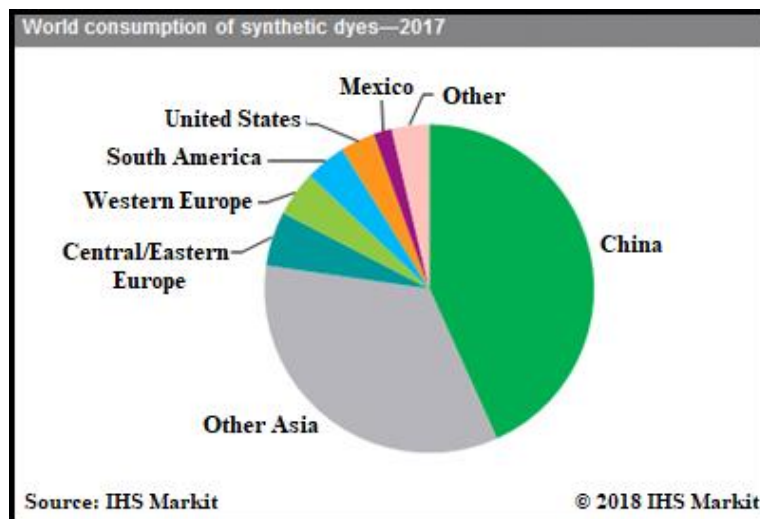


Figure 1. Pie chart showing the world's consumption of organic dyes [18]

The existence of dye waste in domestic and industrial effluents is an established health hazard. These poisonous dyes lower the quantity of dissolved oxygen in lakes and ponds hence limiting the downstream consumption of water for drinking and irrigation. Exposure to these dye polluted sewages can cause severe health damage to humans such as allergic reactions, reproductive system, circulatory problem, liver, neurobehavioral, kidney dysfunction, immune suppression disorders, and central nervous system [19-22]. The laborers in textiles industries have been reported to suffer from numerous types of cancers of the liver, urinary bladder, and kidney, due to high exposure to benzene, phenols, toluene, and other hydrocarbons that are highly carcinogenic.

Dyestuff industrial and textile trade can have a significant effect on mammals and bacteriological inhabitants. Azo dyes that form 60-70% of the total dyes produced are widely used in food, leather, pharmaceuticals, cosmetics, painting, paper, and textile industries. These dyes not only cause lungs, skin, and gastrointestinal problems but are also very stable in the environment hence can persist for a very long time. They can damage the deoxyribonucleic acid (DNA) material, haemoglobin, and even accelerates cancer in humans and animals. The gaseous products released by the fabric industries are toxic leading to air pollution. [Table 1](#)

shows the health hazards caused by organic dyes. Before the wastewaters containing dyes are released into the environment, the wastes should be treated up to the required standards, unfortunately, these dyes are difficult to remove from the polluted wastewater due to their resistance to oxidizing agents, temperature, detergents, soaps, biological, and chemical treatment [19,23,24]. Thus, an effective technique needs to be urgently developed to monitor and reduce the toxicity of organic dyes to the environment.

Table 1. Health hazards of the commonly used azo dyes [25]

Dye Name	Health Hazard
Malachite Green	DNA damage, chronic toxicity, mitochondrial toxicity, Genotoxicity
Auramine O	DNA damage, carcinogenicity, mutagenicity, genotoxicity, and cytotoxicity
Alizarin	Hypersensitivity, estrogenicity, mutagenicity, genotoxicity, acute oral toxicity, photoinduced toxicity, clastogenicity,
Rhodamine 6 G	DNA damage, genotoxicity, mutagenicity, and carcinogenicity
Crystal Violet	Chromosome destruction, genotoxicity, mutagenicity, acute oral toxicity, percutaneous toxicity
Congo Red	Carcinogenicity, protozoan toxicity, microbial toxicity, cytotoxicity, mutagenicity, algal toxicity, and genotoxicity
Methylene Blue	Microbial toxicity, photodynamic toxicity, effluent toxicity mutagenicity, hematotoxicity, teratogenicity, reproductive toxicity, and nucleic acid damage
Methyl Orange	Mutagenicity, genotoxicity, carcinogenicity
Eosin Y	Nucleic acid damage, reproductive toxicity, mutagenicity, skin toxicity, cardiotoxicity, pulmonary toxicity, microbial toxicity, carcinogenicity

2.4 Basis of color and classification of dyes.

Colour can be described as a perception that arises from the brain due to the interpretation by the eyes when stimulated by light. Therefore, color differs from one observer to another. Dyes or pigments normally formulate the colorants. Whereas pigments can be colorless, colored, and insoluble in water, dyes are colored and soluble in water [26,27]. Besides chromophores, most dyes also contain color helpers known as auxochromes groups. These groups include sulfonic acid, hydroxyl, and amino groups. However, these groups are not liable for color, but their existence can cause a change in the color of a dye and they also influence the solubility of the dyes [26].

Table 2 represents the general classification of dyes other colored pigments. Azo, sulfur, phthalocyanine, nitro and nitroso, and anthraquinone are the frequent classes of dyes applied for industrial scale. The frequently used organic dyes consist of basic, reactive, mordant, azo, sulfur, disperse, naphtha, acid, vat, and direct dyes, where azo derivatives based dyes are the main group of dyes that are currently applied in the industries [10,28].

Table 2. Classification of dyes [29]

Classification	Sub-class
Chemical structure	Triphenylmethane, anthraquinone, azo, indigo
Method and domain of usage	Acid, metal complex, direct, reactive, basic, reductive, sulphuric, chromic, and disperse, pigments.
Chromogen $n \rightarrow \pi^*$	Fluorescent Absorptive, and dyes with energy transfer
Nature of donor-acceptor couple	1-aminoanthraquinone, p-nitroaniline
Nature of polyenes: Acyclic and cyclic b) Cyanine	Polyolefins, annulenes, carotenoids, rhodopsin Hydroxyarylmethanes, cyanines, oxonols,

2.5 Organic dye removal technologies.

Before discharge into the aquatic environment, both municipal and industrial wastewater should be subjected to different types of treatment at sewage treatment plants (STPs) to remove dyes [29]. Recently, several technologies have been employed to monitor and reduce the pollution effect caused by organic dyes to the environment. These technologies are mainly aimed at reducing the harmful effects of these molecules in the liquid phase and decolorization of the effluents through breaking the functional groups responsible for color in the molecule. The commonly used conventional methods include physical, chemical, and biological methods. Apart from these long-established methods for dye removal, there is an emerging technology such as advanced oxidation processes (AOPs). These treatment methods should be highly efficient, multifunctional, environmentally friendly, and have low consumption from the environmental perspective [30,31]. The sections below are a detailed discussion of both the conventional methods and these emerging technologies.

2.6 Conventional wastewater treatment methods

The conventional treatment technique involves the use of physical, chemical, biological methods, or a combination of the two or three techniques depending on the standard of the effluent required before the discharge. These processes form the traditional methods that have always been applied to remove contaminants that are a concern to the surroundings and the health of the public. Before discharging the treated wastewater into the environment, the toxic level is tested to ensure that it is free from the contaminants that might negatively affect the environment and humans. Some of the physicochemical methods include flocculation, kinetic coagulation, gravity separation, membrane filtration, adsorption, electro-floatation, ozonization, ultrafiltration, and irradiation [32] while biological methods include aerobic and anaerobic. [Figure 2](#) is a schematic illustration of conventional wastewater treatment processes.

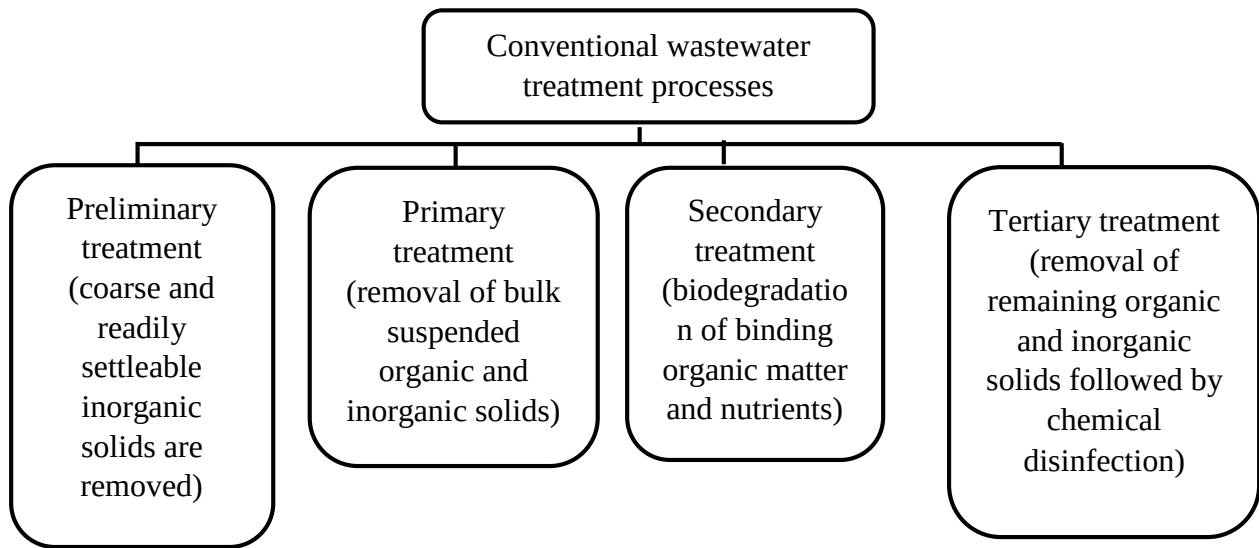


Figure 2. Schematic diagram of conventional wastewater treatment processes

Rough objects and other large substances in raw wastewater are majorly removed at preliminary treatment. This process is beneficial in removing and reducing the large, entrained, and suspended or floating solids such as plastic, cloth, wood, garbage, paper, and some fecal matter. Heavy inorganic solids like gravel and sand as well as glass or metals are removed at this stage [33]. During the primary, secondary, and tertiary treatment stage at STP, either biological, physical, and chemical process is used [34]. Physical and chemical processes such as grinding, flocculation/coagulation, and sedimentation are used at the primary level to remove both organic and inorganic solids. The sedimentation process is used to settle suspended particles of clay and silt. However, for dissolved and colloidal constituents, the application of simple sedimentation is ineffective, therefore the coagulation method is used instead [33,35].

The secondary treatment stage uses the effluents from the primary process, and it is based mainly on biological processes. Aerated lagoons and activated sludge systems are the most used methods. The bacterial biomass formed after 3-8 days of effluent aeration during aerated lagoons treatment is removed as a sludge. The activated sludge method intends to let aerobic bacteria metabolize suspended and dissolve organic substances from wastewater hence generating sludge from the effluent. This method is less costly, but it is difficult to treat the produced watery sludge. Alternatively, the sludge generated can be stabilized by anaerobic

conditions [34,35]. At the tertiary stage, physicochemical processes for example ion exchange, adsorption, AOPs, and reverse osmosis are the main processes applied in removing toxic compounds and additional organic and suspended solids [33]. Figure 3 is a typical illustration of sections of the water treatment plant.

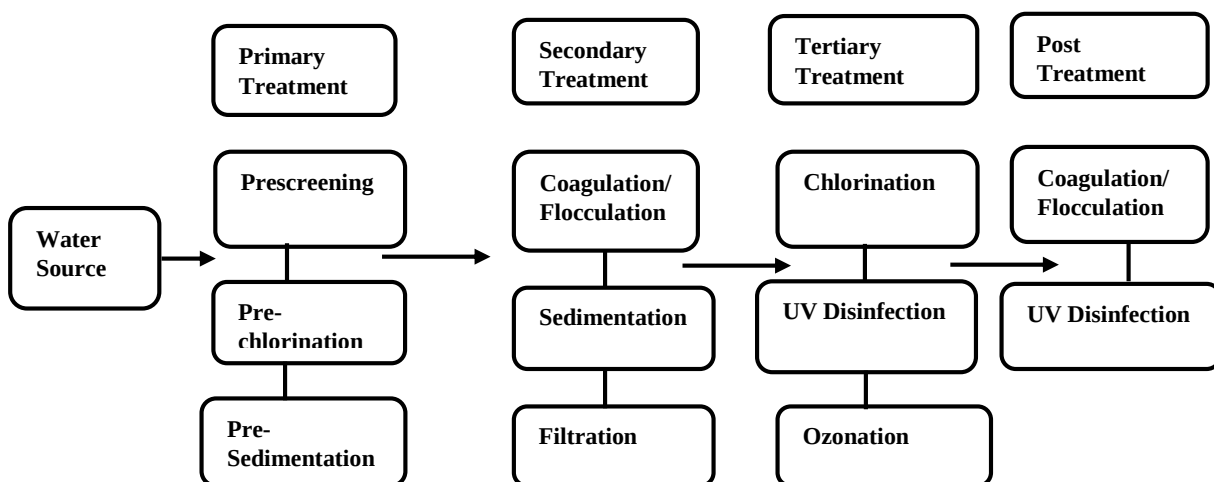


Figure 3. Typical section of the water treatment plant.

2.6.1 Physical methods

Physical approaches such as adsorption techniques and membrane filtration methods for instance reverse osmosis, nanofiltration, and electrodialysis have been widely used. However, the major disadvantages of these methods are fouling of membrane, thus, limiting the membrane lifetime and it is costly as it involves periodic membrane replacement [36]. Despite the extensive application of conventional methods in the treatment of dye-polluted wastewaters, they are costly and thus commercially unattractive. They require high electrical energy in addition to the consumption of a huge amount of chemicals. Additionally, they require long degradation time and have low degradation efficiency hence transmit the waste from one medium to another leading to secondary pollution [30,37].

However, the treatment of these wastewater streams do not guarantee complete removal of toxic compounds, but the expected products or by-products should have a significantly reduced level of toxicity to the threshold levels that are considered safe. These treatment techniques should possess the following characteristics: high efficiency and reliability, multifunctional, environmentally friendly, low construction cost, management, and maintenance supporting

self-sufficiency and acceptance by stakeholders and the general public [31,38]. Various methods of advanced oxidation processes as developing techniques have been exploited for the treatment of dye-polluted waters from textile industries.

2.6.2 Biological treatments

Compared to other physical and chemical processes, biological processes are economical. This process involves the use of biodegradation approaches like bacterial degradation, fungal decolorization, adsorption using living or dead bacterial biomass, and biotechnology systems to treat industrial wastes since microbes such as bacteria, yeasts, algae, and fungi can accumulate and break down different pollutants. However, due to technical constraints, the application of these methods is often restricted. The method is highly sensitive towards the toxicity of some chemicals and diurnal variation, requires a large land area for the establishment, and they are less flexible in design and operation. These current biodegradation methods are less capable of eliminating color to a satisfactory level. Although, the biological method can breakdown some organic molecules, many others particularly the azo dyes are recalcitrant owing to their chemical structural complexity and artificial organic source. Moreover, azo dyes cannot be fully destroyed as a result of their xenobiotic nature [32,36,37].

2.6.3 Chemical methods

Chemical methods such as electrokinetic coagulation, irradiation or electrochemical processes, coagulation/flocculation joined with filtration and flotation, precipitation-flocculation using Fe (II)/Ca(OH)₂ as well as the use of ozone as an oxidizing agent in conventional oxidation system have been applied in the treatment of organic dyes from wastewater. Although the dyes are removed, the use of chemical treatment methods is costly because sludge accumulates creating a discarding problem. The excessive use of chemicals during the treatment process causes the possibility of secondary pollution [32,36].

2.7 Advanced industrial textile wastewater treatment processes

The presence of colored water indicates pollution. Based on the WHO, the permitted limit of color intensity of water for use in industrial or domestic purposes should be between 15–20 units. The important subject should therefore, focus on the removal of these pollutants, which

have proven to be bio-recalcitrant to conventional treatment methods. Several emerging techniques that are environmentally friendly and improved performance have been recently applied for wastewater treatment. These methods include physicochemical methods for example chemical precipitation, membrane filtration, adsorption, flocculation/coagulation, and ozonation whereas AOPs include electro-Fenton, heterogeneous photocatalysis, hydrodynamic cavitation, anodic oxidation, Fenton, peroxicoagulation, photo-Fenton, and persulfate oxidation. The AOPs have received substantial attention owing to their “green” nature in that innovative technologies are promoted that decrease or eradicate the use or production of harmful materials in the design, manufacturing, and use of chemical products. AOPs are effective for removing toxic and non-biodegradable compounds from wastewater [39-42]. In AOPs both organic and inorganic contaminants can simultaneously be targeted for redox reaction hence making the AOPs non-selective which is an advantage [43]. [Figure 4](#) is a summary of advanced oxidation processes used in industrial textile wastewater (ITW)

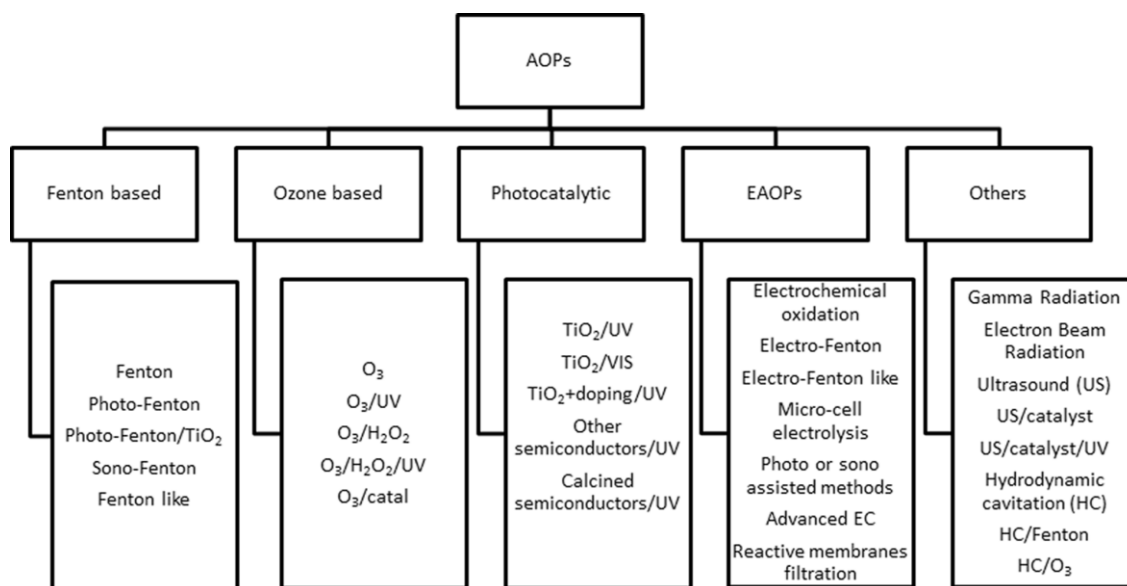


Figure 4. Summary of advanced oxidation processes used in industrial textile wastewater (ITW).

2.7.1 Coagulation-flocculation process

Coagulation is among the most regular and famous methods utilized in the treatment of ITW. During the coagulation treatment process, wastewater is coagulated using ferric sulfate, ferric chloride, and alum coagulants and the settled particles will be collected as sludge. This method is effective for dye removal from wastewater. For example, 96.5% of acid red 119 was efficiently removed with ferric chloride as a coagulant [44]. This method is less costly, simple to operate, and has the potential to handle large initial concentrations of the wastewater. According to their characteristics, coagulants are classified into organic and inorganic coagulants. Examples of inorganic coagulants include calcium oxide, aluminium sulfate, ferric sulfate, aluminum chloride, magnesium oxide, and ferric chloride. The use of inorganic coagulants produces smaller and light flocks that take a longer time to settle down. As soon the salts are added to the wastewater, they dissociate into ions and the resulting cationic species will be in hydrated form. Human diseases like cancer and Alzheimer's are the limitation associated with using chemicals as coagulants [45]

2.7.2 Membrane treatment

The membrane treatment method is among the recent advanced treatment processes that have gained attention due to their capability to eradicate the huge volume of microbes and chemicals from wastewater. The method is highly efficient and less costly compared to AOP. However, the major drawback of this method is fouling phenomena that cause a decrease in membrane performance with time. Due to its complexity, membrane fouling can result in membrane pore plugging, cake formation, clogging, and blocking on the surface of the membrane because of impurities or microbes exist in the form of inorganic and organic compounds. Membrane fouling reduces the life expectancy of the membrane. The three major contributing factors to membrane fouling are water quality feed, membrane characteristics, and process condition. [45-48]. Due to the limitations associated with these treatment methods, numerous studies have been directed towards the exploration of AOPs. These processes are receiving attention due to their ability to destroy pollutants compared to other techniques, in which the pollutant is transferred from one form to another.

2.7.3 Advanced oxidation processes

The AOPs stand out to be an efficient substitute for membrane treatment, coagulation-flocculation, and biological treatments for the elimination of pesticides, synthetic organic dyes, and aromatics from wastewater [49,50]. They are separated into irradiation methods (photolysis, photocatalysis) and non-irradiation methods (electrochemical oxidation, Fenton and photo-Fenton, ozonation, electrical discharge, and sonolysis). The mechanism of AOPs depends on the production of reactive species that attack organic pollutants by redox reaction, dehydrogenation, and hydroxylation. Unless the contaminants have undergone complete mineralization, oxidation will still occur [51,52].

2.7.3.1 Fenton and photo-Fenton reaction

This process leads to the production of $\text{OH}^\bullet$ radicals when hydrogen peroxide (H_2O_2) is decomposed under ferrous (Fe^{2+}) ions as:



Ultraviolet (UV) light can be used to enhance the formation of the $\text{OH}^\bullet$ radicals as:



Photo-Fenton oxidation is the regeneration of the catalyst due to the production of more $\text{OH}^\bullet$ radicals. Fenton reaction is considered to be suitable for the remediation of industrial textile wastewater due to its easiness and fast response in application especially for the removal of colors. These techniques have been effectively used to decolorize and break down organic dyes for example direct blue 71, tartrazine, acid orange 7, red Allura, acid blue 7, methyl violet 6B, and acid red 151 [50,53,54]. However, its major drawbacks include the production of sludge, leftover of unused ferrous (Fe^{2+}) ions, highly sensitive to working parameters along with the existence of other contaminants in wastewater [55-57].

2.7.3.2 Ozonation reaction

This is an environmentally friendly process due to the formation of no sludge, the ability to decolorize and degrade in a single step, little space required for installation, and decomposition of ozone into oxygen and water [58]. Ozone (O_3) is a powerful oxidant that can function under acidic and basic conditions. Ozone acts as an electrophile in acidic conditions in which it promotes a direct reaction with the organic substances. However, the reaction under acidic conditions cannot be classified as AOPs. The ozonation mechanism shifts from a direct mechanism to a complex string radical mechanism under basic pH levels. Therefore, the ozone will rapidly decompose to produce $OH^\bullet$ radicals and other radical species ($HO_2^\bullet$ and $HO_4^\bullet$). The radicals will degrade the organic compounds faster than the ozone itself. The higher the pH, the higher the rate of dye oxidation [56]. The effect of OH^- is beneficial in basic pH because O_3 will directly attack OH^- to generate $HO^\bullet$ as described in the following equations: [59].



A further reaction between $OH^\bullet$ and O_3 produces less reactive hydroperoxyl radicals ($HO_2^\bullet$) which react with O_3 to regenerate the consumed $OH^\bullet$ radicals as illustrated in the following equations [59].



The regeneration of the free radicals from ozone can be significantly increased by adding UV light, the optimum amount of H_2O_2 , or both to the aqueous solution of ozone [57,60]. However, the limitations of this technique include high initial capital, bromated by-products generated during the process may be harmful to human health, it requires energy in form of electricity for the entire process [45].

2.7.3.3 Heterogeneous Photocatalysis

A chemical reaction initiated by photons absorbed by a solid substance (photocatalyst) is referred to as photocatalysis. Nonetheless, this definition is still under deliberation. The photocatalyst remains unchanged during and after the reaction [61]. The photocatalysis process involves the utilization of both semiconductor and light. All photocatalysts are semiconductors. They are categorized into homogenous and heterogeneous photocatalysis. The photocatalysis process is influenced by particle size, unique surface area, bandgap, along with surface morphology. The surface structure of photocatalysts greatly affects the photocatalytic reactions since the reactions are triggered by photoinduced e^- and h^+ on the surface of the photocatalyst [62].

Photocatalysis was first used in the early 1970s. In 1972, Fujishima and Honda [63] applied TiO_2 in the form of anatase electrodes to electrochemically split water into O_2 and H_2 and under the irradiation of UV light. Since this application, semiconductor photocatalysis has gained substantial interdisciplinary attention and research interest owing to its diverse potentials in environmental and energy applications [63,64]. The application of photocatalysis as a means of environmental remediation appears appealing than conventional methods due to high surface area, cost-effective of semiconductors, non-toxicity. The photocatalysts also poses tunable features that can be modified via doping, reducing the size, and sensitizers, the ability for the multielectron transmission process, and reusability of the photocatalyst without losing their photocatalytic efficiency [65]. [Figure 5](#) displays yearly scientific publications showing the application of photocatalysts in the purification and detoxification of wastewaters.

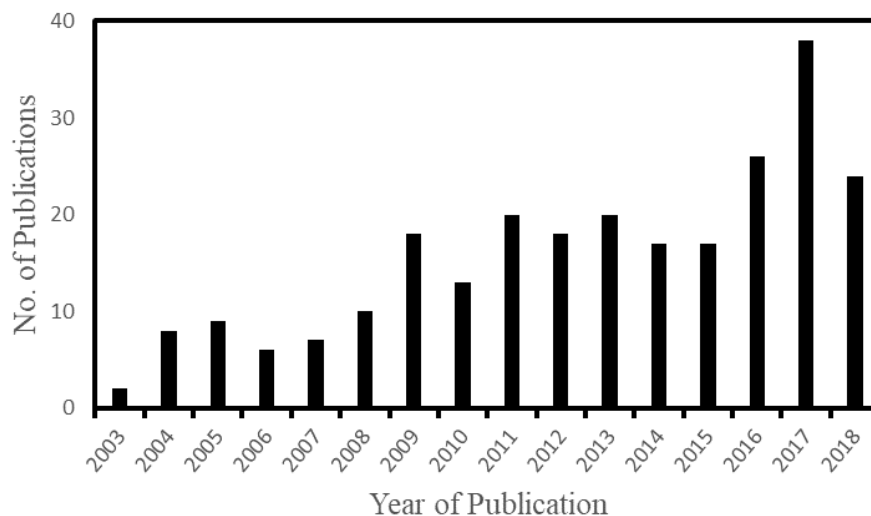


Figure 5. Yearly scientific publications showing the use of photocatalysis in purification and detoxification of wastewaters. (Reprinted with permission from ref. [61]. Copyright (2020) Elsevier.

2.7.3.3.1 Basic Principle of photocatalysis

A photocatalytic reaction is initiated when a photocatalyst absorbs light (photon) with an amount of energy equivalent to or larger than the energy of the bandgap. This energy will cause separation of the charges thus, promoting the electron (e^-) from the VB to CB of the absorbing material henceforth generating a hole (h^+) at the VB as shown in Figure 6 [66]. Oxygen will be reduced to superoxide radicle ($O_2^{\bullet-}$) by the e^- promoted to CB. The positive holes will oxidize water or hydroxide ions to form $OH^{\bullet}$ radicals ($OH^{\bullet}$) which non-selectively oxidizes a wide range of organic contaminants. Additionally, there can be minimal direct oxidation of contaminants by h^+ . This process can be illustrated as follows:



where PC is the semiconductor photocatalyst for example TiO_2 . The formation of $O_2^{\bullet-}$, H_2O_2 , and $HO_2^{\bullet}$ due to photogenerated electrons is illustrated in eqtns. (10) to (17)



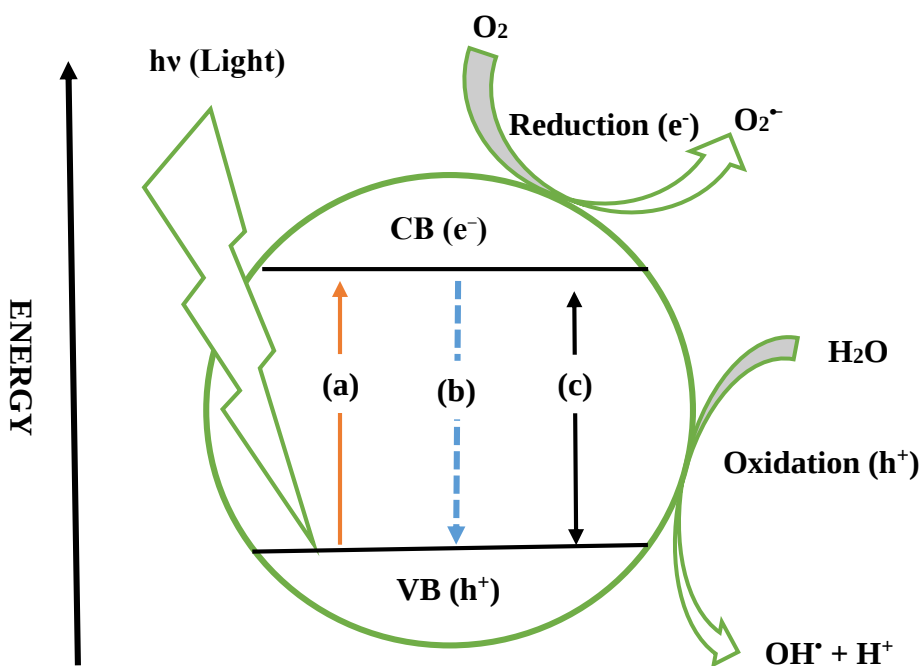


Figure 6. Mechanism of Photocatalysis, (a) photogeneration of electron/hole pair, (b) surface recombination, (c) energy bandgap of SC

Litter (1999) reported that the oxidative pathways performed by direct h^+ attack or $OH^\bullet$ in their free or adsorbed state, in many instances can completely mineralize organic substrates such as insecticides, organic dyes, halo hydrocarbons, aromatics, surfactants, and pesticides to CO_2 and

H₂O. The superoxide radicals (O₂^{•-}) generated due to the reaction between oxygen and the excited electron can further react with H⁺ to produce hydroxyl radicals [67] eqtns. (18) to (19) give the oxidation reactions activated by the photogenerated holes:



The reactions are terminated as; [68]



2.7.3.3.2 Heterogeneous semiconductor photocatalysis

Semiconductors modified into various organic and inorganic materials have recently been of interest due to their outstanding photocatalytic activity [69]. Metal oxides and sulfides, bismuth oxyhalides, and metal-organic frameworks (MOF) have been studied and have shown capability of removing biological and chemical contaminants from raw water and wastewater through photocatalysis [70,71]. Photocatalysts are used for decolorization, wastewater treatment, antifouling, air purification, antifogging, self-cleaning, conservation, and storage of energy, and sterilization. The electronic structure of semiconductors enables them to act as sensitizers for photoredox processes. Hybrid systems can be formed through coupling and integration of heterogeneous photocatalysis processes with other techniques to improve application scope and lower the removal time. Figure 7 is a schematic illustration of the coupling of photocatalysis with other AOPs.

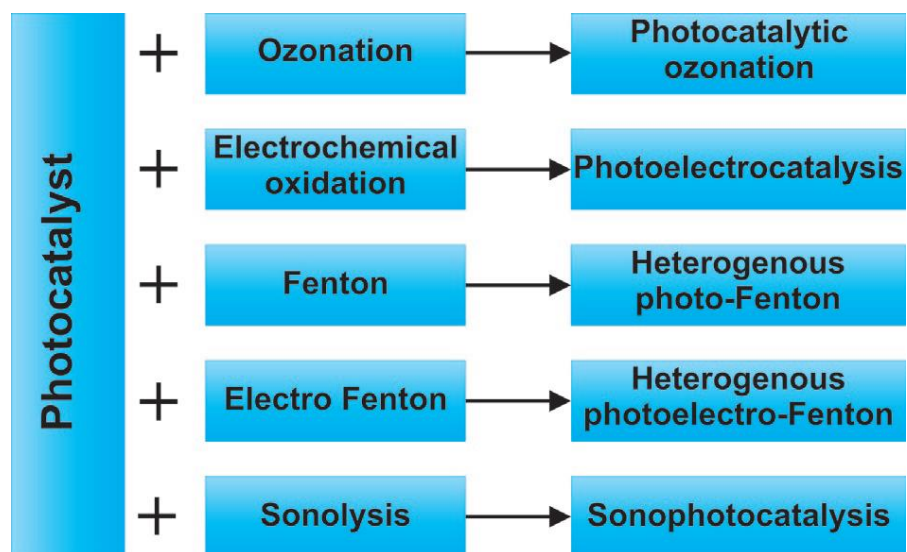


Figure 7. Coupling photocatalysis with other AOPs.

Several metal sulfides and oxides semiconductors photocatalysts for example TiO_2 , CdS , In_2S_3 , CuO , CeO_2 , WO_3 , ZnO , ZrO_2 , SnO_2 , Fe_2O_3 , Sb_2S_3 , AgO , CoS_2 , CdO , and In_2O_3 have been extensively considered for the elimination of organic contaminants [62,71,72]. Cerium(IV) oxide (CeO_2) is used as a key component in catalysts used in the reduction of hydrocarbon emission [73]. As a result of the great surface area available for adsorption, metal oxide nanoparticles show higher photocatalytic activity [68]. ZnO has strong oxidizing power to photogenerated holes because of its valence band position hence very efficient for the photodegradation of several bio-recalcitrant organic compounds [74].

Among the metal oxide photocatalysts, TiO_2 was the first photocatalyst to be discovered, so it has received the most attention in photocatalytic research [63]. The wide utilization and extensive study of TiO_2 are due to its strong oxidizing activity, non-selectivity, non-toxicity, cost-saving, chemical inertness, and good stability against photo corrosion [46,64]. Although TiO_2 has several advantages, its practical application still faces some drawbacks. It has a wide bandgap enabling it to only respond to UV light accounting for only ca. 3 to 5% of the solar hence limiting the utilization of solar as well as its small quantum efficacy attributable to the strong tendency of electron-hole pairs recombination [37,64,75]. Besides metal oxides, metal sulfides semiconductors have also received numerous attention due to their suitable CB and VB location and high sensitivity to visible light. Unfortunately, their poor photostability and photo

corrosion of sulfur ions cause secondary pollution of heavy metal ions [71]. Therefore, alternative photocatalytic materials are highly necessary and desirable.

To overcome these limitations associated with metal oxides and sulfides, several strategies such as doping nonmetal and metal elements, the combination of semiconductor photocatalysts, and surface functionalization have been used to increase the application effectiveness of these photocatalysts in the visible region [76]. The photocatalyst developed should have high stability, low cost, high efficiency, and low toxicity [70]. The photocatalyst should show incredible photocatalysis in the oxidative removal of organic contaminants/substrates to result in complete mineralization giving much safer inorganic products such as water and carbon dioxide when exposed to the visible region of the electromagnetic spectrum. BiOM (M = Cl, Br, I) materials are promising photocatalysts and have thus attracted much attention in recent years.

2.7.3.3.3 Bismuth oxyhalides (BiOM (M = Cl, Br, I))

The layered BiOMs semiconductor compounds crystallize to form a tetragonal matlockite. This layering within the structure form an asymmetric tetrahedral symmetry (M-Bi-O-Bi-M) with every bismuth atom bordered by a halogen and four oxygen atoms [77]. Due to this arrangement, BiOM possesses outstanding characteristics for instance catalytic features, optical, electrical, and mechanical. Hence, BiOMs have been utilized in organic synthesis, purification of indoor-gas, splitting of water, and photocatalytic removal of organic contaminants in wastewater [78].

The p-type semiconductor bismuth oxychloride (BiOCl) possesses remarkable electrical, optical, ionic conduction, and catalytic properties. BiOCl consists of bismuth ions (Bi^{3+}), chloride ions (Cl^-), and oxygen ions (O_2^-) which form $[\text{Cl-Bi-O-Bi-Cl}]$ in the tetragonal design with chlorine atoms held by non-bonding attractions along the c-axis. The four Bi-O and four Bi-Cl bonds are connected to Bi in the center of the structure, forming a tetragonal pyramid phase opposite to each other. The experimental bandgap of BiOCl ranges from 3.1 to 3.5 eV whereas 2.8 to 2.9 eV is the theoretical range, thus BiOCl is only active within the UV range [79].

The p-type semiconductor bismuth oxybromide (BiOBr) nanoparticles is a photocatalyst with outstanding chemical stability, optical properties, and efficient photocatalytic properties. Bismuth oxybromide (BiOBr) have indirect bandgap and layered tetragonal structure with high visible light active effective separation of electrons-hole (e^-/h^+) ability hence high ability of pollutant removal [78]. The Bismuth oxyiodide (BiOI) tetragonal structure is stacked with alternating $[Bi_2O_2]^{2+}$ and I slabs. It has a narrow bandgap between 1.6 to 1.9 eV suitable for visible light photocatalytic applications. The successful application of BiOI in some photocatalytic processes such as degradation of organic contaminants, hydrogen production, and CO_2 conversion is due to its resilient intralayer and interlayer bonding (weak van der Waals) hence high separation of photoexcited e^- and h^+ [80].

From Figure 8, it can be shown that there is an increasing trend in the interest to study bismuth oxy-halides (BiOM (M = Cl Br, I)) photocatalysts. BiOM has benefited from its exceptional layered structures and its complex band structures. The incorporation of $[Bi_2O_2]$ slabs into binary halogen atom slabs make the BiOM exhibit relaxed layered structures. The photocatalyst-layered structure can provide it sufficient space to separate the corresponding atoms that can excite the generation of the internal electric field (IEF) among $[Bi_2O_2]$ and the halogen slab. The separation and migration of photo-generated e^-/h^+ pairs are accelerated by induced IEF thus improving the BiOM photocatalytic activities [81]. Many bismuth-based photocatalysts like $Bi_2W_2O_6$, $BiVO_4$, $BiPO_4$, Bi_xTO_y , Bi_2O_3 , and $BiOCl$ have been reported [82]. From the traditional investigations, BiOM has been considered as catalysts, materials storage, and ferroelectric. Nevertheless, these compounds have displayed some promising photocatalytic aptitudes of organic dyes [83]. BiOM-based photocatalysts have a higher photocatalytic activity under visible light compared to TiO_2 and they are comparatively convenient to synthesize. By compositing bismuth oxy-halide with other different materials, there is an increasing photocatalytic activity of the material [84].

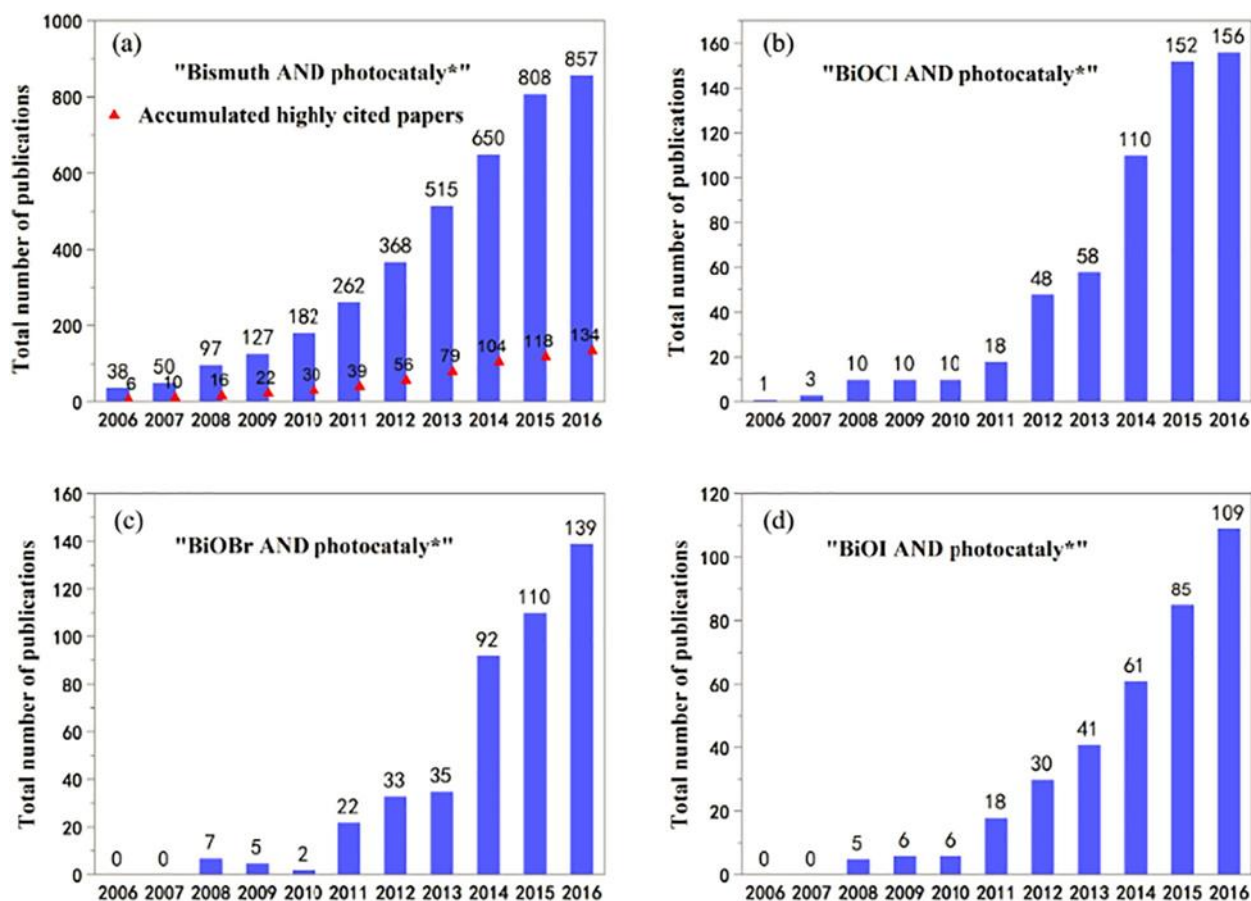


Figure 8. Yearly publications on (a) bismuth-based photocatalysts, (b) BiOCl, (c) BiOBr, and (d) BiOI photocatalysts. (Reprinted with permission from ref. [81]. Copyright (2018) Elsevier.

2.7.3.3.4 Modifications of BiOM photocatalysts

Although BiOM exhibits excellent photocatalytic activity, its photocatalytic efficacy is still generally low and making it far from real-world applications in terms of the utilization of solar energy. Several modification methods such as doping, surface plasmon resonance, dehalogenation, coupling, and solid solutions, have been applied to improve the charge separation and solar light-harvesting of BiOM, thus enhancing their photocatalytic performance [85,86]. These modification methods have successfully enhanced the photocatalytic activity of BiOM in remediating the environment and conserving solar energy. This study seeks to investigate how the modification through the formation of solid solutions will influence the photocatalytic ability of bismuth oxy-halides.

2.8.3.3.5 Synthesis of Solid solutions

Apart from doping that involves the introduction of foreign atoms into a structure, thus isolating their energy states above VB or below CB, the formation of a solid solution easily allows the engineering of photocatalysts band gaps. In solid solution, bandgaps can easily be adjusted by decreasing the CB level and/or increasing the VB level, this modification will tailor the electronic structures to maximize their photocatalytic performance. Unlimited solubility has been reported between BiOM semiconductors [87], offering the possibility of performing theoretical calculations demonstrating the alloying effect in the BiOM – BiON (M, N = Cl, Br, I)) solid solutions. Additionally, e^-/h^+ recombination is considerably reduced [88]. Until now, several solid solution photocatalysts such as $\text{BiOCl}_{1-m}\text{Br}_m$, $\text{BiOCl}_m\text{Br}_{1-m}$, and $\text{BiOCl}_{1-m}\text{I}_m$ [89-91] have been synthesized by various synthetic methods/routes. Table 3 represents the examples of solid solutions and their corresponding photocatalytic applications.

Table 3. Recent studies on solid solutions and their corresponding photocatalytic applications

Solid solutions	Synthetic method	Model contaminant	Photocatalytic results	Ref.
$m\text{BiOBr}-(1-m)\text{BiOI}$	Soft chemical method	MO decomposition under UV-light and visible light	5.8 times higher MO removal rate than P25 (Vis)	[92]
3D Flowerlike $\text{BiOCl}_m\text{Br}_{1-m}$	Precipitation	Removal of aqueous RhB under visible light	Total decomposition of aqueous RhB solution within 120 s	[93]
$\text{BiOBr}_m\text{I}_{1-m}$	Alcoholysis method	Removal of RhB under irradiation from artificial sunlight	$\text{BiOBr}_{0.75}\text{I}_{0.25}$ is about 15.1 times greater than BiOI and 3.4 times higher than BiOBr	[94]
$\text{BiO}(\text{Cl}_m\text{Br}_{1-m})$	Simple hydrothermal method	Removal of RhB under visible light.	$\text{BiO}(\text{Cl}_{0.5}\text{Br}_{0.5})$ showed 3.15 times greater reactivity than P25.	[95]

$\text{BiOCl}_m\text{Br}_n\text{I}_z$ ($m + n + z = 1$)	Hydrolysis method	Removal of MO under visible light	8.5, 2, and 3 times than that of individual BiOCl , BiOBr , and BiOI	[96]
Ultrathin 2D $\text{BiOBr}_m\text{I}_{1-m}$	Hydrothermal method.	Removal of 4-chlorophenol (4-CP)	90.2% of 4-CP can be removed after 30 min irradiation $\text{BiOBr}_{0.85}\text{I}_{0.15}$ nanoplates	[97]
Bismuth-rich $\text{Bi}_4\text{O}_5\text{Br}_m\text{I}_{2-m}$	Hydrothermal method	Photocatalytic CO_2 conversion and Cr (VI) removal under irradiation of visible light	$\text{Bi}_4\text{O}_5\text{BrI}$ was 8.4 times than individual $\text{Bi}_4\text{O}_5\text{Br}_2$ and 1.4 times than individual $\text{Bi}_4\text{O}_5\text{I}_2$	[98]
$\text{BiOBr}_m\text{Cl}_{1-m}$	Simple precipitation method	Photocatalytic reduction of CO_2	$\text{BiOBr}_{0.6}\text{Cl}_{0.4}$ was 7.5 times than individual BiOCl and 10.2 times than pure BiOBr	[99]

2.8 Applications of BiOM Photocatalysts

Many reports have been presented on the study of the application of bismuth oxyhalides for environmental remediation. However, there is still minimal investigation of the industrial application. The summary of the BiOM photocatalysis background is given in the sections below.

2.8.1 Environmental Application of BiOM Photocatalysts

The studies on the degradation of organic pollutants such as industrial effluents, pharmaceuticals, and dyes using BiOM have been previously reported [85,86,100-107]. It is established that the superoxide radicals and holes are the elementary active species that facilitate the photocatalytic performance of BiOM [100,105,106].

The application of BiOM for remediating the environment was first reported by Zhang *et al.*, [79] group. They demonstrated that under irradiation of 365 nm, the photodegradation of methyl orange dye solution over BiOCl was higher than Degussa P25 TiO₂ [79]. They calculated the electronic structure and showed that in BiOCl, Cl 3p orbitals were the highest occupied molecular orbitals, while Bi 6p orbitals were the lowest unoccupied unit orbitals [79]. After Zhang *et al.*, report, Lei *et al.*, [108] later reported on the photocatalytic removal of methylene blue, ethylene violet, and rhodamine B over BiOCl. The photocatalytic performance was majorly dependent on the morphology, where the highest rate of degradation was presented by the catalysts with flower-like microspheres under 254 nm irradiation [108]. From the photocatalytic evaluation of BiOBr and BiOCl microspheres for the removal of ibuprofen under irradiation from visible light, the authors established that adsorption was the major contributing factor for the enhanced removal of ibuprofen [109,110]. The synthesized BiOCl_{0.875}Br_{0.125} as a novel photocatalyst was found to remove pharmaceuticals like bezafibrate, propranolol, and ibuprofen under simulated solar irradiation [111].

Several reports have been presented on the use of BiOI for water treatment and environmental remediation. Wang *et al.*, [112] synthesized BiOI nanoplates and evaluated its photocatalytic ability towards the degradation of phenol and methyl orange [112]. The radical scavenging experiments revealed that superoxide radicals and holes were the primary active species responsible for the observed photocatalytic performance [112]. Under photocatalytic conditions of visible light, the application of ionic liquid-modified BiOI was demonstrated to be effective in degrading methyl orange [113]. The radical scavenging experiments revealed that the elementary species liable for the photocatalytic activity were the h⁺ radicals, the authors further established that modification through ionic liquid acted as an electron trap (Figure 9) [113].

When the ratios of Bi: O: I is varied and the hydrothermal temperature changed during the synthesis of BiOI, a series of BiOI compounds with varying bandgap energies ranging from 1.86 to 3.32 eV are obtained. High iodine content results in a smaller bandgap. The authors established that superoxide radicals were the key species involved in the photodegradation of crystal violet dye [114]. Hao *et al.*, [104] reported, the usage of polyvinylpyrrolidone (PVP) as a directing agent during the synthesis of BiOI, the microspheres obtained were found to be

effective in degrading tetracycline under irradiation from visible light. Thus, this demonstrates that BiOI is a potential candidate for the removal of persistent organic contaminants [104].

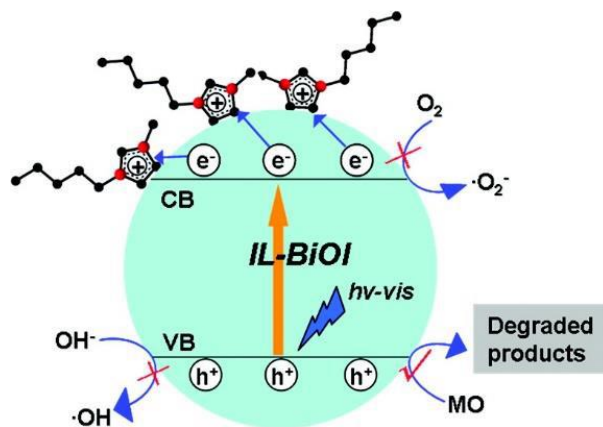


Figure 9. Schematic illustration of the degradation of methyl orange over modified BiOI. Reprinted (adapted) from [113], copyright (2011), with permission from the American Chemical Society.

2.8.2 Industrial Applications of BiOM Photocatalysts

Up to date, the industrial application of BiOM materials is still limited. The industrial application of TiO_2 and BiOM for cyclohexane selective oxofunctionalization in water with O_2 was first demonstrated by Henriquez *et al.*, [115]. The products obtained from the use of both photocatalysts were cyclohexanol and cyclohexanone. Figure 10 illustrates the reaction pathways for the oxidation of cyclohexane over the photocatalysts. These proposed reaction mechanisms suggest that the reaction involving the cyclohexane oxidation is initiated by an e^-/h^+ in the VB of the photocatalyst. Hence, the formation of cyclohexyl radicals on the surface of the photocatalyst which reacts with oxygen species to generate the ultimate oxidized products.

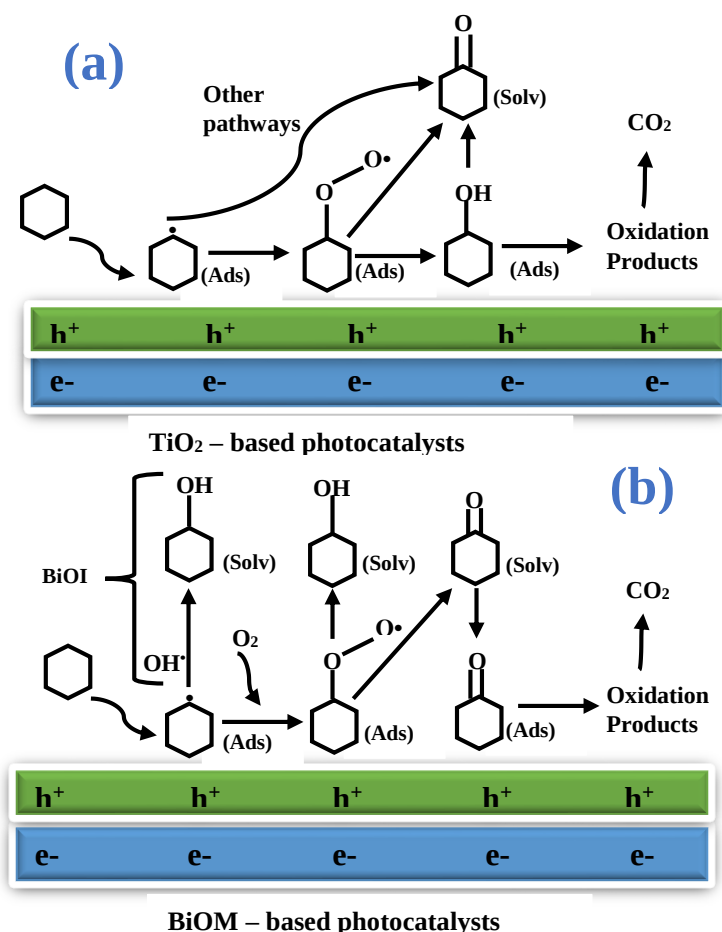


Figure 10. The suggested oxidation mechanism for cyclohexane over (a) TiO₂ and (b) BiOM photocatalysts. (Reprinted with permission from ref. [115]. Copyright (2017) Elsevier.

2.9 Knowledge gaps

From the reviewed literature, effective treatment of textile wastewater characterized by a high concentration of organic dyes has been reported to be very challenging. Biological techniques have been employed for the removal of these organic dyes, unfortunately, owing to the bio recalcitrant nature of these dyes; the biological technique is ineffective. Other treatment approaches such as adsorption and flocculation/coagulation have also been applied for textile wastewater treatment. However, these methods despite being effective are expensive and can lead to secondary pollution. Moreover, adsorption is unable to fully eliminate the contaminant, but only transform it from one form to another. Heterogeneous photocatalysis, which involves

the use of semiconductor photocatalysts, can be used to completely mineralize organic dyes. This technique has shown remarkable success in the removal of organic dyes and it was adopted for this study.

Physical, biological, and chemical approaches such as ionothermal, sol-gel, solvothermal, co-precipitation, hydrolysis, and reverse micro-emulsion are some of the methods that have been recently used in the fabrication of nanomaterials [116,117]. However, among these methods, the hydrothermal method has been extensively used in the preparation of BiOM because of its versatility and capability to regulate the shape and size of the particle, and crystallinity by regulating the hydrothermal operational conditions [117]. The major focus of this research project is to develop bismuth oxy-halide ($\text{BiOBr}_m\text{I}_{(1-m)}$) solid solutions for environmental and industrial applications. Chapter 3 gives an overview of the methods, material, experimental setup, and experimental procedure involved in the preparation of $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions. The techniques used for characterization of the material are also described as well as the description of the photocatalytic performance of the prepared materials. In this work, hydrothermal was used to synthesize $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions and the photocatalytic performance was tested through the degradation of MB dye

References

1. C. S. Meena Palaniappan, Peter H. Gleick, Lucy Allen, Michael J. Cohen, Juliet Christian-Smith, *Clearing the Waters over A focus on water quality solutions.*, vol. 96, p. 36. 2010.
2. N. R. N. Yusoff, "Photolytic Degradation of Acephate, Glyphosate, and Malathion," *Brunel Univ. Inst. Environ.*, p 20-70. April 2013.
3. K. M. Mezughi, "Heterogeneous photocatalytic degradation of organic pollutants in water over nanoscale powdered titanium dioxide," *Univ. Bradford Open Access*, p. 114-190, 2010. Available: <http://hdl.handle.net/10454/4865>.
4. J. Campo and Y. Picó, *Chapter 10: Emerging Contaminants*, vol. 68. Elsevier, p. 111-234, 2015.
5. L. Wang, W. Ben, Y. Li, C. Liu, and Z. Qiang, "Behavior of tetracycline and macrolide antibiotics in activated sludge process and their subsequent removal during sludge reduction by ozone," *Chemosphere*, vol. 206, pp. 184–191, 2018.
6. A. Gogoi, P. Mazumder, V. K. Tyagi, G. G. Tushara Chaminda, A. K. An, and M. Kumar, "Occurrence and fate of emerging contaminants in the water environment: A review," *Groundw. Sustain. Dev.*, vol. 6, no. January, pp. 169–180, 2018.
7. M. Taheran, M. Naghdi, S. K. Brar, M. Verma, and R. Y. Surampalli, "Emerging contaminants: Here today, there tomorrow!," *Environ. Nanotechnology, Monit. Manag.*, vol. 10, no. May, pp. 122–126, 2018.
8. S. Sakthivel, M. V Shankar, M. Palanichamy, B. Arabindoo, D. W. Bahnemann, and V. Murugesan, "Enhancement of photocatalytic activity by metal deposition : characterization and photonic efficiency of Pt, Au, and Pd deposited on TiO₂ catalyst," *Water Res.*, vol. 38, pp. 3001–3008, 2004, doi: 10.1016/j.watres.2004.04.046.
9. R. Vinu, S. U. Akki, and G. Madras, "Investigation of dye functional group on the photocatalytic degradation of dyes," *J. Hazard. Mater. J.*, vol. 176, pp. 765–773, 2010, doi: 10.1016/j.jhazmat.2009.11.101.
10. D. Ayodhya and G. Veerabhadram, "A review on recent advances in photodegradation of dyes using doped and heterojunction based semiconductor metal sul fi de nanostructures for environmental protection," *Mater. Today Energy*, vol. 9, no. May,

- pp. 83–113, 2018, doi: 10.1016/j.mtener.2018.05.007.
11. G. Guo, X. Li, F. Tian, T. Liu, F. Yang, K. Ding, C. Liu, J. Chen, C. Wang. “Azo dye decolorization by a halotolerant consortium under microaerophilic conditions,” *Chemosphere*, vol. 244, p. 125-510, 2020, doi: 10.1016/j.chemosphere.2019.125510.
 12. K. Klaus, “Pharmaceuticals in the Environment,” p. 4-56, 2010, doi: 10.1146/annurev-environ-052809-161223.
 13. P. G. W. Bauer, H. Berneth, T. Clausen, A. Engel, M. Filosa, *Industrial Dyes*. p. 10-67 2003.
 14. S. Arora, “Textile Dyes : Its Impact on Environment and its Treatment,” *J. Bioremediation Biodegrad.*, vol. 5, no. 3, p. 61-99, 2014, doi: 10.4172/2155-6199.1000e146.
 15. Y. C. Wong, Y. S. Szeto, W. H. Cheung, and G. McKay, “Adsorption of acid dyes on chitosan - Equilibrium isotherm analyses,” *Process Biochem.*, vol. 39, no. 6, pp. 695–704, 2004, doi: 10.1016/S0032-9592(03)00152-3.
 16. Z. Carmen and S. Daniel, “Textile Organic Dyes – Characteristics, Polluting Effects and Separation/Elimination Procedures from Industrial Effluents – A Critical Overview,” *Org. Pollut. Ten Years After Stock. Conv. - Environ. Anal. Updat.*, 2012, doi: 10.5772/32373.
 17. G. A. R. de Oliveira, D. M. Leme, J. de Lapuente, L. B. Brito, C. Porredón, L. de Brito Rodrigues, N. Brull, J. T. Serret, M. Borràs, G. R. Disner, M. M. Cestari, D. P. de Oliveira “A test battery for assessing the ecotoxic effects of textile dyes,” *Chem. Biol. Interact.*, vol. 291, no. February, pp. 171–179, 2018, doi: 10.1016/j.cbi.2018.06.026.
 18. IHS Inc., “Chemical Economics Handbook,” *IHS Markit*, no. July, pp. 1–2, 2018, doi: 608.50000.
 19. Md. Aminul Islama, Imran Alic, S.M. Abdul Karimb, Md. Shakhawat Hossain Firoz, Al-Nakib Chowdhury, David W. Mortona, Michael J. Angove “Removal of dye from polluted water using novel nano manganese oxide-based materials,” *J. Water Process Eng.*, vol. 32, no. June, p. 100-911, 2019, doi: 10.1016/j.jwpe.2019.100911.
 20. B. Mu, L. Liu, W. Li, and Y. Yang, “A water/cottonseed oil bath with controllable dye sorption for high dyeing quality and minimum discharges,” *J. Clean. Prod.*, vol. 236, p. 117-566, 2019, doi: 10.1016/j.jclepro.2019.07.041.
 21. Ji Wu, Qimeng Li, Wentao Li, Yan Li, Guoxiang Wang b, Aimin Li, Haibo L. “Efficient

- removal of acid dyes using permanent magnetic resin and its preliminary investigation for advanced treatment of dyeing effluents,” *J. Clean. Prod.*, vol. 251, p. 119694, 2020, doi: 10.1016/j.jclepro.2019.119694.
22. K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani, and S. Pattabhi, “Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions,” *Bioresour. Technol.*, vol. 87, no. 1, pp. 129–132, 2003, doi: 10.1016/S0960-8524(02)00201-8.
 23. Thalles M.F. Marques, Débora A. Sales, Lucinaldo S. Silva, Roosevelt D.S. Bezerra, Mateus S. Silva, Josy A. Osajima, Odair P. Ferreira, Anupama Ghoshe, Edson C. Silva Filho, Bartolomeu C. Vianab, José M.E. Matosh “Amino-functionalized titanate nanotubes for highly efficient removal of anionic dye from aqueous solution,” *Appl. Surf. Sci.*, vol. 512, no. February, p. 145659, 2020, doi: 10.1016/j.apsusc.2020.145659.
 24. G. Oros, E. Forgacs, and T. Cserha, “Removal of synthetic dyes from wastewaters : a review,” *Environ. Int.*, vol. 30, pp. 953–971, 2004, doi: 10.1016/j.envint.2004.02.001.
 25. Aminul Islama, Imran Alic, S.M. Abdul Karimb, Md. Shakhawat Hossain Firoz, Al-Nakib Chowdhury, David W. Mortona, Michael J. Angove “Removal of dye from polluted water using novel nano manganese oxide-based materials,” *J. Water Process Eng.*, vol. 32, no. July, p. 100911, 2019, doi: 10.1016/j.jwpe.2019.100911.
 26. A. ’t M. Tania Carreón-Valencia, King-Thom Chung, Silvia de Sanjosé, Harold S Freeman, Shoji Fukushima, Charles William Jameson, “IARC Monographs on the Evaluation of Carcinogenic Risks of Some Aromatic Amines, Organic Dyes, and Related Exposures to Humans,” vol. 99, p 34-112, 2010.
 27. M. S. G. Ahmet Gürses, Metin Açıkyıldız, Kübra Güneş, *Dyes and Pigments*. Springer, p. 13-29, 2016.
 28. C. Belpaire, T. Reyns, C. Geeraerts, J. Van Loco, M. Green, and C. Violet, “Toxic textile dyes accumulate in the wild European eel *Anguilla anguilla* highlights,” *Chemosphere*, vol. 138, pp. 784–791, 2015, doi: 10.1016/j.chemosphere.2015.08.007.
 29. Zaharia Carmen and Daniela Suteu. Organic pollutants ten years after the – environmental and analytical update *Edited by Tomasz Puzyn*. p. 55-86, 2012.
 30. B. Zhao, Z. Zhu, X. D. Qin, Z. Li, and H. Zhang, “Highly efficient and stable CuZr-based metallic glassy catalysts for azo dye degradation,” *J. Mater. Sci. Technol.*, vol.

- 46, pp. 88–97, 2020, doi: 10.1016/j.jmst.2019.12.012.
31. L. Yang, Y. Liu, C. Liu, Y. Fu, and F. Ye, “A cationic metal-organic framework for dye adsorption and separation based on column-chromatography,” *J. Mol. Liq.*, vol. 300, no. 3, p. 112311, 2019, doi: 10.1016/j.molliq.2019.112311.
 32. S. Noreen, H. Nawaz, M. Iqbal, F. Hussain, and F. Malik, “International Journal of Biological Macromolecules Chitosan, starch, polyaniline and polypyrrole biocomposite with sugarcane bagasse for the efficient removal of Acid Black dye,” *Int. J. Biol. Macromol.*, vol. 147, pp. 439–452, 2020, doi: 10.1016/j.ijbiomac.2019.12.257.
 33. A. Sonune and R. Ghate, “Developments in wastewater treatment methods,” *Desalination*, vol. 167, no. February, pp. 55–63, 2004, doi: doi: 10.1016/3.desal.2004.06.113.
 34. M. Samer, “Wastewater Treatment Engineering,” no. October, p. 210, 2015, doi: 10.5772/59384.
 35. A. E. Ghaly, R. Ananthashankar, M. Alhattab, and V. V Ramakrishnan, “Chemical Engineering & Process Technology Production, Characterization, and Treatment of Textile Effluents : A Critical Review,” *Chem. Eng. Process Technol.*, vol. 5, no. July, p. 2-18, 2013, doi: 10.4172/2157-7048.1000182.
 36. G. Crini, “Non-conventional low-cost adsorbents for dye removal : A review,” *Bioresour. Technol.*, vol. 97, no. June, pp. 1061–1085, 2005, doi: 10.1016/j.biortech.2005.05.001.
 37. G. Singh, M. Sharma, and R. Vaish, “Exploring the piezocatalytic dye degradation capability of lithium niobate,” *Adv. Powder Technol.*, pp. In press, 2020, doi: 10.1016/j.appt.2020.01.031.
 38. G. Libralato, G. Lofrano, A. Siciliano, E. Gambino, G. Boccia, C. Federica, A. Francesco, E. Galdiero, R. Gesuele, M. Guida. 8 - *Toxicity assessment of wastewater after advanced oxidation processes for emerging contaminants*; degradation & lowast; Elsevier Inc., p. 195-211, 2020.
 39. M. Navgire, A. Yelwande, D. Tayde, B. Arbad, and M. Lande, “Photodegradation of Molasses by a MoO₃-TiO₂ Nanocrystalline Composite Material,” *Chinese J. Catal.*, vol. 33, no. 2–3, pp. 261–266, 2012.
 40. J. Khatri, P. V Nidheesh, T. S. A. Singh, and M. S. Kumar, “Advanced oxidation

- processes based on zero-valent aluminum for treating textile wastewater,” *Chem. Eng. J.*, vol. 348, no. February, pp. 67–73, 2018, doi: 10.1016/j.cej.2018.04.074.
41. M. Gałol, A. Przyjazny, and G. Boczkaj, “Wastewater treatment through advanced oxidation processes based on cavitation – A review,” *Chem. Eng. J.*, vol. 338, no. September 2017, pp. 599–627, 2018, doi: 10.1016/j.cej.2018.01.049.
 42. S. N. Malik, P. C. Ghosh, A. N. Vaidya, and S. N. Mudliar, “Journal of Water Process Engineering Hybrid ozonation process for industrial wastewater treatment : Principles and applications : A review,” *J. Water Process Eng.*, vol. 35, no. October 2018, 2020, doi: 10.1016/j.jwpe.2020.101193.
 43. E. T. Anthony, M. O. Ojemaye, O. O. Okoh, and A. I. Okoh, “A critical review on the occurrence of resistors in the environment and their removal from wastewater using apposite treatment technologies: Limitations, successes and future improvement,” *Environ. Pollut.*, vol. 263, p. 113791, 2020, doi: 10.1016/j.envpol.2019.113791.
 44. S. S. Moghaddam, M. R. A. Moghaddam, and M. Arami, “Coagulation/flocculation process for dye removal using sludge from water treatment plant : Optimization through response surface methodology,” *J. Hazard. Mater.*, vol. 175, no. October, pp. 651–657, 2009, doi: 10.1016/j.jhazmat.2009.10.058.
 45. K. G. Pavithra, P. S. Kumar, V. Jaikumar, and P. S. Rajan, “Removal of colorants from wastewater: A review on sources and treatment strategies,” *J. Ind. Eng. Chem.*, vol. 75, no. March, pp. 5–19, 2019.
 46. X. Z. Tong Zhang, Xiaoguang Wang, “Recent Progress in TiO₂-Mediated Solar Photocatalysis for Industrial Recent Progress in TiO₂ -Mediated Solar Photocatalysis for Industrial Wastewater Treatment,” *Int. J. Photoenergy*, vol. 2014, no. July, p. 12, 2014, doi: 10.1155/2014/607954.
 47. T. Ahmad, T. Belwal, L. Li, S. Ramola, R. Muhammad, A. Abdullah, Y. Xu, L. Zisheng. “Trends in Food Science & Technology Utilization of wastewater from the edible oil industry, turning waste into valuable products : A review,” *Trends Food Sci. Technol.*, vol. 99, no. February, pp. 21–33, 2020, doi: 10.1016/j.tifs.2020.02.017.
 48. A. Tkaczyk, K. Mitrowska, and A. Posyniak, “Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review,” *Sci. Total Environ.*, vol. 717, p. 137222, 2020, doi: 10.1016/j.scitotenv.2020.137222.

49. A. Gnanaprakasam, V. M. Sivakumar, P. L. Sivayogavalli, and M. Thirumarimurugan, "Ecotoxicology and Environmental Safety Characterization of TiO₂ and ZnO nanoparticles and their applications in photocatalytic degradation of azodyes," *Ecotoxicol. Environ. Saf.*, vol. 121, pp. 121–125, 2015, doi: 10.1016/j.ecoenv.2015.04.043.
50. V. Vaiano and G. Iervolino, "Journal of Colloid and Interface Science Facile method to immobilize ZnO particles on glass spheres for the photocatalytic treatment of tannery wastewater," *J. Colloid Interface Sci.*, vol. 518, no. February, pp. 192–199, 2018, doi: 10.1016/j.jcis.2018.02.033.
51. S. Hisaindee, M. A. Meetani, and M. A. Rauf, "Trends in Analytical Chemistry Application of LC-MS to the analysis of advanced oxidation process (AOP) degradation of dye products and reaction mechanisms," *TRENDS Anal. Chem.*, vol. 49, pp. 31–44, 2013, doi: 10.1016/j.trac.2013.03.011.
52. P. V Nidheesh, M. Zhou, and M. A. Oturan, "Chemosphere An overview on the removal of synthetic dyes from water by electrochemical advanced oxidation processes," *Chemosphere*, vol. 197, pp. 210–227, 2018, doi: 10.1016/j.chemosphere.2017.12.195.
53. C. Bouasla, M. E. H. Samar, and F. Ismail, "Degradation of methyl violet 6B dye by the Fenton process," *Desalination*, vol. 254, no. 1–3, pp. 35–41, 2010, doi: 10.1016/j.desal.2009.12.017.
54. S. Garcia-segura *et al.*, "Electrochimica Acta Comparative decolorization of monoazo , diazo and triazo dyes by electro-Fenton process," *Electrochim. Acta*, vol. 58, no. September, pp. 303–311, 2011, doi: 10.1016/j.electacta.2011.09.049.
55. M. Liu, H. Zhu, B. Dong, Y. Zheng, and S. Yu, "Submerged nanofiltration of biologically treated molasses fermentation wastewater for the removal of melanoidins," *Chem. Eng. J.*, vol. 223, no. March, pp. 388–394, 2013, doi: 10.1016/j.cej.2013.02.107.
56. S. Amat, M. Saisriyoot, A. Thanapimmetha, and P. Srinophakun, "Decolorization and COD reduction of wastewater from ethanol production by Fenton oxidation," *26th Annual Meet. of the Thai Soc. Biotechnol. Int. Conf.*, pp. 417–423, 2014.
57. K. Paździor, L. Bilińska, and S. Ledakowicz, "A review of the existing and emerging technologies in the combination of AOPs and biological processes in industrial textile wastewater treatment," *Chem. Eng. J.*, vol. 376, no. December, p. 120597, 2018, doi:

- 10.1016/j.cej.2018.12.057.
58. A. Asghar, A. Aziz, A. Raman, W. Mohd, and A. Wan, "Advanced oxidation processes for in-situ production of hydrogen peroxide / hydroxyl radical for textile wastewater treatment : a review," *J. Clean. Prod.*, vol. 87, no. September, pp. 826–838, 2014, doi: 10.1016/j.jclepro.2014.09.010.
 59. G. Boczkaj and A. Fernandes, "Wastewater treatment through advanced oxidation processes at basic pH conditions : A review," *Chem. Eng. J.*, vol. 320, pp. 608–633, 2017, doi: 10.1016/j.cej.2017.03.084.
 60. G. Sigge, "Investigating the Effect of Ozone on the Biodegradability of Distillery Wastewater," *South African J. Enol. Vitic.*, vol. 28, no. July, pp. 155–162, 2007, doi: 10.21548/28-2-1469.
 61. J. J. Rueda-Marquez, I. Levchuk, P. Fernández Ibañez, and M. Sillanpää, "A critical review on application of photocatalysis for toxicity reduction of real wastewaters," *J. Clean. Prod.*, vol. 258, p. 120694, 2020, doi: 10.1016/j.jclepro.2020.120694.
 62. R. Ameta, M. S. Solanki, S. Benjamin, and S. C. Ameta, *CHAPTER 6: Photocatalysis*. Elsevier Inc., p. 10-20, 2018.
 63. A. Fujishima and K. Honda, "Electrochemical Photolysis of Water at a Semiconductor Electrode One and Two-dimensional Structure of Alpha-Helix and Beta-Sheet Forms of Poly (L-Alanine) shown by Specific Heat Measurements at Low Temperatures (1 . 5-20 K)," *Nature*, vol. 238, no. March, pp. 37–38, 1972, doi: 10.1038/239137a0.
 64. L. Qi, Y. Yang, P. Zhang, Y. Le, C. Wang, and T. Wu, "Hierarchical flower-like BiOI_xBr_(1-x) solid solution spheres with enhanced visible-light photocatalytic activity," *Appl. Surf. Sci.*, vol. 467–468, no. October, pp. 792–801, 2019.
 65. D. Chatterjee and S. Dasgupta, "Visible light-induced photocatalytic degradation of organic pollutants," *J. Photochem. Photobiol.*, vol. 6, no. May, pp. 186–205, 2005, doi: 10.1016/j.jphotochemrev.2005.09.001.
 66. U. G. Akpan and B. H. Hameed, "Parameters affecting the photocatalytic degradation of dyes using TiO₂-based photocatalysts: a review.," *J. Hazard. Mater.*, vol. 170, no. May, pp. 520–9, Oct. 2009.
 67. M. I. Litter, "Heterogeneous photocatalysis: Transition metal ions in photocatalytic systems," *Appl. Catal. B Environ.*, vol. 23, no. 2–3, pp. 89–114, Nov. 1999, doi:

- 10.1016/S0926-3373(99)00069-7.
68. S. Baruah, S. K. Pal, and J. Dutta, "Nanostructured Zinc Oxide for Water Treatment," *Nanosci. Nanotechnol.*, vol. 2, pp. 90–102, 2012.
69. A. Avci, V. Eskizeybek, H. Gülce, B. Haspulat, and Ö. S. Şahin, "ZnO-TiO₂ nanocomposites formed under submerged DC arc discharge: Preparation, characterization and photocatalytic properties," *Appl. Phys. A Mater. Sci. Process.*, vol. 116, no. 3, pp. 1119–1125, 2014, doi: 10.1007/s00339-013-8194-1.
70. J. Šíma and P. Hasal, "Photocatalytic degradation of textile dyes in aTiO₂/UV system," *Chem. Eng. Trans.*, vol. 32, no. 1999, pp. 79–84, 2013.
71. Luo-hong, Y. Zhu, B. Lei, Y. Li, W. Zhu, and Q. Li, "Trichromatic dyes sensitized HKUST-1 (MOF-199) as scavenger towards reactive blue 13 via visible-light photodegradation," *Inorg. Chem. Commun.*, vol. 94, no. May, pp. 27–33, 2018.
72. Adina Elena Segneanu, Cristina Orbeci, Carmen Lazau, Paula Sfirloaga, Paulina Vlazan, Cornelia Bandas, and Ioan Grozescu "Waste Water Treatment Methods," pp. 53–80, 2013, doi: <http://dx.doi.org/10.5772/53755>.
73. M. Fernández-garcia and J. A. Rodriguez, "Metal Oxide Nanoparticles," *Nanomater. Inorg. Bioinorg. Perspect.*, no. October, p. 60, 2007.
74. A. Hamrouni, N. Moussa, F. Parrino, A. Di, A. Houas, and L. Palmisano, "Journal of Molecular Catalysis A : Chemical Sol – gel synthesis and photocatalytic activity of ZnO – SnO₂ nanocomposites," *J. Mol. Catal. A Chem.*, vol. 390, no. April, pp. 133–141, 2014, doi: 10.1016/j.molcata.2014.03.018.
75. L. Wu, J. C. Yu, and X. Fu, "Characterization and photocatalytic mechanism of nanosized CdS coupled TiO₂ nanocrystals under visible light irradiation," *J. Mol. Catal. A Chem.*, vol. 244, no. 1–2, pp. 25–32, 2006, doi: 10.1016/j.molcata.2005.08.047.
76. X. Jin, L. Ye, H. Xie, and G. Chen, "Bismuth-rich bismuth oxyhalides for environmental and energy photocatalysis," *Coord. Chem. Rev.*, vol. 349, pp. 84–101, 2017.
77. H. Peng, C. K. Chan, S. Meister, X. F. Zhang, and Y. Cui, "Shape Evolution of Layer-Structured Bismuth Oxychloride Nanostructures via Low-Temperature Chemical Vapor Transport," no. 2, pp. 247–252, 2009.
78. Jun Zhang, Fengjun Shi, Jing Lin, Dongfeng Chen, Jianming Gao, Zhixin Huang, Xiaoxia Ding, and Chengcun Tang. "Self-assembled 3-D architectures of BiOBr as a

- visible-light-driven photocatalyst,” *Chem. Mater.*, vol. 20, no. 9, pp. 2937–2941, 2008.
79. K. L. Zhang, C. M. Liu, F. Q. Huang, C. Zheng, and W. D. Wang, “Study of the electronic structure and photocatalytic activity of the BiOCl photocatalyst,” *Appl. Catal. B Environ.*, vol. 68, no. 3–4, pp. 125–129, 2006.
 80. W. William, S. O. B. Oppong, O. B. Oppong, W. Anku, P. P. Govender, and P. Govender, “Bismuth-Based Nanoparticles as Photocatalytic Materials Materials,” 2018.
 81. Y. Yang, C. Zhang, C. Lai, G. Zeng, D. Huang, M. Cheng, J. Wang, F. Chen, C. Zhou, W. Xiong. “BiOX (X = Cl, Br , I) photocatalytic nanomaterials : Applications for fuels and environmental management,” *Adv. Colloid Interface Sci.*, vol. 254, pp. 76–93, 2018.
 82. X. Jin, L. Ye, H. Xie, and G. Chen, “Bismuth-rich bismuth oxyhalides for environmental and energy photocatalysis,” *Coord. Chem. Rev.*, vol. 349, pp. 84–101, 2017.
 83. Davinder S. Bhachu, Savio J.A. Moniz, Sanjayan Sathasivam, David O. Scanlon, Aron Walsh, Salem M. Bawaked, Mohamed Mokhtar, Abdullah Y. Obaid, Ivan P. Parkin, Junwang Tang, and Claire J. Carmalt. Bismuth Oxyhalides: Synthesis, Structure and Photoelectrochemical Activity “Chemical Science,” vol. 7, p. 8, 2016, doi: 10.1039/c6sc00389c.
 84. R. Bibi, Q. Shen, L. Wei, D. Hao, N. Li, and J. Zhou, “Hybrid BiOBr UiO-66-NH₂ composite with enhanced visible-light-driven photocatalytic activity toward RhB dye degradation,” *RSC Adv.*, vol. 8, no. 4, pp. 2048–2058, 2018, doi: 10.1039/c7ra11500h.
 85. Jun Di, Jiexiang Xi, Mengxia Ji, Sheng Yin, Hongping Li, Hui Xu, Qi Zhang, and Huaming Li. “Controllable synthesis of Bi₄O₅Br₂ ultrathin nanosheets for photocatalytic removal of ciprofloxacin and mechanism insight,” *J. Mater. Chem. A* vol. 3, no. 29, pp. 15108–15118, 2015.
 86. H. Cheng, B. Huang, and Y. Dai, “Engineering BiOX (X = Cl, Br, I) nanostructures for highly efficient photocatalytic applications,” *Nanoscale*, vol. 6, no. 4, pp. 2009–2026, 2014.
 87. P. Schultz and E. Keller, “A Strong Deviation from Vegard’s Rule: X-Ray Powder Investigations of the Three Quasi-Binary Phase Systems BiOX–BiOY (X, Y = Cl, Br, I),” *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.*, vol. 70, no. 2, pp. 372–378, 2014.
 88. H. Zhang, L. Liu, and Z. Zhou, “Towards better photocatalysts: First-principles studies

- of the alloying effects on the photocatalytic activities of bismuth oxyhalides under visible light,” *Phys. Chem. Chem. Phys.*, vol. 14, no. 3, pp. 1286–1292, 2012.
89. Y. Liu, W. J. Son, J. Lu, B. Huang, Y. Dai, and M. H. Whangbo, “Composition dependence of the photocatalytic activities of $\text{BiOCl}_{1-x}\text{Br}_x$ solid solutions under visible light,” *Chem. - A Eur. J.*, vol. 17, no. 34, pp. 9342–9349, 2011.
 90. H. Gnaïem and Y. Sasson, “Nanostructured 3D Sun flower-like Bismuth Doped $\text{BiOCl}_x\text{Br}_{1-x}$ Solid Solutions with Enhanced Visible Light Photocatalytic Activity as a Remarkably Efficient Technology for Water Purification,” 2015.
 91. Z. Y. Zhao, Q. L. Liu, and W. W. Dai, “Structural, electronic, and optical properties of $\text{BiOX}_{1-x}\text{Y}_x$ ($X, y = \text{F, Cl, Br, and I}$) solid solutions from DFT calculations,” *Sci. Rep.*, vol. 6, no. November 2015, pp. 4–12, 2016.
 92. W. Wang, F. Huang, X. Lin, and J. Yang, “Visible-light-responsive photocatalysts $x \text{ BiOBr} - (1-x) \text{ BiOI}$,” *Catal. Commun.*, vol. 9, pp. 8–12, 2008.
 93. H. Gnaïem and Y. Sasson, “Hierarchical nanostructured 3D flowerlike $\text{BiOCl}_x\text{Br}_{1-x}$ semiconductors with exceptional visible light photocatalytic activity,” *ACS Catal.*, vol. 3, no. 2, pp. 186–191, 2013.
 94. H. Y. Xu, X. Han, Q. Tan, X. L. He, and S. Y. Qi, “Structure-dependent photocatalytic performance of $\text{BiOBr}_{1-x}\text{I}_x$ nanoplate solid solutions,” *Catalysts*, vol. 7, no. 5, 2017.
 95. S. Shenawi-Khalil, V. Uvarov, Y. Kritsman, E. Menes, I. Popov, and Y. Sasson, “A new family of $\text{BiO}(\text{Cl}_x\text{Br}_{1-x})$ visible light-sensitive photocatalysts,” *Catal. Commun.*, vol. 12, no. 12, pp. 1136–1141, 2011.
 96. X. Sun, Y. Zhang, C. Li, Z. Zhang, Z. Peng, H. Si, J. Zhang, Y. Li. “ $\text{BiOCl}_x\text{Br}_y\text{I}_z(x + y + z = 1)$ solid solutions with controllable bandgap and highly enhanced visible-light photocatalytic performances,” *J. Alloys Compd.*, vol. 638, no. March, pp. 254–260, 2015.
 97. Q. Wang, Z. Liu, D. Liu, G. Liu, M. Yang, F. Cui, W. Wang. “Ultrathin two-dimensional $\text{BiOBr}_x\text{I}_{1-x}$ solid solution with rich oxygen vacancies for enhanced visible-light-driven photoactivity in environmental remediation,” *Appl. Catal. B Environ.*, vol. 236, no. March, pp. 222–232, 2018.
 98. Y. Bai, L. Ye, T. Chen, P. Wang, L. Wang, and X. Shi, “Synthesis of hierarchical bismuth-rich $\text{Bi}_4\text{O}_5\text{Br}_x\text{I}_{2-x}$ solid solutions for enhanced photocatalytic activities of CO_2

- conversion and Cr (VI) reduction under visible light,” *Applied Catal. B, Environ.*, vol. 203, pp. 633–640, 2017.
99. M. Gao, J. Yang, T. Sun, Z. Zhang, D. Zhang, H. Huang, H. Lin, Y. Fang, X. Wang “Persian buttercup-like $\text{BiOBr}_x\text{Cl}_{1-x}$ solid solution for photocatalytic overall CO_2 reduction to CO and O_2 ,” *Appl. Catal. B Environ.*, vol. 243, pp. 734–740, 2019.
 100. Y. Yu, C. Cao, H. Liu, P. Li, F. Wei, Y. Jiang, and W. Song. “A Bi/BiOCl heterojunction photocatalyst with enhanced electron-hole separation and excellent visible light photodegrading activity,” *J. Mater. Chem. A* vol. 2, no. 6, pp. 1677–1681, 2014.
 101. X. Jia, J. Cao, H. Lin, M. Zhang, X. Guo, and S. Chen, “Transforming type-I to type-II heterostructure photocatalyst via energy band engineering: A case study of I-BiOCl/I-BiOBr,” *Appl. Catal. B Environ.*, vol. 204, pp. 505–514, 2017.
 102. L. Ye, Y. Su, X. Jin, H. Xie, and C. Zhang, “Recent advances in BiOX (X = Cl, Br and I) photocatalysts: Synthesis, modification, facet effects, and mechanisms,” *Environ. Sci. Nano*, vol. 1, no. 2, pp. 90–112, 2014.
 103. Jun Di, Jiexiang Xia, Sheng Yin, Hui Xu, Li Xu, Yuanguo Xu, Minqiang He, and Huaming Li. “Preparation of sphere-like $\text{g-C}_3\text{N}_4/\text{BiOI}$ photocatalysts via a reactable ionic liquid for visible-light-driven photocatalytic degradation of pollutants,” *J. Mater. Chem. A* vol. 2, no. 15, pp. 5340–5351, 2014.
 104. R. Hao, X. Xiao, X. Zuo, J. Nan, and W. Zhang, “Efficient adsorption and visible-light photocatalytic degradation of tetracycline hydrochloride using mesoporous BiOI microspheres,” *J. Hazard. Mater.*, vol. 209–210, pp. 137–145, 2012.
 105. J. Di, J. Xia, M. Ji, B. Wang, S. Yin, Q. Zhang, Z. Chen, H. Li. “Advanced photocatalytic performance of graphene-like BN modified BiOBr flower-like materials for the removal of pollutants and mechanism insight,” *Appl. Catal. B Environ.*, vol. 183, pp. 254–262, 2016.
 106. F. Chen, Q. Yang, J. Sun, F. Yao, S. Wang, Y. Wang, X. Wang, X. Li, C. G. Niu, D. Wang, and G. Zeng “Enhanced Photocatalytic Degradation of Tetracycline by AgI/BiVO_4 Heterojunction under Visible-Light Irradiation: Mineralization Efficiency and Mechanism,” *ACS Appl. Mater. Interfaces*, vol. 8, no. 48, pp. 32887–32900, 2016.
 107. S. Gao, C. Guo, J. Lv, Q. Wang, Y. Zhang, S. Hou, J. Gao, J. Xu. A novel 3D

- hollow magnetic Fe₃O₄/BiOI heterojunction with enhanced photocatalytic performance for bisphenol A degradation, vol. 307. Elsevier B.V., 2017.
108. Y. Lei, G. Wang, S. Song, and H. Zhang, "Synthesis, characterization, and assembly of BiOCl nanostructure and their photocatalytic properties," *Cryst. Eng. Commun.*, vol. 11, pp. 1857–1862, 2009.
 109. J. Li, S. Sun, R. Chen, T. Zhang, and B. Ren, "Adsorption behavior and mechanism of ibuprofen onto BiOCl microspheres with exposed {001} facets," *Env. Sci Pollut Res*, vol. 24, pp. 9556–9565, 2017.
 110. Ian Li, S. Sun, C. Qian, L. He, K. K. Chen, T. Zhang, Z. Chen, M. Ye. "The role of adsorption in photocatalytic degradation of ibuprofen under visible light irradiation by BiOBr microspheres," *Chem. Eng. J. J.*, vol. 297, pp. 139–147, 2016.
 111. Y. Lester, D. Avisar, and H. Gnayem, "Demonstrating a New BiOCl_{0.875}Br_{0.125} Photocatalyst to Degrade Pharmaceuticals Under Solar Irradiation," *Water Air Soil Pollut*, vol. 225, p. 2132, 2014.
 112. Y. Li, J. Wang, H. Yao, L. Dang, and Z. Li, "Efficient decomposition of organic compounds and reaction mechanism with BiOI photocatalyst under visible light irradiation," *Journal Mol. Catal. A, Chem.*, vol. 334, no. 1–2, pp. 116–122, 2011.
 113. Y. Wang, K. Deng, and L. Zhang, "Visible light photocatalysis of BiOI and its photocatalytic activity enhancement by in situ ionic liquid modification," *J. Phys. Chem. C*, vol. 115, no. 29, pp. 14300–14308, 2011.
 114. W. W. Lee, C. S. Lu, C. W. Chuang, Y. J. Chen, J. Y. Fu, C. W. Siao, "Synthesis of Bismuth Oxyiodides and Their Composites: Characterization, Photocatalytic Activity, and Degraded Mechanisms," *RSC Adv.*, pp. 2– 17, 2015.
 115. A. Henríquez, H. D. Mansilla, A. Martínez, M. Cruz, J. Freer, and D. Contreras, "Selective oxofunctionalization of cyclohexane over titanium dioxide-based and bismuth oxyhalide (BiOX, X = Cl⁻, Br⁻, I⁻) photocatalysts by visible light irradiation," *Applied Catal. B, Environ.*, vol. 206, pp. 252–262, 2017.
 116. A. Gnanaprakasam, V. M. Sivakumar, and M. Thirumarimurugan, "Influencing Parameters in the Photocatalytic Degradation of Organic Effluent via Nanometal Oxide Catalyst : A Review," *Indian J. Mater. Sci.*, vol. 2015, no. September, p. 16, 2015, doi: 10.1155/2015/601827.

117. I.D. Sharma, Gagan Kant Tripathi, Vinod Kumar Sharma, Sandeep N. Tripathi, Rajnish Kurchania, Chander Kant, Amit Kumar Sharma, and K.K. Saini “One-pot synthesis of three bismuth oxyhalides (BiOCl, BiOBr, BiOI) and their photocatalytic properties in three different exposure conditions One-pot synthesis of three bismuth oxyhalides,” *Cogent Chem.*, vol. 43, no. 1, pp. 1–15, 2015, doi: 10.1080/23312009.2015.1076371.

CHAPTER 3

3. Materials and Methods

3.1 Introduction

This chapter presents a summary of the methods, material, experimental setup, and experimental procedure involved in the preparation of $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions. The techniques used for characterization of the material are also described as well as the description of the photocatalytic activities of the prepared materials. The hydrothermal method was used for the synthesis of the materials. Optical properties, functional groups, morphologies, surface areas, Raman vibrational modes, crystal structure, shapes, sizes, and distribution were determined through photocatalyst characterization. The performance of the photocatalyst was evaluated through color removal and COD reduction during the photodegradation of methylene blue dye. Various parameters were investigated to find out their effects on the removal of the MB dye. The absorbance of the dye was monitored using UV-Vis spectrometer (UV201, Shimadzu) at 661 nm maximum wavelengths.

Photodegradation of the MB dye was performed under solar and UV lamp irradiation and the two sources of photons were compared against each other to determine their efficiency in the degradation of the dye. Reaction kinetics and best model were determined through fitting the photodegradation data to zero, first, and second-order reaction kinetics. The stability of the catalyst and its efficiency and possible practical application was determined from its reusability.

3.2 Chemicals and materials.

The chemicals applied in this work were used without purification because they were of analytical grade. The following chemicals were acquired from:

1. Sigma-Aldrich; Bismuth (III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 98%), Sodium hydroxide (NaOH , 98%), 99% Tert-butanol, 98% P-benzoquinone, Methylene blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$, 98%).
2. Merck; Glacial acetic Acid (CH_3COOH , 98%), Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na , 99%).

3. Rochelle chemicals; potassium iodide (KI, 99.5%), Sodium nitrate (NaNO_3 , 98.5%), Silver nitrate (AgNO_3 , 99.8%).
4. Associated chemical enterprises (Ace); Sodium bromide (NaBr , 99%).
5. Alpha chemika; Nitric acid (HNO_3 , 38%).
6. Glassworld; Absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.9%). UV lamp (UVP UVG-54) with 254 nm output.

3.3 Experimental set up.

The setup consists of a reaction vessel (250 mL beaker) and a magnetic stirrer that performs the function of mixing the catalyst, and the MB dye solution in the beaker through vigorous stirring. A 6 W UVP UVG-54 lamp (378 x 81 x 64 mm in length, width, and height, respectively) was applied as a source of UV light. The lamp was operating at 254 nm that is imperative to produce reactive radicals that are crucial for photocatalysis. The extremely low penetrating ability of UVC past dead cell layers on the skin was important in minimizing skin damage in case of accidental exposure. The UV lamp was placed above the reaction vessel at 10 cm from the bottom of the beaker containing the mixture (Figure. 11a) whereas for solar, the mixture was exposed to open air (Figure. 11b). During sampling in each case, the stirrer was stopped to allow sampling to be done

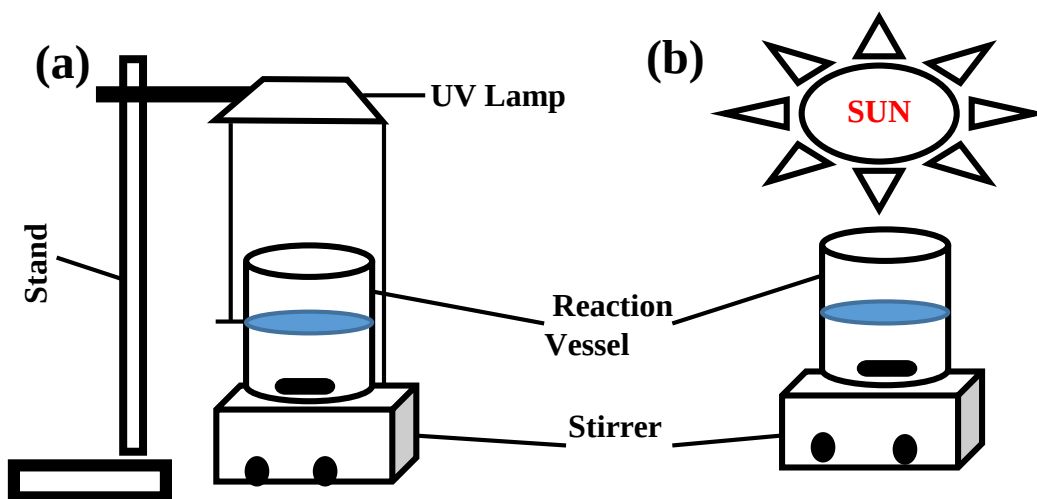


Figure 11. Experimental set up (a) UV-lamp and (b) solar.

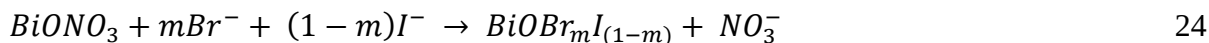
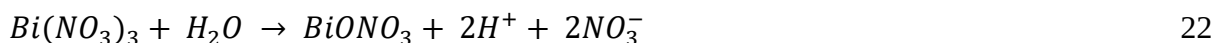
3.4 Experimental procedure

3.4.1 Preparation of synthetic wastewater

Synthetic wastewater was synthesized by dissolving a certain amount of the commercially acquired methylene blue crystals in distilled water to obtain a required initial concentration. A concentration of 10 mgL⁻¹ methylene blue solution was obtained by dissolving an accurately weighed 10 mg of MB into 1000 mL of distilled water.

3.4.2 Synthesis of the photocatalysts.

Bismuth oxyhalide (BiOBr_mI_{1-m}) materials were synthesized via the hydrothermal method at 160 °C. Typically, 0.4123 mM Bi(NO₃)₃·5H₂O solution was prepared by dissolving a certain amount (2.0 g) of bismuth nitrate pentahydrate into 5 mL acetic acid. A solution containing a stoichiometric quantity of KI and NaBr was carefully added to the above Bi-based solution while continuously stirring. The resulting mixture was then transferred into 23 mL sealed Teflon-stainless steel autoclave and put into an oven at 160 °C for 24 h under normal atmospheric conditions. When Bi(NO₃)₃ hydrolyses in water, BiONO₃ is produced [1]. According to Wu *et al.*, [1] the formation of BiOBr_mI_(1-m) solid solutions follows the equations (22 – 24) starting from the Bi(NO₃)₃ compound.



Upon the completion of the reaction, the sample was naturally cooled to room temperature, centrifuged several times at 6000 rpm, and washed 4 times with distilled water and ethanol. Drying the sample was done in an air convection oven at 70 °C for 24 h and kept for further characterization and photodegradation reactions. Depending on the molar ratio of Br⁻ and I⁻, BiOBr_mI_{1-m} solid solutions (M = 0, 0.2, 0.4, 0.6, 0.8, and 1) were successfully prepared following the same procedure. The samples were labeled as BiOI, BiOBr_{0.2}I_{0.8}, BiOBr_{0.4}I_{0.6}, BiOBr_{0.6}I_{0.4}, BiOBr_{0.8}I_{0.2}, and BiOBr, respectively.

3.5 Photocatalysts characterization

Characterization of the photocatalysts is a very important aspect of photocatalysis. The main reason for photocatalysts characterization was to determine physical and chemical properties and determine how these properties affect the photocatalytic performance of the material. Crystallinity, elemental composition, chemical bonds, surface area, morphologies and shapes, particle size, and optical properties were the main properties under investigation. Characterization studies of these properties are crucial in explaining the photocatalytic ability of $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions. It will help to identify the effects of changes in the surface after engineering individual BiOBr and BiOI via doping. The studies were also important in explaining the stability/recyclability of the photocatalyst. The analyses carried out included crystallography (X-ray diffraction, Raman), electron microscopy (Scanning and Transmission), elemental composition (EDS), spectroscopy (Fourier transform infrared), spectrophotometry (UV-Visible), and surface area (Brunauer-Emmett-Teller)

3.5.1 Surface morphology

3.5.1.1 Scanning electron microscope

Gemini SEM 500 (Carl Zeiss, Japan) was used to determine the surface morphology of the prepared materials. The SEM was operating at a voltage of 0.02 - 30 kV with a probe current of 3 pA - 20 nA. The SEM was operating at 50 – 2,000,000 magnification. Before analyzing the surface morphology of the material, it is necessary to carry out sample preparation to help avoid the charging of the samples during analysis. A thin layer of conductive material was used to coat the dry samples to prevent the build-up of the charges. The samples were mounted on an SEM sample holder known as a stub and coated with carbon graphite using a sputter coater.

3.5.1.2 Transmission electron microscopy

The particle average size and shape of the prepared photocatalysts were determined by TEM, FEI Tecnai G2 Spirit (Hillsboro, USA). Before the TEM analysis, the sample drop is placed on a copper grid coated with carbon. The sample is then dried to room temperature. The remaining solution is removed using blotting paper. A voltage of 20-120 kV accelerated the beam of

electrons. To allow the visibility of a large number of photocatalysts within the microscopic field view, the TEM was well aligned and operating at a magnification of 18-650 kx.

3.5.2 Structural analysis

3.5.2.1 X-ray diffraction crystallography

The XRD was used to determine the phase composition as well as the crystal structure of the prepared materials. The information was obtained at room temperature by a Bruker D8 Advance powder diffractometer, with a Cu X-ray source, and a LynxEye XE energy-dispersive strip detector. The radiation used was a $\text{Cu-K}\alpha$ ($\lambda=1.54056$ nm, 40 kV, 40 mA). The XRD was operating at a scan rate of 0.500 sec/step covering 0.02 degrees of 2θ . The patterns formed because of diffraction were recorded over diffraction angle $2\theta = 5^\circ \sim 90^\circ$. The average crystallite size of the prepared $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions was calculated from the XRD peak with the highest intensity using Scherrer relation. Analysis of the influence of doping on the crystallinity of pure BiOBr and BiOI was also done by XRD. Moreover, it was also used to determine whether the materials were successfully prepared and were free from impurities.

3.5.2.2 Raman Spectroscopy and Fourier-transform infrared spectroscopy

Raman LabRAM HR800 (Horiba Jobin Yvon, Villeneuve d'Ascq, France) was used to obtain the Raman shift of the synthesized materials. The Raman shift was collected between 25 – 500 cm^{-1} . The FTIR Bruker Vertex 80v vacuum (Bruker, Germany) technique as the name implies, uses low energy infrared radiation (IR) for qualitative and quantitative analysis of a sample and components making up that sample. The data was collected from 400 to 4000 cm^{-1} .

3.5.3 Brunner-Emmett-Teller

The porosity and surface area investigations of the solids were performed through Brunauer-Emmett-Teller (BET: Micrometrics Tristar 3000 porosity analyzer, Norcross, USA). For BET analysis, the degassing of the prepared materials was carried out at 150°C for 5 h in N_2 gas flow before sample analysis at 77.350 K, the temperature of liquid nitrogen.

3.5.4 Ultraviolet-visible spectroscopy.

UV-Vis Spectroscopy (UV201, Shimadzu, Japan) is a technique that involves the use of UV radiations (200-400 nm) range and visible (400-700 nm) range to characterize the samples. Running the blank suppresses the background absorption. Once this was done the sample holder containing pure water was taken out, the water discarded, and then the cuvette was filled with the dye sample being measured.

3.6 Determination of point of zero charge (pH_{PZC}) by Salt Addition Procedure

The procedure employed in this work was adapted from Tahira *et al.*, [2]. The 0.1 M NaNO₃ solution was used for determining the PZC values for BiOBr_mI_(1-m) solid solutions at 298 K. Typically, 0.1 g of the samples were added into 30 mL of 0.1 M NaNO₃ solution in various reaction vessels. The initial pH of the mixtures was adjusted to 2, 3, 4, 5, 6, 7, 8, 9, 10, or 11 using 0.1 M HNO₃ or 0.1 M NaOH. Each reaction vessel was then agitated at 130 rpm in a shaker for 24 h. The resultant pH of the mixtures was determined using a Basic20 pH-meter (ShangHai Shilu Instruments, China). A graph of change in pH (initial and final) against initial pH values was then plotted. The pH_{PZC} was taken to be the pH at which ΔpH is zero.

3.7 Photodegradation studies

Before the exposure to the source of light for the photodegradation process, a catalyst loading of 1 g/L was dispersed in 0.05 L MB solution (10 mg/L) and the adsorption-desorption experiments were carried out in absence of light for 30 min. The amount of MB (adsorbate) adsorbed on the surface of adsorbent (catalyst) at equilibrium was determined from [equation 25](#) below:

$$q_e = \left(\frac{C_0 - C_e}{W} \right) V \quad 25$$

where C₀ and C_e (ppm) are initial concentration and concentration at a time interval, t, respectively. V is the volume of MB solution (L) and W is the quantity (g) of catalyst used

The photocatalytic investigations were carried out in a beaker (250 mL) under a 6 W UVP lamp ([Figure. 11a](#)) and solar ([Figure. 11b](#)) irradiations. To monitor the degradation process, a given amount of aliquot (2 mL) was pipetted from the mixture at a given time interval (30 min). The

catalyst in the aliquot was then separated from the solution through centrifugation for 7 min at 13000 rpm. The degradation of the MB dye was monitored through color and COD reduction. The color reduction was monitored via the reduction in MB UV-Vis absorbance at a maximum wavelength ($\lambda_{\max}$) of 661 nm. The degradation efficiencies, μ of the prepared solid solutions were obtained using the following equation. 26.

$$\mu = \frac{A_0 - A_t}{A_0} = \frac{C_0 - C_t}{C_0} \times 100\% \quad 26$$

where A_0 and C_0 are initial absorbance and concentration at equilibrium while A_t and C_t are the absorbance and concentration at a time interval, t .

3.8 Estimation of chemical oxygen demand

Chemical oxygen demand (COD) has extensively been used to estimate the organic matter of wastewater. The COD of the MB dye solution was assessed before and after treatment. To calculate the COD, glasses of 0-1500 mg/L were used to obtain the amount of oxygen required to oxidize MB dye. The COD was determined by the HACH method. To prepare a reference sample, 2 mL of distilled water was placed in a COD sample vial before shaking and placing it in the reactor. To determine the COD of the treated dye, 2 mL of treated MB solution was mixed with 1.9 mL of deionized water in the sample vials, shaken, and placed the reactor. The vials were then positioned in the DRB 200 HACH digester and left for 2 h at a temperature of 150 °C. After this time, the reactor temperature was decreased to 60 °C, for 30 min, so that the samples could be measured as they were removed from the digester. The COD (mg/L) values were then read from the instrument. The proportion of COD removed ϕ , was calculated as:

$$\phi = \frac{\Delta COD}{COD_0} \times 100 \quad 27$$

where ΔCOD is a change in experimental COD in mg/L, COD_0 is the corresponding initial COD value before treatment.

3.9 Investigation of the catalyst stability/recyclability

To test the stability/reusability/recyclability of the synthesized solid solutions for MB dye, $\text{BiOBr}_{0.6}\text{I}_{0.4}$ sample was used for analysis and the degradation cycles were performed. Initially,

50 mg of $\text{BiOBr}_{0.6}\text{I}_{0.4}$ was added to the MB dye solution (10 mg/L) at natural pH 7.0 of the dye solution. The dye degradation efficiency of the $\text{BiOBr}_{0.6}\text{I}_{0.4}$ was evaluated for the first cycle. After completion of the degradation process for the first cycle, the MB dye loaded $\text{BiOBr}_{0.6}\text{I}_{0.4}$ sample was separated and washed. After the first degradation, the $\text{BiOBr}_{0.6}\text{I}_{0.4}$ sample was subsequently reused for the second cycle. Similarly, the reusability study was conducted for five consecutive cycles.

References

1. T. Wu, X. Li, D. Zhang, F. Dong, and S. Chen, "Efficient visible-light photocatalytic oxidation of NO with hierarchical nanostructured 3D flower-like $\text{BiOCl}_x\text{Br}_{1-x}$ solid solutions," *J. Alloys Compd.*, vol. 671, no. February, pp. 318–327, 2016.
2. T. Mahmood, M. T. Saddique, A. Naeem, P. Westerhoff, S. Mustafa, and A. Alum, "Comparison of different methods for the point of zero charge determination of NiO ," *Ind. Eng. Chem. Res.*, vol. 50, no. 17, pp. 10017–10023, 2011, doi: 10.1021/ie200271d.

CHAPTER 4

4 Results and Discussion.

4.1 Structural Analysis of photocatalysts.

4.1.1 X-ray powder diffractometer analysis

The XRD, which is an accurate, rapid, and non-destructive technique, was used for the crystalline phase and phase purity examination of the prepared materials. The measurement was taken from the same 2θ range per sample. Figure 12 represents the XRD patterns of $\text{BiOBr}_m\text{I}_{(1-m)}$ combined samples of solid solutions.

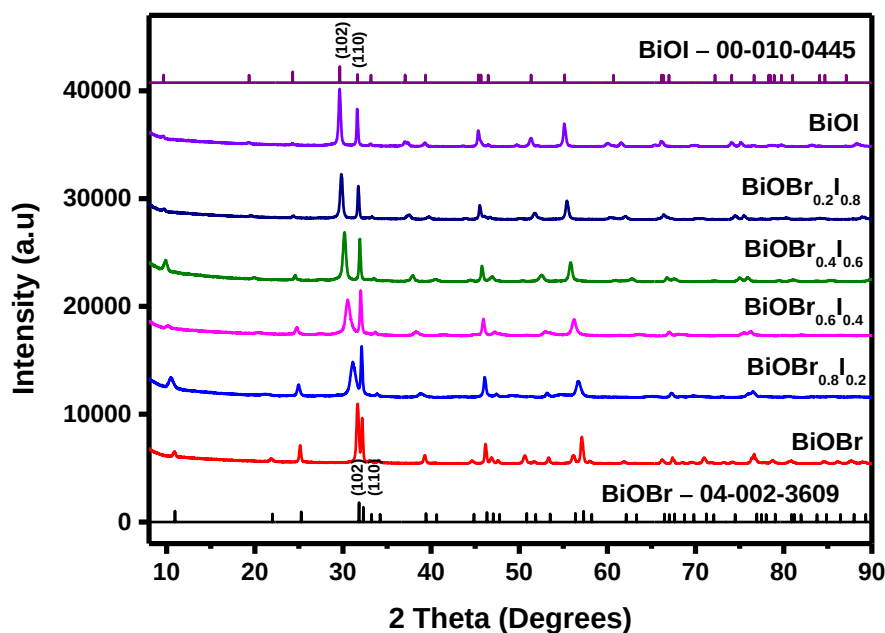


Figure 12. XRD patterns of $\text{BiOBr}_m\text{I}_{(1-m)}$ samples

Sun *et al.*, [1] reported that the dominating facets of BiOI crystals are (001) and (110) [1]. However, the results of this study show that the dominating facets are (102) and (110) positioned at $2\theta = 31.8$ and 32.3° for BiOBr and $2\theta = 29.6$ and 31.6° for BiOI as shown in Figure 12. All the prepared materials were well crystallized and the observed peaks pointed to $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions tetragonal PbFCI type structure with space of $p4/mmm$ and a space

group D_{4h}. The prepared materials were all indexed to the database of PDF card numbers 04-002-3609 and 00-010-0445 for BiOBr and BiOI, respectively.

When the composition of I⁻ increases, the BiOBr_mI_(1-m) peaks broadens and the diffraction peaks shift to a smaller angle, for example, the (102) plane angle shifts from 31.8 to 29.6 °, this change could be associated with the doping of iodine with a greater ionic radius of I⁻ (2.2 Å) into Br⁻ (1.96 Å) [2]. This successive shift of the angles displayed by XRD patterns is a clear indication that doping BiOI into BiOBr was successful. Lu *et al.*, [3] reported that the consecutive change in the diffraction peaks showed that the prepared materials are BiOBr_mI_(1-m) solid solutions, not a combination of separate phases of BiOBr and BiOI [3]. The intensity of (102) plane in BiOBr is higher than other planes indicating a preferred orientation along (102) plane. As the amount of I⁻ increases from 0 to 0.4 the intensity of (110) plane becomes pronounced than (102) leading to preferred orientation along the (110) plane. Additionally, as the amount of I⁻ increases from 0.4 to 1, the preferred orientation shifts to be along the (102) plane. No impurity peaks were observed hence the samples were described to be a pure phase.

The Miller indices (hkl) and unit cell were used in determining the crystallographic planes of the samples. Various materials exhibit different crystal structures therefore different lattice geometry equations are used to calculate the lattice parameters (a, b, and c) of each structure. The volume of the unit cell structure can be determined from the calculated lattice parameters. The observed structure of pure BiOBr and BiOI was tetragonal. The lattice parameters of the material with a tetragonal cell structure can be calculated as:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad 28$$

where *h*, *k*, and *l* signifies the miller indices, *d* is the interplanar distance, *a* and *c* are the lattice constant of the unit cell. These parameters were obtained from the (001) and (200) planes. The unit cell volume of materials were calculated using [equation 29](#) as:

$$V = a^2c \quad 29$$

The calculated lattice constants, lattice parameters, and unit cell volume are shown in [Table 4](#).

Table 4. Lattice parameters (a, b, c), constants (c/a) and unit volume of BiOBr_mI_(1-m) samples.

Parameters	Values (Å)					
	M = 1.0	M = 0.8	M = 0.6	M = 0.4	M = 0.2	M = 0
a= b (Å)	3.928	3.935	3.948	3.960	3.980	3.994
c (Å)	8.128	8.430	8.722	8.955	9.192	9.243
c/a	2.069	2.142	2.209	2.261	2.310	2.314
Volume(Å)	125.41	130.53	135.95	140.43	145.60	147.44

The lattice parameters and unit volume increase with an increase in the amount of Γ . This increase in calculated parameters could be as a result of the stretching of the unit cell. The average FWHM was obtained using the Lorentz system from Origin (9.0) software whereas the average crystallite size (D) of BiOBr_mI_(1-m) samples was determined by Debye Scherrer's formula (eqtn 30) [4,5] from (102), (110), (200), and (212) planes and the results presented in Table 5

$$D = \frac{\kappa\lambda}{\beta\cos\theta} \quad 30$$

where, κ is a constant, about 0.94, λ is the wavelength of the X-ray (1.5406 Å), β is FWHM of the diffraction peak in radians, and θ is Bragg diffraction angle. The strength of the XRD peaks is proportional to the content of the corresponding crystallites, the sharpness of the peaks indicates higher crystallinity [6]. Therefore, the BiOBr_mI_(1-m) samples with sharp and intense XRD peaks show high crystallinity.

Table 5. The calculated FWHM and crystallite size from XRD measurements

Parameters	Samples					
	M = 1.0	M = 0.8	M = 0.6	M = 0.4	M = 0.2	M = 0.0
FWHM (Rad)	0.251	0.464	0.397	0.295	0.282	0.257
Crystallite size (D) (nm)	364.5	255.9	272.4	239.3	332.8	359.2

4.1.2 Raman spectroscopy

The Raman vibrational modes are expressed as “Raman shift”, which is directly related to the energy. Figure 13 represents the Raman spectra of $\text{BiOBr}_m\text{I}_{(1-m)}$ materials prepared by varying amounts of Br^- and I^- ions.

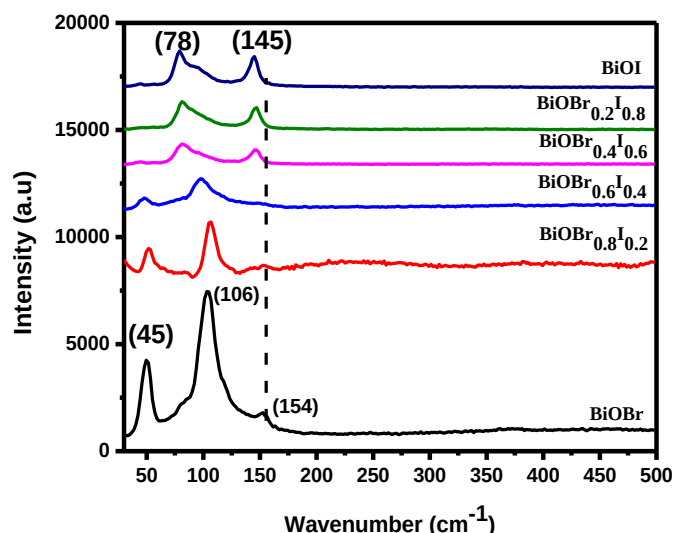


Figure 13. Raman shift spectra for $\text{BiOBr}_m\text{I}_{(1-m)}$ samples.

To show a variation in structural features of $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions, the Raman spectra was recorded ranging from 25 to 500 cm^{-1} . The Raman spectra data was acquired from a random-selected area exposed by excitation light with a focus beam diameter of 2 μm . BiOM as mentioned in XRD analysis belongs to the tetragonal structure of PbFCI type with $p4/mmm$ spacing. The A_{1g} , B_{1g} , and E_g are the Raman active modes. Zhang *et al.*, [7] explained that the optical modes can be applied to explore the correlation within this kind of structure [7]. Raman vibrational modes are explained as $4, \Gamma = 2A_{1g} + B_{1g} + 3E_g + 2E_u + 2A_{2u}$, where A_{1g} , B_{1g} , and $3E_g$ are Raman active while $2E_u$ and $2A_{2u}$ are infrared active [8]

For the BiOBr material, the Raman spectrum peak at 45 cm^{-1} is assigned to vibration of the first-order of Bi metal, the high-intensity band at 106 cm^{-1} corresponds to the A_{1g} mode of internal Bi–Br enlargement. The weakest band at 159 cm^{-1} was attributed to the E_g mode of internal Bi–Br enlargement [9,10]. The high-intensity bands in BiOI at 78 and 145 cm^{-1} are ascribed to the A_{1g} mode of internal Bi–I enlargement. As the composition of I increases, the 78 and 145 cm^{-1} bands are increasingly become prominent. These changes agree with the XRD

results. The 106 band broadening with increasing I^- composition reveals that the mode frequency distribution arises mainly from chemical disorder [11].

4.1.3 Fourier-transform infrared spectroscopy

The FTIR spectra of the $\text{BiOBr}_m\text{I}_{(1-m)}$ samples were examined between 400 to 4000 cm^{-1} to explore the functional groups within the as-prepared materials. Figure 14 displays the FTIR results.

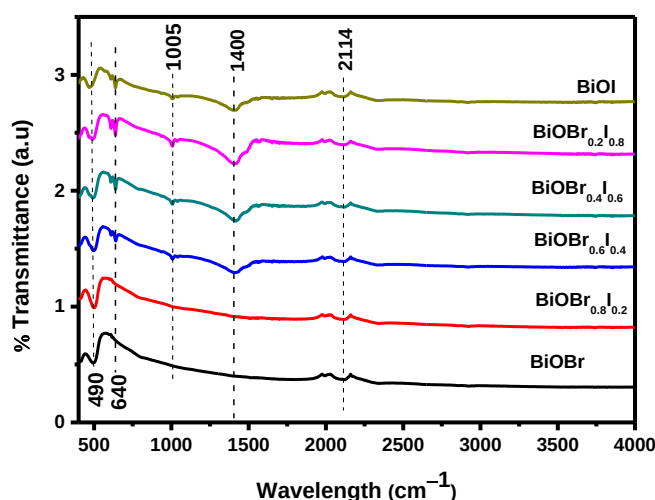


Figure 14. FTIR spectra of $\text{BiOBr}_m\text{I}_{(1-m)}$ samples

The strong absorption bands are mainly located between wavelengths of 400 to 1500 cm^{-1} . These bands are as a result of the enlargement vibrations of Bi O Br, Bi O I, Bi O, and Bi O Bi in $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions [12]. In the $\text{BiOBr}_m\text{I}_{(1-m)}$ spectra, the peak at 490 cm^{-1} was ascribed to the stretching vibrations of the Bi – O bond in crystal tetragonal BiOBr [13-15]. As the amount of iodide (I^-) composition increases from $M = 0.6$, many additional peaks were observed appearing at 640, 1005, 1400, and 2114 cm^{-1} . For individual BiOI, the IR peak observed at 1005 cm^{-1} results from the stretching of Bi – I chemical bound. All these observations point to the successful synthesis of $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions.

4.2 Morphological analysis.

4.2.1 Scanning electron microscopy.

The $\text{BiOBr}_{1-m}\text{I}_m$ solid solutions micrographs are displayed in Figure 15 (a-f).

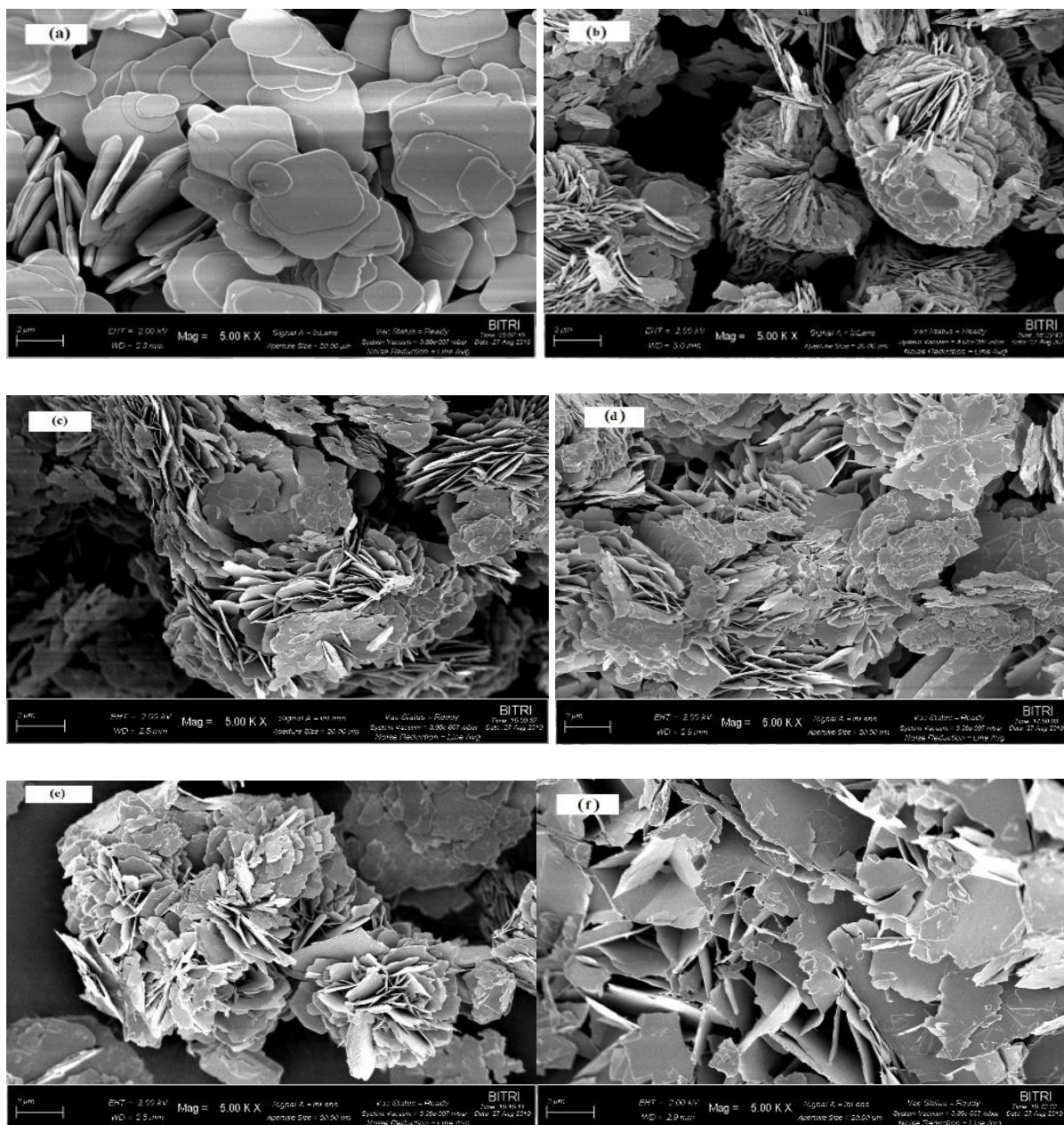


Figure 15. SEM micrographs of (a) BiOBr , (b) $\text{BiOBr}_{0.8}\text{I}_{0.2}$, (c) $\text{BiOBr}_{0.8}\text{I}_{0.2}$, (d) $\text{BiOBr}_{0.6}\text{I}_{0.4}$, (e) $\text{BiOBr}_{0.4}\text{I}_{0.6}$, (f) BiOI

The SEM micrographs display flower-like microspheres as the main structure constituting mainly of microplates and micro sheets. The structures displayed by pure BiOBr photocatalyst (Figure 15a) are regular ultrathin microplate structures, which consist of nanoplates. This formation of ultrathin micronanoplate is due to the crystal growth along the predominant (102) facet in preference to the crystallographic axis (001) plane. This compared to the result obtained from the XRD analysis which showed the preferred orientation along (102) plane because the intensity of (102) plane is higher than (001) plane hence the formation of microplates. These findings agree with literature [16]. The samples with $M = 0.8$ and 0.6 display a flake-like morphology with average diameters of $2\ \mu\text{m}$. The flake-like structure consists of multi-layered nanosheets that are vertically assembled on the surface. The morphologies of $M = 0.4$ and 0.2 samples are similar to that of $M = 0.8$ and 0.6 , however, their flake-like structures are slightly different. For the $M = 0.8$ and 0.6 there are more nanosheets assembled within the structure [17].

An increase in the composition of iodide ion from 0 to 1 results in the aggregation of nanoplates to form 3-dimensional flower-like structures. Bismuth oxy-iodide (BiOI) form flower-like hierarchical micro flowers which consist of loosely packed nanosheets with a thickness of $1 - 2\ \mu\text{m}$ that intercrossed together to form a 3D structure [1]. The formation of these hierarchical 3D flower-like structures is usually attributed to a self-assembly process [18]. The SEM results indicate that introducing iodine into the bismuth structure resulted in an obvious change in morphology from ultrathin nanoplates to flower-like morphology. The difference between the particle size obtained by SEM and the crystallite size calculated using XRD is owing to the fact that the particles are composed of several crystallization domains, which are measured using X-rays, while with SEM the whole particle is seen. The shape of the crystal is known to be controlled by the growth rates along with different directions [19]. To confirm the formation of $\text{BiOBr}_m\text{I}_{(1-m)}$, EDX analysis was performed. The Bi, Br, O, and I are confirmed in the synthesized materials in the EDX spectrum. In the spectrum, the quantities of Bi, Br, O, and I vary in each compound as presented in inserts in Appendix A.

4.2.2 Transmission electron microscopy

The BiOBr, $\text{BiOBr}_{0.6}\text{I}_{0.4}$, and BiOI were chosen as the representatives for the TEM analysis. The particle sizes as revealed by the TEM micrographs are $2\ \mu\text{m}$. As displayed in Figure 16 the

TEM images also show that the BiOBr plate-like morphology, the BiOBr_{0.6}I_{0.4} flake-like structure, and BiOI 3D flower-like structures consist of microplates. The inter microplates distance can be seen that might be ascribed to the strain in the BiOBr_mI_(1-m) inner structure. This strain within the inner structure of the materials can modify the structure of the band and promote the separation of the charges, thus, enhancing the photocatalytic performance of BiOM [20]. The micro sheets are advantageous to the separation and transport of photoexcited electrons and hole [21].

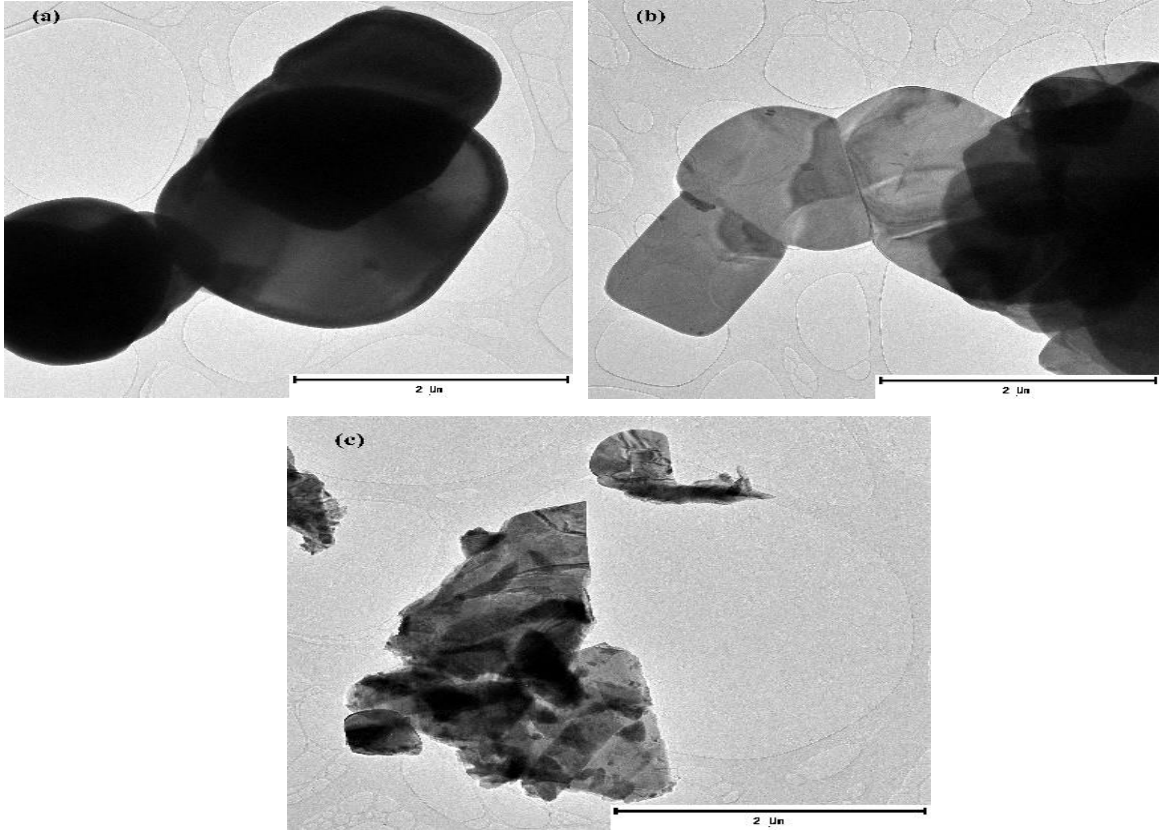


Figure 16. TEM images of (a) BiOBr, (b) BiOBr_{0.6}I_{0.4}, and (c) BiOI

4.3 Brunauer-Emmett-Teller (BET)

The pores sizes and the BET surface area (S_{BET}) of the prepared materials were determined using Micro metrics Tristar 3000 instrument. The BET isotherm model was applied in its linearized form [22,23].

$$\frac{P/P_o}{V_{ads}(1-\frac{P}{P_o})} = \frac{1}{V_{m1} \cdot C_{BET}} + \frac{C_{BET}-1}{V_{m1} \cdot C_{BET}} \cdot \frac{P}{P_o}$$

31

where P/P_0 is relative pressure, V_{ads} is the quantity adsorbed, V_{m1} is the adsorbed monolayer volume, and C_{BET} is a constant. Figure 17, represents corresponding N_2 isotherms and BJH pore size distribution.

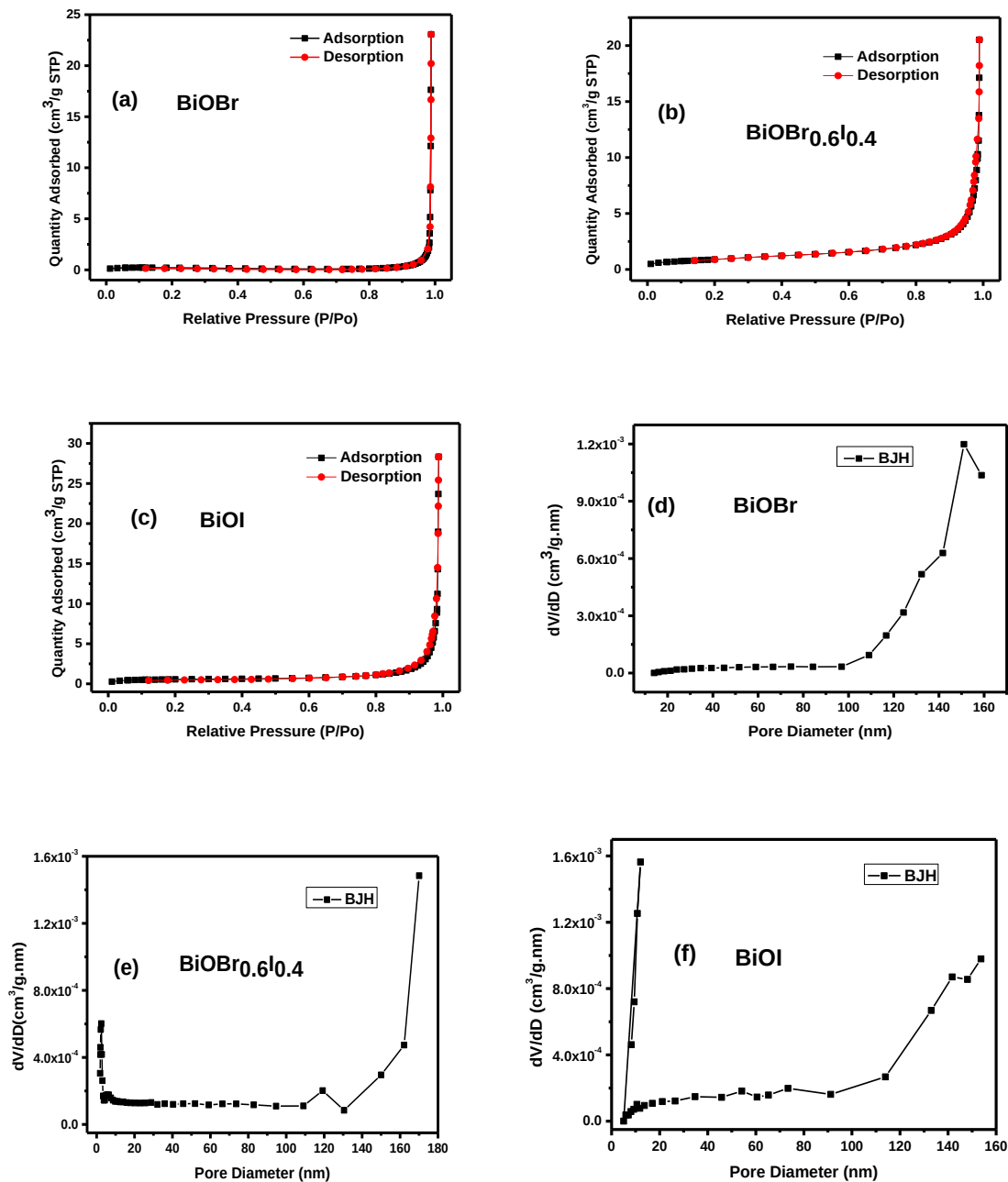


Figure 17. (a-c) N_2 adsorption-desorption isotherms of $M = 1.0$, 0.6 , and 0.0 , respectively (d-f) BJH distribution of the pore sizes of $M = 1.0$, 0.6 , and 0.0 , respectively.

The performance of photocatalysts is widely influenced by the pore structure and surface area. Figure 17 (a-c) represents the N₂ adsorption-desorption isotherms of M = 1.0, 0.8, 0.6, 0.4, 0.2, and 0.0. The isotherms are of type-III based on Brunauer, Deming, Deming, and Teller (BDDT) IUPAC classification. The materials exhibit type H3 hysteresis loops at P/P₀ of 0.5 to 1.0 showing the presence of mesopores [24,25]. The shape of the loops is linked with the pores having slit-shaped within the material microstructures. These slit-shaped pores suggest that there is self-assembly of nanoplates and nanosheets thus forming hierarchical architectures.

The corresponding Barrett-Joyner-Halenda (BJH) curves are shown in Figure 17 (d-f). From the BiOBr BJH curve, the strongest peak is at 150 nm indicating that BiOBr contains macropores. The BiOBr_{0.6}I_{0.4} and BiOI display a bimodal distribution. The BiOBr_{0.6}I_{0.4} shows a peak pore at 5 and 120 nm indicating that it is composed of mesopores and macropores, respectively whereas BiOI shows a peak pore at 10 and 140 nm. The BiOI pore distribution also indicates that BiOI is composed of mesopores and macropores. Generally, the distribution of bimodal is usually linked with different pore sizes that are shaped through intra and inter aggregation within the microplates [26]. Clearly, BiOI contains both mesopores and macropores and BiOBr_{0.6}I_{0.4} has several small mesopores (ca. 5 nm) which increases the BET surface area. The surface area of a material is generally known to influence its photocatalytic performance hence the higher the surface area to volume ratio the greater the photocatalytic performance. However, the samples have a lower surface area (Table 6) but higher photocatalytic performance towards the removal of MB, this is due to a unique (102) facet with specific electronic structure and broader light absorption which are the main contributing factors [27]. Table 6 shows the surface areas, pore diameters and pore volume.

Table 6. BET surface areas and pore volume of the BiOBr, BiOBr_{0.6}I_{0.4}, and BiOI

Photocatalyst	BET surface area (m ² g ⁻¹)	Pore volumes (cm ³ g ⁻¹)	Pore diameter (nm)
BiOBr	0.517	0.000477	127.0
BiOBr _{0.6} I _{0.4}	3.249	0.000218	32.4
BiOI	1.890	0.000292	76.8

4.4 Optical properties

The energy bandgap of a semiconductor photocatalyst plays a significant function in photocatalytic performance. The UV– Vis spectrometer was used to investigate the optical features of $\text{BiOBr}_m\text{I}_{(1-m)}$ materials and the results are displayed in Figure 18a.

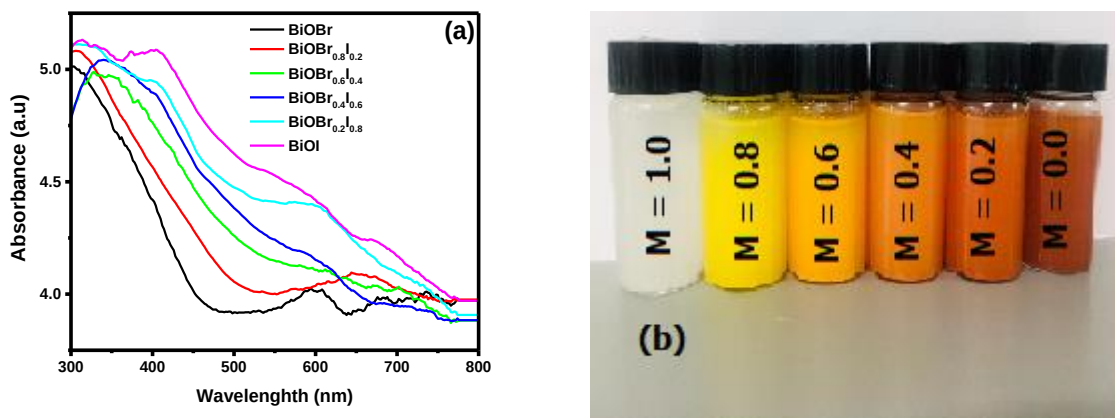


Figure 18. (a) Absorption spectra from UV- vis analysis (b) Optical images showing resultant colors of $\text{BiOBr}_m\text{I}_{(1-m)}$.

It is shown that the absorption threshold of $M = 1.0$ is about 478.2 nm, whereas that of $M = 0.0$ is about 631.7 nm. This suggests that both BiOBr and BiOI are active within the visible light. As estimated, the absorption edges of $M = 0.8, 0.6, 0.4, 0.2$ are found between those of individual BiOBr and BiOI, and the absorption thresholds increase with an increase in the amount of I (Table 7). The color corresponding to the samples was seen to be shifting from light yellow to red with an increase in the composition of iodine (Figure 18b). The energy bandgap (E_g) of the prepared $\text{BiOBr}_m\text{I}_{(1-m)}$ materials were determined by:

$$\alpha h\nu = A(h\nu - E_g)n/2 \quad 32$$

where α , h , ν , E_g , and A are absorption coefficient, Planck's constant, frequency of light, the energy of the bandgap, and a constant, respectively [1], and n is a subject to transition properties of a semiconductor. BiOM has an indirect band structure hence n is 4. The bandgap changes from 2.59 to 1.96 eV with increasing the composition of I from 0 to 1 (as shown in Table 7), indicating that the $\text{BiOBr}_m\text{I}_{(1-m)}$ bandgaps can be tailored through incorporating I atoms into the BiOBr structure. Apart from tailoring the bandgap, the absorption range of $\text{BiOBr}_m\text{I}_{(1-m)}$

can also be extended. Therefore, modifying the bandgap via doping bromide and iodide ions can improve the photocatalytic performance of BiOM based photocatalysts.

Table 7. The absorption edges and the calculated optical band gaps.

Photocatalyst	M = 1.0	M = 0.8	M = 0.6	M = 0.4	M = 0.2	M = 0
Absorption thresholds (nm)	478.2	546.4	576.6	590.6	610.6	631.7
Optical band gap (eV)	2.59	2.27	2.15	2.10	2.03	1.96

The photocatalytic reduction activity of a photocatalyst is well known to be decided by the conduction band minimum (CBM). The photocatalytic activity of a material depends on the position of the CBM and VBM. When the position of CBM is high, the photocatalytic reduction activity will be higher. For semiconductors, the VBM and CBM can be obtained from the following equations [29-32].

$$E_{CBM} = \chi - E^c - 0.5 E_g \quad 33$$

$$E_{VBM} = E_{CBM} + E_g \quad 34$$

where E_{CBM} and E_{VBM} are CBM and VBM are edge potentials edge, respectively. E^c is the energy of the free electrons on the hydrogen scale (ca. 4.5 eV), E_g is the bandgap energy. Finally, χ is the electronegativity of the semiconductor (geometric mean of the electronegativity of the atoms in the compound) and was obtained using the equation below [33]

$$\chi = [\chi(A)^a \chi(B)^b \chi(C)^c]^{1/(a+b+c)} \quad 35$$

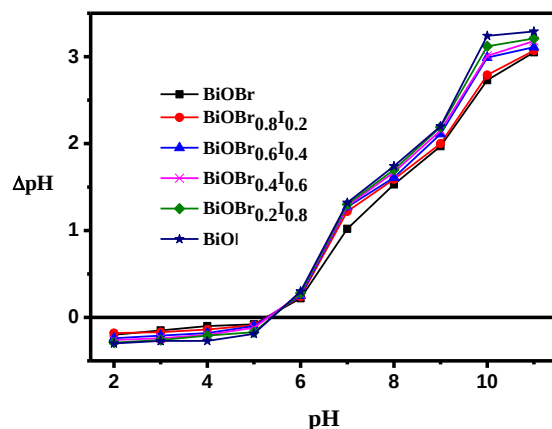
where A, B, C are the elements forming the compound, a, b, and c are the number of atoms in the compounds. The calculated values of E_g and χ for $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions are recorded in Table 8. When the position of VB is lifted and/or CB is lowered in BiOM, the energy bandgap will be narrowed which can improve their photocatalytic efficiencies. Doping not only leads to the creation of solid solutions but also introduces a different element foreign to the host material that leads to raising the VB or lowering the CB, hence narrowing the energy bandgap.

Table 8. Calculated band gaps (E_g) and electronegativity (χ) of $\text{BiOBr}_m\text{I}_{(1-m)}$ samples

Photocatalyst	M = 1.0	M = 0.8	M = 0.6	M = 0.4	M = 0.2	M = 0
Electronegativity (χ)	6.25	4.03	4.46	4.46	4.03	6.01
The optical band gap (eV)	2.59	2.27	2.15	2.10	2.03	1.96
E_{CBM}	0.46	-1.61	-1.12	-1.09	-1.49	0.53
E_{VBM}	3.05	0.66	1.03	1.01	0.54	2.49

4.5 Point of zero charge (pH_{PZC}) or isoelectric point (pH_{IEP})

The pH at which the overall charge on the material surface is zero is called a point of zero charges (pH_{PZC}). Several approaches have been used to find the pH_{PZC} of a range of nanomaterials for instance Tahira *et al.*, [34] determined the pH_{PZC} of nickel oxide (NiO) using the salt addition method, fast titration method, and mass titration method. This is important as it helps to understand the degradation mechanism. This factor plays a significant function in the characterization of compound surfaces. Adsorption of harmful compounds is determined by PZC of the materials. In this study, the PZC of $\text{BiOBr}_m\text{I}_{(1-m)}$ compounds was determined by the Salt Addition Method [34,35].

**Figure 19.** ΔpH against initial pH of $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions at 298 K

When the pH is higher than the pH_{PZC} , the $\text{BiOBr}_m\text{I}_{(1-m)}$ materials surface will acquire negative charges and attracts cations. On the other hand, at a pH less than the pH_{PZC} , the surface will be

positively charged and repels cations [36]. Thus, this parameter determines the potential of the photocatalysts to adsorb MB. When $\text{BiOBr}_m\text{I}_{(1-m)}$ was added to the NaNO_3 solution, and the measurements of changes in pH taken at fixed ionic strength, are presented in Figure 19. The pH_{PZC} was obtained from the plotted curves. The results revealed that the PZC of BiOI, $\text{BiOBr}_{0.2}\text{I}_{0.8}$, $\text{BiOBr}_{0.4}\text{I}_{0.6}$, $\text{BiOBr}_{0.6}\text{I}_{0.4}$, $\text{BiOBr}_{0.8}\text{I}_{0.2}$, and BiOBr, were found to be and 5.39, 5.38, 5.31, 5.29, 5.27, and 5.27, respectively.

4.6 Photocatalytic activity Evaluation

4.6.1 Adsorption

Adsorption studies for $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions were carried out with catalysts loading of 50 mg and initial concentration of 10 mgL^{-1} MB solution. The results are shown in Figure 20

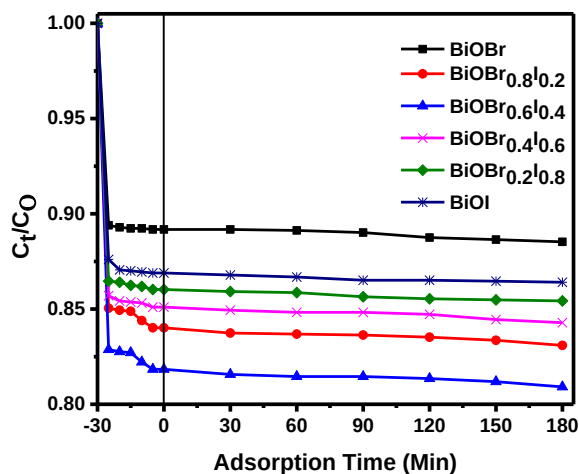


Figure 20. Adsorption efficiencies of MB over $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions

After 30 min of adsorption in the dark (Figure 20) there was no significant change in the adsorption of capacities of the materials implying that after 30 min, the adsorption of MB by the photocatalysts attains equilibrium. These results clearly show that the adsorption capacities of the prepared materials are very low hence; the catalysts cannot be used as an adsorbent. Table 9 shows the adsorption capacities of the prepared materials. The reduction of color of MB through photodegradation was monitored at the wavelength (λ_{max}) of 661 nm that is a maximum characteristics absorption band of MB.

Table 9. The adsorption capacity of $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions

Photocatalyst	Blank	M = 1.0	M = 0.8	M = 0.6	M = 0.4	M = 0.2	M = 0.0
Adsorption capacity (mg/g)	0.0	12	17	19	16	15	14

4.6.2 Photocatalytic activity evaluation under solar irradiation

Before the exposure to the solar irradiation, a mixture of the dye and the photocatalyst was stirred in the dark for 30 min to obtain the adsorption-desorption equilibrium (Figure 20). To determine the best composition of BiOBr and BiOI that possess the highest photocatalytic ability under solar, the photocatalytic efficiency of $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions synthesized under varying Br and I molar ratios were evaluated and the result is shown in Figure 21.

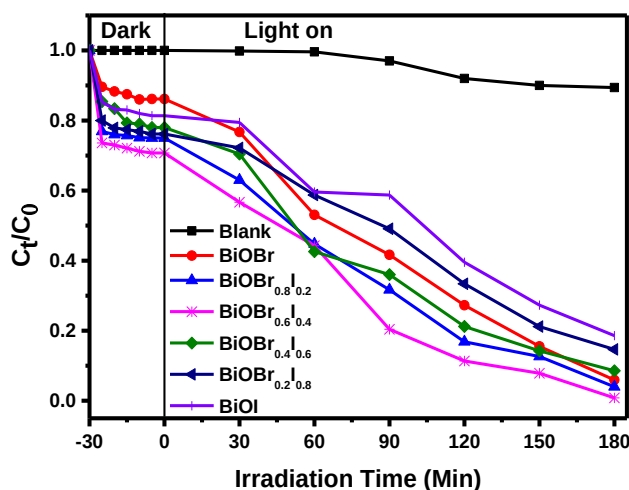
**Figure 21.** Degradation efficiencies of MB over $\text{BiOBr}_m\text{I}_{(1-m)}$ materials under solar irradiation.

Table 10 displays photodegradation efficiencies of $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions after 3 h of irradiation under solar. The removal effectiveness of MB without catalyst under solar (photolysis) is insignificant because the dye is expected to be almost completely removed after 3 h of irradiation. The low percentage removal indicates that the dye is stable under solar irradiation. Therefore, the photolysis of MB can be neglected. The results show that the

BiOBr_mI_(1-m) materials with the composition of BiOBr_{0.6}I_{0.4} showed the highest efficiency compared to other materials. This could be attributed to its optimal composition of Br⁻ and I⁻ in the compound.

Table 10. Degradation efficiencies of BiOBr_mI_(1-m) solid solutions under solar irradiation

Photocatalyst	Blank	M = 1.0	M = 0.8	M = 0.6	M = 0.4	M = 0.2	M = 0.0
Degradation, %	9	93	95	99	89	81	77

4.6.3 Photocatalytic evaluation under irradiation from UV light

Figure 22 represents the variations in the UV-vis spectra during the degradation of MB over BiOBr_mI_(1-m) under irradiation from the UV lamp. Before the mixture exposure to the irradiation from UV light, the adsorption equilibrium was established for 30 min in the dark (Figure 20). The most efficient BiOBr_mI_(1-m) solid solutions for the removal of MB was determined under UV irradiation with other factors (irradiation time, catalyst dosage, and pollutant initial concentration) kept constant. Figure 22 (a-g) illustrates the efficiencies of the prepared materials through the reduction of MB color leading to a reduction in absorbance. After 3 h of irradiation from UV light, the photocatalytic activities of doped BiOBr_mI_(1-m) were higher than those of individual BiOBr and BiOI. The result is shown in Figure 22(h). The degradation efficiencies are shown in Table 11. The lower degradation efficiency as a result of photolysis indicates that the MB dye is stable under UV light, therefore photolysis can be ignored. As was with the case of solar, BiOBr_mI_(1-m) solid solution with the Br⁻ and I⁻ composition of BiOBr_{0.6}I_{0.4} recorded the highest degradation efficiency. Figure 23 shows the color reduction as a result of the degradation of MB over BiOBr_{0.6}I_{0.4} photocatalyst under UV- light irradiation.

The most efficient photocatalyst among the BiOBr_mI_(1-m) materials was selected and used in investigating the degradation parameters for example temperature, catalyst loading, pH, oxidant, and scavengers. The activities of different BiOBr_mI_(1-m) samples are also presented for comparison. The experimental conditions are outlined in more detail in the experimental procedure/methodology. It is generally acknowledged that the photocatalytic property of a

photocatalyst is dependent on the surface areas, component contents, absorbance ability, and band structure matching.

However, from the BET analysis, the BET surface area was relatively low, which demonstrates that the improved photocatalytic performance was not as a result of high surface area. The major factor for the improved photocatalytic efficiency of the prepared materials is more likely to be the formation and built-in of electric field between the layers of $(\text{Bi}_2\text{O}_2)^{2+}$ and 2M^- that increases the separation of photoexcited e^-/h^+ , thus improving the photocatalytic performance. Additionally, the flower-like and the flake-like hierarchical architecture possess a longer optical path length than the BiOBr plate-like structures. Since the optical path length transport light, the longer the optical path length, the higher the number of photoexcited electrons and holes available to take part degradation process.

Table 11. Degradation efficiencies of $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions under UV light irradiation

Photocatalyst	Blank	M = 1.0	M = 0.8	M = 0.6	M = 0.4	M = 0.2	M = 0.0
Degradation, %	2.9	54.2	83.1	88.2	78.3	70.8	33.0

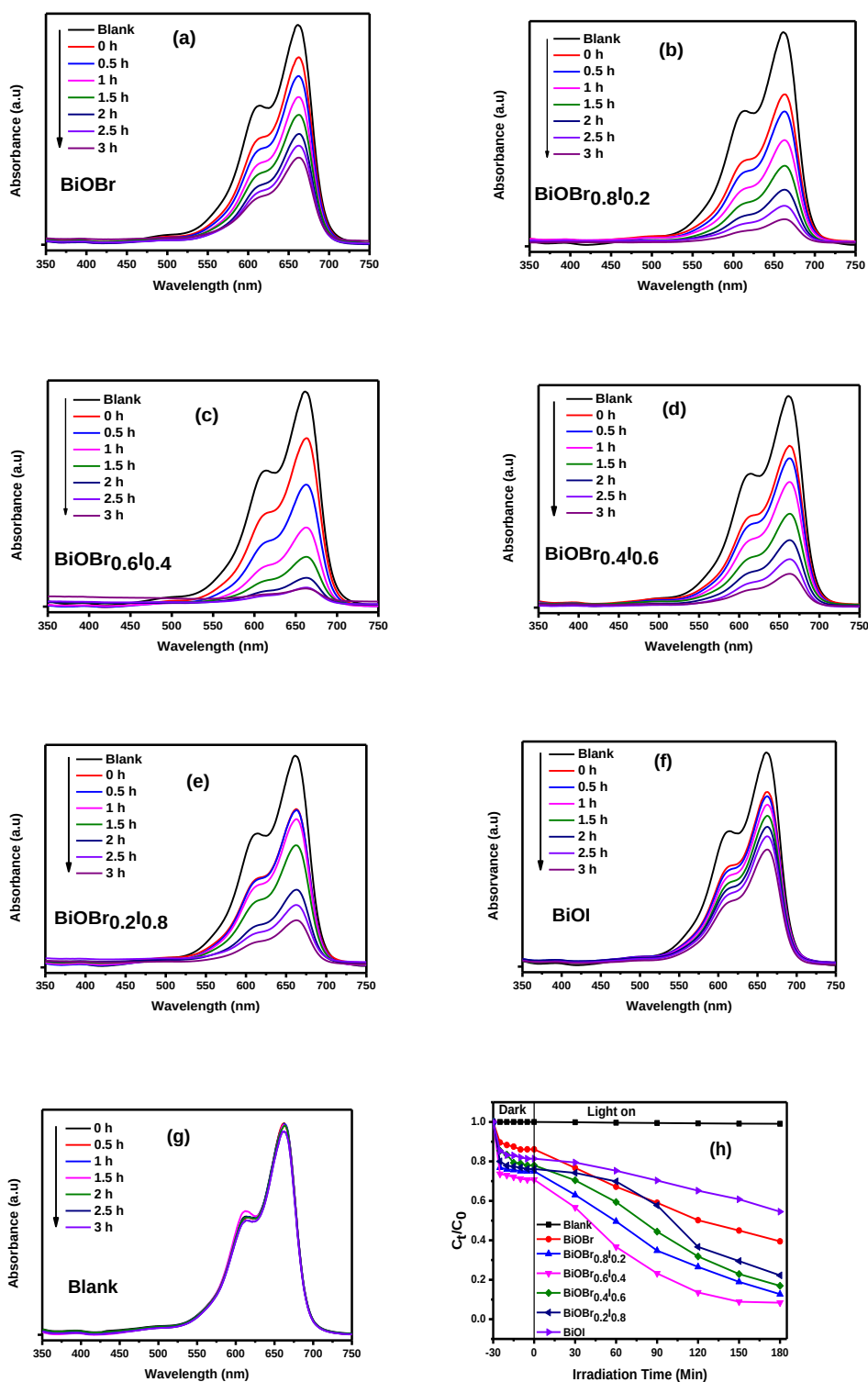


Figure 22. (a-g) UV-Vis MB absorption spectra over BiOBr_mI_(1-m) photocatalysts (h) Photodegradation efficiencies of MB over BiOBr_mI_(1-m) under UV light irradiation. (The blank is the absorbance of 10 ppm MB without catalyst whereas the 0 h is the absorbance 10 ppm MB and photocatalyst after equilibration).

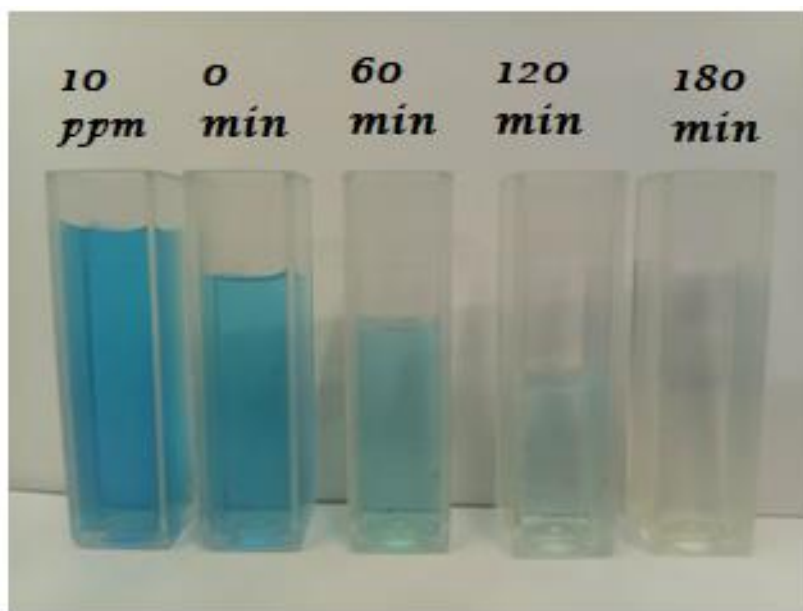


Figure 23. Photodegradation of MB over $\text{BiOBr}_{0.6}\text{I}_{0.4}$ under UV-light irradiation

4.6.4 A study of the thermal effect on the MB photodegradation under solar

It has been observed that the photocatalytic degradation under solar radiation is greater than that of UV light. Compared to the controlled conditions under which MB was performed, the degradation under solar was done in the open air under sunlight, which may have introduced other factors that have led to increased degradation. It was speculated that the increased performance was as a result of the thermal contribution. Therefore, a study of thermal contribution, in particular, was conducted with other factors such as catalyst loading and initial dye concentration constant. $\text{BiOBr}_{0.6}\text{I}_{0.4}$ was selected as the best photocatalyst for the study. An experiment was performed with a setup with four different reaction vessels: two aluminum foil-covered vessels, one with catalyst and another without and another two uncovered vessels with similar catalyst conditions (with/without) were set up. The temperature of the four samples were recorded as 27°C before exposure to sunlight ([Table 12](#)).

Table 12. Change in temperature with irradiation time under solar

Reaction vessel	Temperature (°C) at Time interval (Min)						
	0	30	60	90	120	150	180
Covered with catalyst	27	36	40	42	44	45	45
Covered blank	27	36	40	42	44	45	45
Uncovered with catalyst	27	35	38	40	41	41	41
Uncovered blank	27	35	38	40	41	41	41

For the covered vessels, the temperature increases steadily up to the 150th minute whereas for the uncovered vessels, the temperature increases up to the 120th minute, with no noticeable change thereafter. The covered vessels recorded the highest temperature due to the build-up of heat that could not escape as the vessels were covered. Covering the vessels prevented all the light from reaching the reaction mixture. Further, MB degradation still occurred in the covered vessels, despite the absence of light, which may be ascribed to the build-up of heat energy. [Figure 24](#) illustrates the photocatalytic change for MB both from covered and uncovered flasks. The degradation efficiency under solar irradiation was higher than that under UV irradiation. This could be due to the additional contribution of visible light and infrared radiation (heat) in solar. An increase in temperature as a result of solar irradiation leads to an increase in degradation efficiency. This conclusion is further supported by the studies on the effects of temperature on photodegradation.

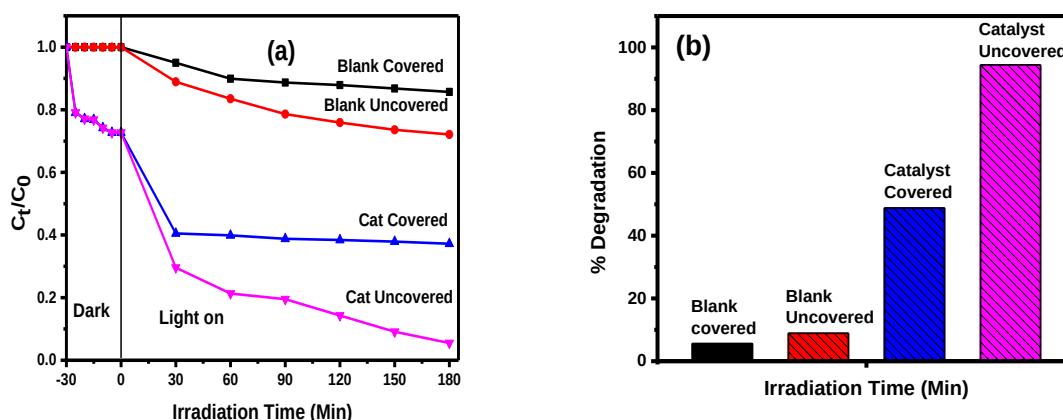


Figure 24. (a) Photodegradation efficiency due to thermal contribution and (b) corresponding % removal of MB after 3 h of solar irradiation.

4.6.4 Kinetic study of the photocatalytic process

The experimental data obtained under the effects of change in time were subjected to three kinetic models i.e. zero, first, and second-order. The equation of pseudo-first-order is generally applied in photodegradation processes if the initial concentration of the contaminant is low [37]. The apparent first-order kinetics is generally depicted by the Langmuir–Hinshelwood model as follows [38]

$$r = -\frac{dC}{dt} = \frac{\kappa KC}{1 + \kappa C} \quad 36$$

where r is dye degradation rate (mg/L min), C dye concentration (mg/L), t is time irradiation, K is dye adsorption coefficient (L/mg), and k is the reaction rate constant (mg/L min). The equation can be simplified as shown below if the amount of C is very low.

$$\ln \frac{C_0}{C_t} = \kappa K t = k_{app} t \quad 37$$

where C_0 is the contaminants' initial concentration [mol/L], C_t is the concentration of the contaminant at time interval t , while k_{app} is the apparent first-order rate constant. Among the prepared materials, $\text{BiOBr}_{0.6}\text{I}_{0.4}$ compound recorded the highest removal rate constant (Table 14). The rate of reaction was approximately 3 and 6 times higher than that of individual BiOBr and BiOI , respectively. As shown in Figure 25, all the plots of rate constants show linear trends,

indicating that the degradation of MB is well defined by the first-order model. The k values for MB removal are recorded in [Table 13](#).

Table 13. Apparent constants rate for the photodegradation of MB

Photocatalysts	MB photodegradation rate (Kapp)								
	Ko	1/ Ko	R ²	K	1/ K	R ²	K ₂	1/ K ₂	R ²
Blank	1.0E-04	9969.3	0.9776	5.3E-05	1887.1	0.9780	2.8E-05	35720.8	0.9783
BiOBr	0.00499	200.40	0.9861	0.00441	226.8	0.9983	0.00405	246.9	0.9837
BiOBr _{0.8} I _{0.2}	0.00675	148.15	0.9740	0.00995	100.5	0.9864	0.01801	55.5	0.8644
BiOBr _{0.6} I _{0.4}	0.00692	144.51	0.9021	0.01322	75.6	0.9743	0.03458	28.9	0.9145
BiOBr _{0.4} I _{0.6}	0.00693	144.30	0.9854	0.00887	112.7	0.9703	0.01329	75.2	0.8756
BiOBr _{0.2} I _{0.8}	0.00644	155.28	0.9343	0.00736	135.9	0.9077	0.00935	107.0	0.8456
BiOI	0.0029	344.83	0.9839	0.00224	446.4	0.9681	0.00175	571.4	0.9449

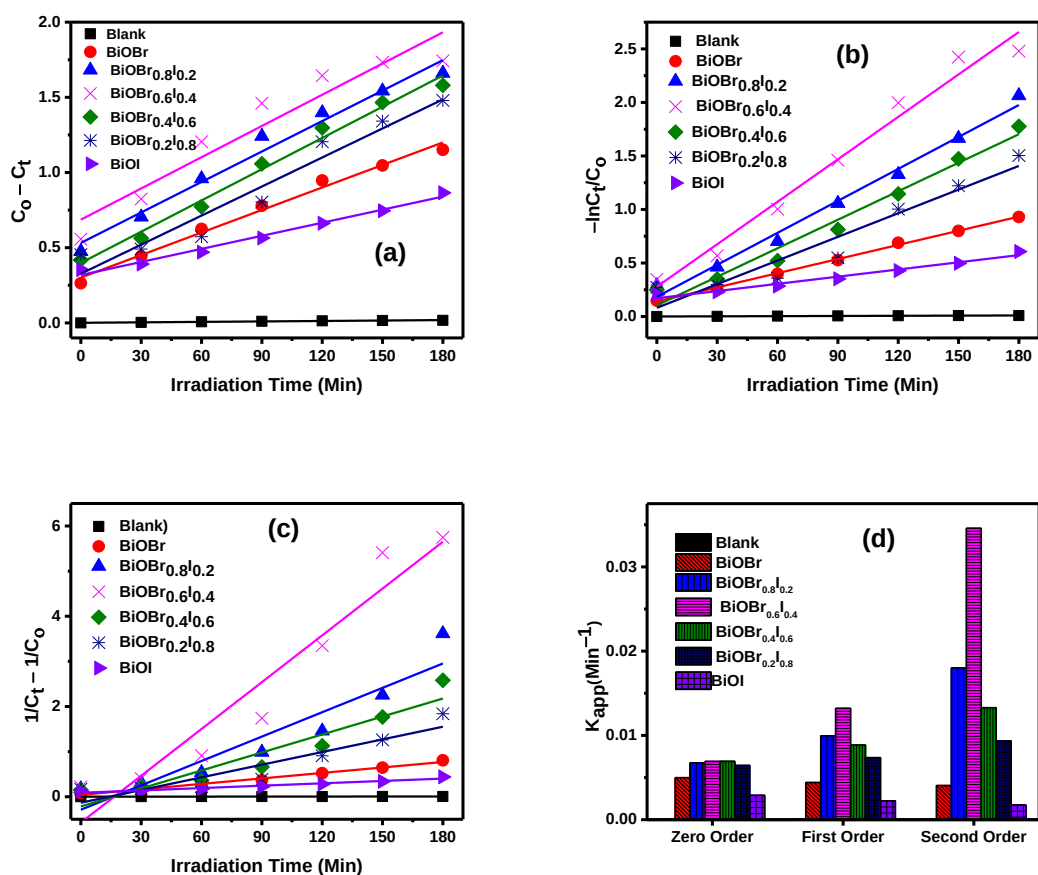


Figure 25. (a) Zero (b) First (c) Second-order for the removal of MB under UV light and (d) corresponding pseudo kinetics rate constants K_{app} with different catalysts.

4.6.5 Photocatalytic mechanisms

A series of photo-induced reactive species for example $O_2^{\bullet-}$, e^- , h^+ , and $HO^{\bullet}$ are directly involved in the photodegradation of MB under the light source. However, to establish the impact of these reactive species on photocatalytic degradation of MB over BiOBr_mI_(1-m) solid solutions, BiOBr_{0.6}I_{0.4} was selected for the quenching experiment for MB removal under irradiation from the UV light. The concentration of 1 mM of P-benzoquinone (BQ) traps $O_2^{\bullet-}$, 1 mM silver nitrate ($AgNO_3$) traps e^- , 1 mM EDTA-2Na traps h^+ , and 1 mM tert-butanol (TBA) traps $OH^{\bullet}$. The variation of percentage degradation efficiency of MB over BiOBr_{0.6}I_{0.4} solid solution is shown in Figure 26. The degradation efficiency shows a little change compared with the no-scavenger experiment when $AgNO_3$ and TBA were added, implying that the e^- and $OH^{\bullet}$ were not the key active species in the catalytic reaction system.

Additionally, the VB edge potential of BiOBr_{0.6}I_{0.4} sample (1.03 eV) is less positive than E° (OH[•]/H₂O) (2.68 eV), signifying that H₂O molecules cannot be oxidized by h⁺ to form OH[•] radicals. In contrast, the removal efficiency is suppressed in EDTA-add for h⁺ and BQ-add for O₂^{•-} experiments, revealing that O₂^{•-} and h⁺ are the dominant active species in this catalytic degradation system.

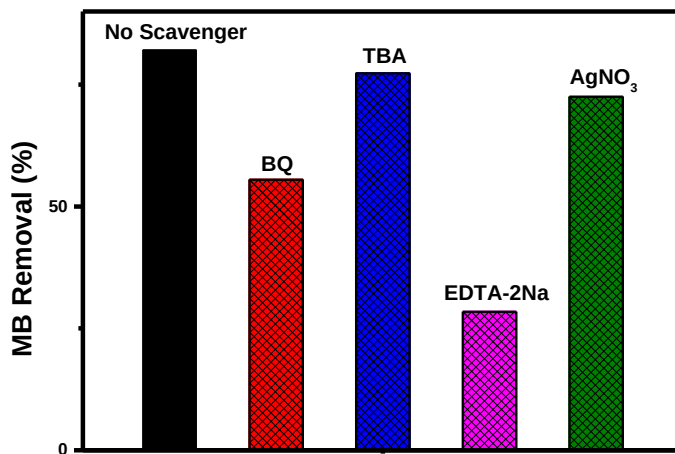


Figure 26. Effects of scavenger on degradation efficiencies of MB over BiOBr_{0.6}I_{0.4} photocatalyst.

The CB edge potential of BiOBr_{0.6}I_{0.4} (-1.12 eV) is highly negative than the E° (O₂/O₂^{•-}) (-0.046 eV) CB, this indicates that O₂ can be thermodynamically reduced to yield O₂^{•-} radicals this explains why the inhibition of O₂^{•-} by adding BQ reduced the degradation efficiency. The CB edge potential of BiOBr_{0.6}I_{0.4} catalyst (-1.12 eV) is more negative than O₂ (0.68 eV), thus the formation of H₂O₂ as shown in the following equation. [39]:



Previous studies have reported that OH[•] radicals can be formed from the reaction between H₂O₂ and the photoinduced electron [40]. Nevertheless, the scavenging experiment showed that OH[•] was not the major reactive species for MB degradation (Figure 30). Hence, it was speculated that H₂O₂ can directly oxidize MB molecules [41]. This hypothesis can be verified by the examination of the effects of H₂O₂ on the removal efficiency of MB, where it was clearly shown in section 4.8.5 that the removal of MB was increased by adding H₂O₂.

4.7 Estimation of chemical oxygen demand

The amount of the organic strength of wastewater is measured by the COD test, which is considered an effective technique. This test reveals the total amount of oxygen needed to oxidize organic substances to water and carbon dioxide. In this measurement, the COD of the MB dye before treatment and after the treatment at the time interval was estimated. The decrease in COD values after treatment shows the effectiveness of photodegradation in the remediation of textile wastewater [42].

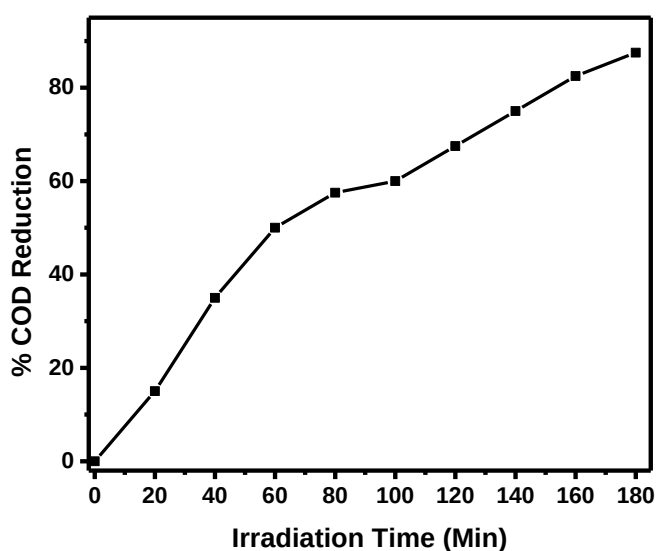


Figure 27. Percentage COD removal over $\text{BiOBr}_{0.6}\text{I}_{0.4}$ with irradiation time.

An initial MB concentration of 10 mgL^{-1} with a COD value of 40 mgL^{-1} and a $0.05 \text{ g BiOBr}_{0.6}\text{I}_{0.4}$ loading was used in all these experiments. During the reaction process, aliquots (4 mL) were drawn at various reaction times and the colorimetric method was used to determine the COD [43], where sulfuric acid and potassium dichromate oxidized the organic matter within the closed system for 120 min at 150°C . The result of the COD examination is shown in Figure 27. The MB COD reduction under solar irradiation after 3 h was 88%, which is lower than the photodegradation efficiency (99%). This difference in efficiency indicates that the photodegradation of MB results in the production of some stable organic intermediates that are biorecalcitrant hence require time to be degraded,

4.8 Degradation parameters

4.8.1 Effect of pH on photocatalysis

To establish the role of pH on photocatalysis efficiency, adjusting the initial pH of the mixture to 3.0, 5.0, 7.0, 8.0, and 14.0 was done by adding 1 M HNO₃ and 1 M NaOH while other conditions were kept constant (BiOBr_{0.6}I_{0.4} dosage of 1.00 g/L and MB concentration of 0.01 g/L). The results are presented in Figure 28a.

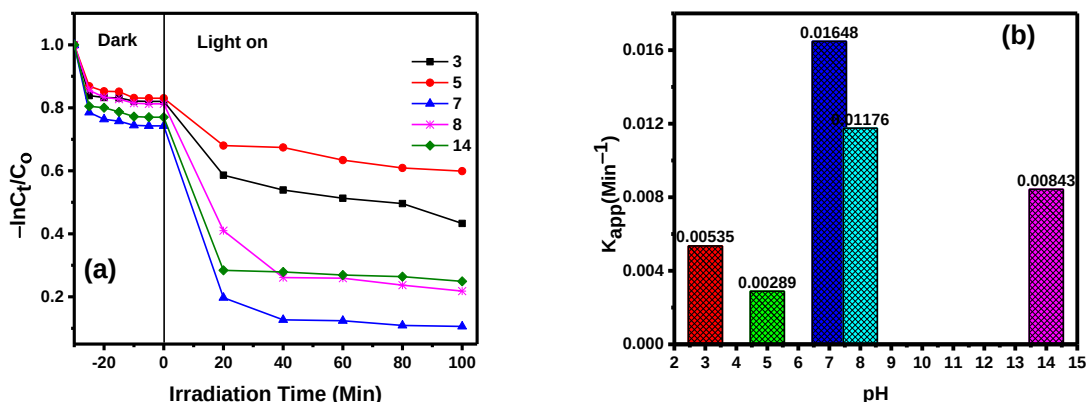


Figure 28. (a) Effects of pH on photodegradation efficiencies of MB over BiOBr_{0.6}I_{0.4} and (b) Degradation rate constants of BiOBr_{0.6}I_{0.4} at different initial pH.

When the pH value is lower than pH_{PZC} , the material surfaces acquire a positive charge, on the other hand, the formation of negative charges on the materials is promoted at higher pH. Photocatalytic degradations of MB in an aqueous suspension of the BiOBr_{0.6}I_{0.4} photocatalyst were carried out to evaluate the effect of pH on degradation efficiency, Figure 28 shows the degradation efficiency of the BiOBr_{0.6}I_{0.4} photocatalyst. The degradation efficiencies recorded are shown in Table 14. The high efficiencies at the pH of 7.0, 8.0, and 14.0 can be ascribed to the existence of a positive charge on BiOBr_{0.6}I_{0.4} ($pH_{PZC} = 5.3$) surface. Thus, adjusting the initial pH of MB to 7.0, 8.0, and 14.0 will result in attraction (electrostatic) between the dye and the positively charged BiOBr_{0.6}I_{0.4}. The electrostatic interaction is useful for improving the adsorptive property thus increasing the degradation efficiencies. On the other hand, adjusting the pH of the pollutant to initial values of 3.0 and 5.0 lowers degradation efficiency due to the electrostatic repulsion between the positively charged BiOBr_{0.6}I_{0.4} surface and the cationic dye

[44]. The degradation rate constants at different initial pH values were obtained and the results are displayed in Figure 28b. The reaction rate constant is higher at a pH of 7.0 indicating the degradation of MB is efficient at neutral pH. Therefore, for ease and cost-effectiveness, the further experiments on degradation parameters were carried out at neutral pH.

Table 14. Degradation efficiencies under different initial pH values.

Initial pH	3.0	5.0	7.0	8.0	14.0
% Degradation	47	28	86	78	75

4.8.2 Catalyst loading

To determine the influence of catalyst loading on the MB removal by the photocatalyst, the dosage of $\text{BiOBr}_{0.6}\text{I}_{0.4}$ was varied from 10 mg to 70 mg under optimum conditions (0.01 g/L, pH, 7.0, and 3 h of reaction time). The removal of MB was enhanced from 38 to 99% with an increasing amount of dosage from 10 mg to 70 mg.

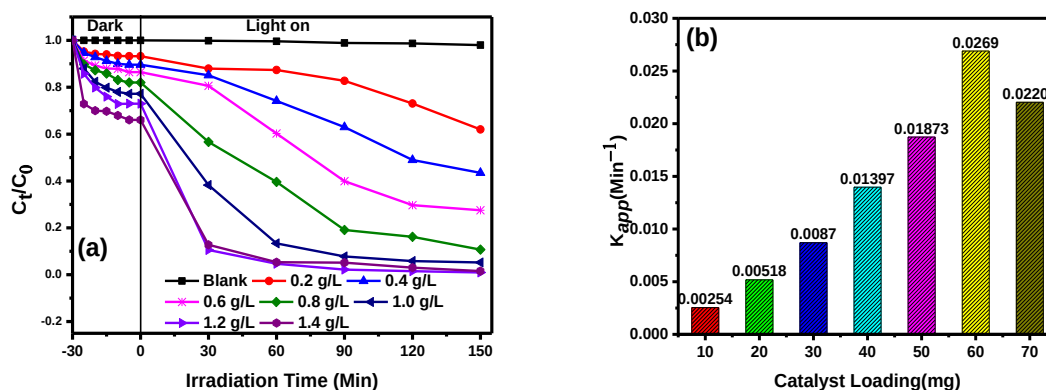


Figure 29. (a) Effects of catalyst loading on photodegradation efficiencies of MB over $\text{BiOBr}_{0.6}\text{I}_{0.4}$ and (b) Degradation rate constants of $\text{BiOBr}_{0.6}\text{I}_{0.4}$ at different catalyst loading.

The number of active sites available is dependant on the catalyst loading which in turn affects photocatalytic process. An increase in active sites will lead to more production of active radicals when the photocatalyst is irradiated. When the catalyst loading is low, the degradation turn over frequency is reduced since a lot of light will be transmitted hence little light will be utilized in

the reaction leading to low degradation. The past studies reported that degradation efficiency increases with an increase in catalyst dosage. However, excessive dosage resulted in a decrease in degradation since the screening effect and light scattering tend to become higher. [45,46]. From Figure 29a it can be observed that the degradation efficiency of $\text{BiOBr}_{0.6}\text{I}_{0.4}$ increases with catalyst loading up to 60 mg. The degradation rate constants for MB removal at different catalyst loading is displayed in Figure 29b. The results show that the rate of reaction increases from $0.00254 - 0.0269 \text{ min}^{-1}$ with increasing catalyst loading from 10 mg to 60 mg, respectively, above 60 mg, the reaction rate reduces to 0.02203 min^{-1} . There is an insignificant difference in the activity of 50 mg and 60 mg. As a result, the dosage of 50 mg is considered as the optimized dosage, therefore, from the economic point of view, 50 mg would be preferred as the optimum catalyst load as less energy would be required for regeneration.

4.8.3 Initial Concentration

The study of the impact of the initial concentration of the pollutant in the photodegradation process is important because it affects the practical application of the photocatalysts.

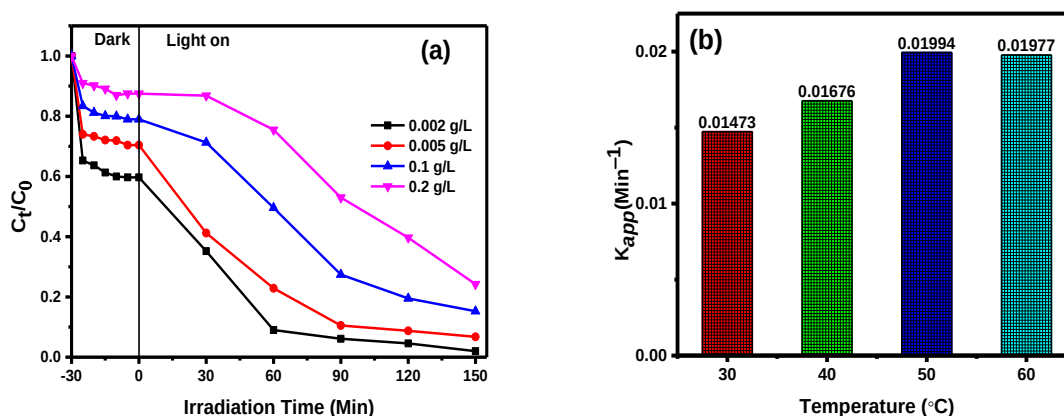


Figure 30. (a) Effects of initial concentration on photodegradation efficiencies of MB over $\text{BiOBr}_{0.6}\text{I}_{0.4}$ and (b) Removal rate constants of $\text{BiOBr}_{0.6}\text{I}_{0.4}$ at various dye concentrations.

To investigate the dependence of degradation effects on the initial contaminant concentration, MB solutions of various initial concentrations ($0.002, 0.005, 0.01, \text{ and } 0.02 \text{ gL}^{-1}$) were degraded using the same catalyst and amount of photocatalyst ($\text{BiOBr}_{0.6}\text{I}_{0.4}$ and 50 mg, respectively). The

results of this study displayed in Figure 30a show that the photocatalyst activity reduces with increasing the initial pollutant concentration, which is in agreement with the literature [47,48]. The photocatalytic performance of a material is influenced by the adsorption of contaminants onto the photocatalyst surface, which depends on the initial concentration of the pollutants [48]. Therefore, the availability of active sites on the photocatalyst surface for adsorbing the contaminant reduces with increasing the initial pollutant concentration hence reducing the activity.[49]. This is due to the fact that the pollutant molecules will compete for the available active sites.

Additionally, with increasing initial contaminant concentration, several organic intermediates will compete with reactive particles for adsorption at the active sites of BiOBr_{0.6}I_{0.4} photocatalyst, thus reducing the generation of these particles responsible for MB degradation [50,51]. Moreover, the reduction in degradation with increasing concentration is due to screening effect that inhibits the penetration of light hence decreasing the number of photons striking the photocatalyst surface. Thereby reducing the generation of an electron from the VB to the CB [50,52,53]. Studying the kinetic curves and degradation rate constants for this study demonstrates that all reaction rates obey the first-order kinetic equation and that the rate constants decrease accordingly with increasing MB concentrations (Figure 30b) as established by other studies [54,55].

4.8.4 Temperature

Several experiments were conducted to study the influence of temperature on the reaction rate of MB photodegradation under UV light irradiation and plots of C_t/C_0 against time, t in the temperature range of 30 to 60 °C are shown in Figure 31a. From the kinetics model fitting, the reaction rate constants increase constantly from 0.01473 to 0.01994 min⁻¹ (Figure 31b) over the temperature range 30 to 50 °C.

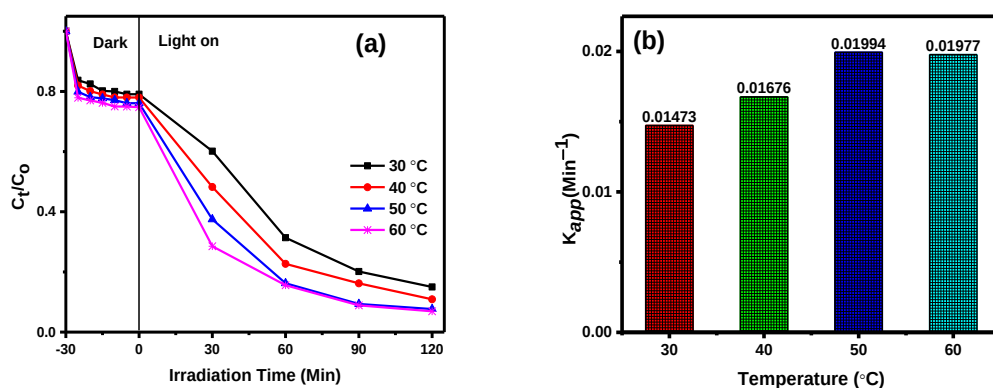


Figure 31. (a) Effects of temperature on photodegradation efficiencies of MB over BiOBr_{0.6}I_{0.4} as and (b) Degradation rate constants of BiOBr_{0.6}I_{0.4} at different temperatures.

The results indicate that degradation generally increases with an increase in reaction temperature. When the temperature rises during the reaction the separation of photoexcited electrons and holes are enhanced, which may improve the photocatalytic activity [56]. Additionally, electron-hole recombination is restrained by increasing the reaction temperature up to a certain limit. The oxidation rate of organic substances at the interface will be enhanced. However, when the reaction temperature rises to a beyond 60 °C, the reaction rates gradually start to reduce due to a decrease of adsorption of MB on the BiOBr_{0.6}I_{0.4} surface and higher recombination of charge carriers hence reducing the activity [57].

4.8.5 Effects of H₂O₂ oxidant

Many studies have reported that the recombining of the photoexcited e^-/h^+ pairs is the main factor limiting the rate of photocatalytic degradation organic compounds.

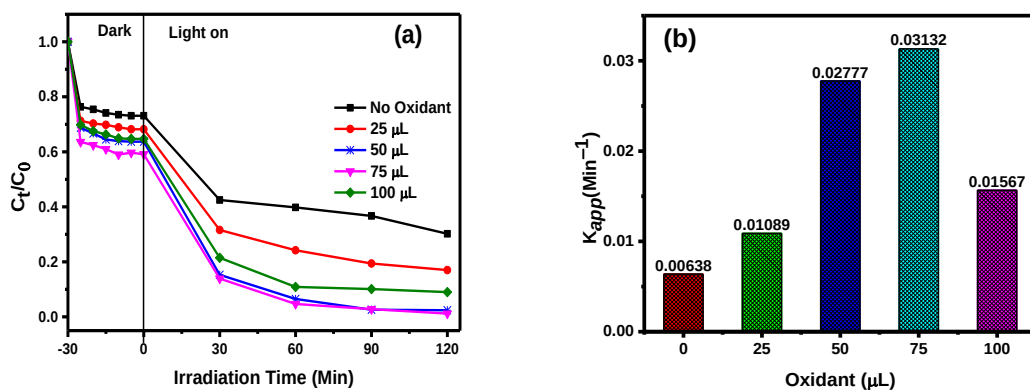


Figure 32. (a) Effects of oxidant on photodegradation efficiencies of MB over BiOBr_{0.6}I_{0.4} and (b) Degradation rate constants of BiOBr_{0.6}I_{0.4} at different amounts of oxidant.

The degradation rates and efficiencies of organic substrates under the light of enough photon energy are significantly improved in the presence of peroxides [58]. In this study, the effect of the addition of H₂O₂ as an oxidant on the MB degradation rate was investigated experimentally. The results are shown in Figure 32a. According to the results displayed in Figure 32b, an increase in the amount of oxidant from 25 to 75 μL , results in a steady rise in the degradation rate of MB, and the value of degradation rate reached the maximum at 75 μL .

Further increase in the amount of oxidant to 100 μL led to a substantial reduction in the rate of removal. When the H₂O₂ is added in excess, it will absorb UV light, thus reducing the average intensity of the light within the solution [58]. Adding a proper amount of H₂O₂ during the reaction process enhances the rate of MB degradation. The proper amount of the oxidant will inhibit the e^-/h^+ pairs from recombination according to the equation below [58]. When H₂O₂ was added in excess, less reactive HO₂[•] (Equation. 39) will be generated that inhibits the subsequent degradation reaction [59].



4.8.6 Investigation of the catalyst stability/recyclability

The stability and recyclability of the photocatalyst are two important factors for the real-time application of photocatalyst. The degradation process was performed five times to investigate the recyclability of the BiOBr_{0.6}I_{0.4} (Figure 33).

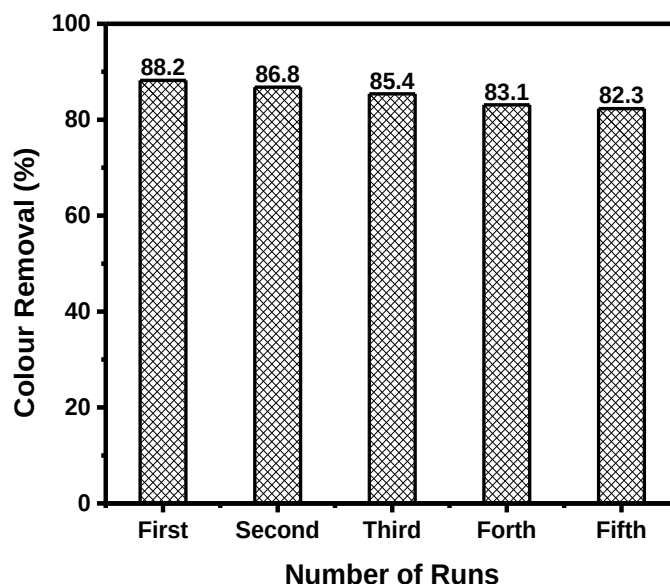


Figure 33. Recyclability test for $\text{BiOBr}_{0.6}\text{I}_{0.4}$ for the removal of 10 mgL^{-1} MB after 3 h of UV-light irradiation at pH 7.0 with 50 mg catalyst dosage.

For MB degradation, the efficiency of $\text{BiOBr}_{0.6}\text{I}_{0.4}$ was reduced to 82 from 88%. There was a 1.4% reduction in efficiency between the 1st and 2nd cycle, 1.4% between the 2nd and 3rd cycle, 1.3% between the 3rd and 4th cycle, whereas between the 4th and 5th cycle the efficiency reduced by 0.8%. It is established that the degradation efficiency slightly drops compared to the fresh catalyst. However, a small decrease in degradation efficiency between the 4th and 5th cycles shows that some of the active sites opened during the reaction process in previous cycles. There is a slight drop in the overall photocatalytic efficiency of $\text{BiOBr}_{0.6}\text{I}_{0.4}$ even after five cycles, signifies that the $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions showed remarkable good stability and efficiency. Therefore, the results establish that the $\text{BiOBr}_m\text{I}_{(1-m)}$ synthesized by simple hydrothermal technique is stable for the photodegradation of contaminants that is a key factor for its practical application.

4.9 Comparison of the performance of TiO₂ and ZnO with BiOBr_mI_(1-m) solid solutions.

The degradation efficiency of MB over TiO₂ and ZnO reported by some authors and the present study is presented in Table 15.

Table 15. Comparison of the degradation of MB over TiO₂, ZnO, and the present study.

Photocatalyst	MB Initial concentration	Catalyst loading (g)	Source of light	Irradiation time (Min)	Percentage degradation (%)	Ref.
TiO ₂	10 mg/L, 200 mL	100	UV	90	98	[60]
	(1.6 × 10 ⁻⁴ M, 10 mg of MB in 200 mL	0.5 g/L	UV-light	40	40	[61]
	30 mg/L, 50 mL	0.01	Mercury lamp (300 W)	60	17	[62]
	10 ppm	0.05	UV light	100	54	[63]
	3 mg/L, 100 mL	0.06	100 mW/cm ² (AM 1.5G one Sun)	30	20	[64]
ZnO	2.87 × 10 ⁻⁵ M	0.08	11 W Uv-lamp	120	83	[65]
	3 × 10 ⁻⁵ M, 3 mL	-	200 W mercury lamp	4.5	34	[66]
	10 mg/L, 250 ml	-	Sunlight	4320	100	[67]
	20 ppm	0.2 g/L	Philips 20 WUV-B lamp	150	100	[68]

Bismuth oxyhalide	10 mg/L. 50 mL	0.05	Solar	180	99	Present study
			UV-light	180	88	

References

1. X. Sun, Y. Zhang, C. Li, Z. Zhang, Z. Peng, H. Si, J. Zhang, Y. Li. “BiOCl_xBr_yI_z (x + y + z = 1) solid solutions with controllable bandgap and highly enhanced visible-light photocatalytic performances,” *J. Alloys Compd.*, vol. 638, no. March, pp. 254–260, 2015.
2. Y. Bai, L. Ye, T. Chen, P. Wang, L. Wang, and X. Shi, “Synthesis of hierarchical bismuth-rich Bi₄O₅Br_xI_{2-x} solid solutions for enhanced photocatalytic activities of CO₂ conversion and Cr (VI) reduction under visible light,” *Applied Catal. B, Environ.*, vol. 203, pp. 633–640, 2017.
3. J. Lu, Q. Meng, H. Lv, L. Shui, M. Jin, Z. Zhang, Z. Chen, M. Yuan, X. Wang, J. M. Liu, G. Zhou. “Synthesis of visible-light-driven BiOBr_xI_{1-x} solid solution nanoplates by ultrasound-assisted hydrolysis method with tunable bandgap and superior photocatalytic activity,” *J. Alloys Compd.*, vol. 732, no. October, pp. 167–177, 2018.
4. J. Cao, B. Xu, H. Lin, B. Luo, and S. Chen, “Chemical etching preparation of BiOI/BiOBr heterostructures with enhanced photocatalytic properties for organic dye removal,” *Chem. Eng. J.*, vol. 185–186, no. January, pp. 91–99, 2012, doi: 10.1016/j.cej.2012.01.035.
5. A. G. Habte, F. G. Hone, and F. B. Dejene, “The influence of malonic acid on the structural, morphological and optical properties of CdSe thin films prepared by a chemical bath deposition method,” *Inorg. Chem. Commun.*, vol. 103, no. January, pp. 107–112, 2019, doi: 10.1016/j.inoche.2019.03.017.
6. B. Ohtani, “Photocatalysis A to Z — What we know and what we do not know in a scientific sense,” *Journal Photochem. Photobiol. C Photochem. Rev.*, vol. 11, no. February, pp. 157–178, 2011, doi: 10.1016/j.jphotochemrev.2011.02.001.
7. K. Zhang, J. Liang, S. Wang, J. Liu, K. Ren, X. Zheng, H. Luo, Y. Peng, X. Zou, X. Bo, J. Li, and X. Yu “BiOCl sub-microcrystals induced by citric acid and their high photocatalytic activities,” *Cryst. Growth Des.*, vol. 12, no. 2, pp. 793–803, 2012.
8. D. T. Durig and J. R. Durig, “Phonon Modes of Molecular Crystals,” *Low Temp. Mol.*

- Spectrosc.*, pp. 477–504, 1996.
9. Y. Na, Y. Il Kim, D. Won Cho, D. Pradhan, and Y. Sohn, “Adsorption/photocatalytic performances of hierarchical flowerlike $\text{BiOBr}_x\text{Cl}_{1-x}$ nanostructures for methyl orange, Rhodamine B and methylene blue,” *Mater. Sci. Semicond. Process.*, vol. 27, no. 1, pp. 181–190, 2014.
 10. W. Maisang, A. Phuruangrat, and C. Randorn, “Enhanced photocatalytic performance of visible-light-driven $\text{BiOBr}/\text{BiPO}_4$ composites,” *Mater. Sci. Semicond. Process.*, vol. 75, no. September 2017, pp. 319–326, 2018.
 11. Y. Liu, W. J. Son, J. Lu, B. Huang, Y. Dai, and M. H. Whangbo, “Composition dependence of the photocatalytic activities of $\text{BiOCl}_{1-x}\text{Br}_x$ solid solutions under visible light,” *Chem. - A Eur. J.*, vol. 17, no. 34, pp. 9342–9349, 2011.
 12. Y. Lee, Y. Dai, J. Fu, and C. Chen, “A series of bismuth-oxychloride/bismuth-oxyiodide/graphene-oxide nanocomposites : Synthesis, characterization, and photocatalytic activity and mechanism,” *Mol. Catal.*, vol. 432, pp. 196–209, 2017.
 13. Z. S. Liu, J. L. Liu, H. Y. Wang, G. Cao, and J. N. Niu, “Boron-doped bismuth oxybromide microspheres with enhanced surface hydroxyl groups: Synthesis, characterization and dramatic photocatalytic activity,” *J. Colloid Interface Sci.*, vol. 463, pp. 324–331, 2016.
 14. M. Yadav, S. Garg, A. Chandra, and K. Hernadi, “Fabrication of leaf extract mediated bismuth oxybromide/oxyiodide ($\text{BiOBr}_x\text{I}_{1-x}$) photocatalysts with tunable bandgap and enhanced optical absorption for degradation of organic pollutants,” *J. Colloid Interface Sci.*, vol. 555, pp. 304–314, 2019.
 15. G. Cheng, J. Xiong, and F. J. Stadler, “Facile template-free and fast refluxing synthesis of 3D desertrose-like BiOCl nanoarchitectures with superior photocatalytic activity,” *New J. Chem.*, vol. 37, no. 10, pp. 3207–3213, 2013.
 16. K. Natarajan, H. C. Bajaj, and R. J. Tayade, “Photocatalytic efficiency of bismuth oxyhalide (Br, Cl and I) nanoplates for RhB dye degradation under LED irradiation,” *J. Ind. Eng. Chem.*, vol. 34, no. November, pp. 146–156, 2016.
 17. L. Qi, Y. Yang, P. Zhang, Y. Le, C. Wang, and T. Wu, “Hierarchical flower-like $\text{BiOI}_x\text{Br}_{(1-x)}$ solid solution spheres with enhanced visible-light photocatalytic activity,” *Appl. Surf. Sci.*, vol. 467–468, no. August 2018, pp. 792–801, 2019, doi: 10.1016/j.apsusc.2018.10.184.

18. S. Cao, C. Guo, Y. Lv, Y. Guo, and Q. Liu, "A novel BiOCl film with flowerlike hierarchical structures and its optical properties," *Nanotechnology*, vol. 20, no. 27, 2009.
19. W. Lei *et al.*, "Synthesis and magnetic properties of octahedral Fe₃O₄ via a one-pot hydrothermal route," *Phys. Lett. Sect. A Gen. At. Solid State Phys.*, vol. 381, no. 4, pp. 314–318, 2017.
20. H. Y. Xu, X. Han, Q. Tan, X. L. He, and S. Y. Qi, "Structure-dependent photocatalytic performance of BiObRxi1-x nanoplate solid solutions," *Catalysts*, vol. 7, no. 5, 2017.
21. Xiufeng Wu, Guangshe Li, Zhihua Leng, Shuo Wang, Nannan Zhang, Yan Wang, Jing Li, and Liping Li "Effect of Alloyed BiOCl_xBr_{1-x} Nanosheets Thickness on the Photocatalytic Performance," *ChemistrySelect*, vol. 4, no. 5, pp. 1757–1762, 2019, doi: 10.1002/slct.201803935.
22. M. Naderi, "Surface Area : Brunauer – Emmett – Teller (BET)," pp. 585–608, 2015, doi: 10.1016/B978-0-12-384746-1.00014-8.
23. S. Zhou, D. Zhang, H. Wang, and X. Li, "A modified BET equation to investigate supercritical methane adsorption mechanisms in shale," *Mar. Pet. Geol.*, vol. 105, no. March, pp. 284–292, 2019, doi: 10.1016/j.marpetgeo.2019.04.036.
24. C. J. Chang, P. Y. Chao, and K. S. Lin, "Flower-like BiOBr decorated stainless steel wire-mesh as immobilized photocatalysts for photocatalytic degradation applications," *Appl. Surf. Sci.*, vol. 494, no. July, pp. 492–500, 2019, doi: 10.1016/j.apsusc.2019.07.203.
25. T. S. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, "Reporting physisorption data for gas/solid systems with Special Reference to the Determination of Surface Area and Porosity," *Pure Appl. Chem.*, vol. 57, no. 4, pp. 603–619, 1985.
26. L. Qi, Y. Yang, P. Zhang, Y. Le, C. Wang, and T. Wu, "Hierarchical flower-like BiOI_xBr_(1-x) solid solution spheres with enhanced visible-light photocatalytic activity," *Appl. Surf. Sci.*, vol. 467–468, no. August 2018, pp. 792–801, 2019, doi: 10.1016/j.apsusc.2018.10.184.
27. R. Li, X. Gao, C. Fan, X. Zhang, Y. Wang, and Y. Wang, "A facile approach for the tunable fabrication of BiOBr photocatalysts with high activity and stability," *Appl. Surf. Sci.*, vol. 355, no. August, pp. 1075–1082, 2015, doi: 10.1016/j.apsusc.2015.07.216.
28. Q. C. Liu, D. K. Ma, Y. Y. Hu, Y. W. Zeng, and S. M. Huang, "Various bismuth oxyiodide

- hierarchical architectures: Alcohothermal- controlled synthesis, photocatalytic activities, and adsorption capabilities for phosphate in water,” *ACS Appl. Mater. Interfaces*, vol. 5, no. 22, pp. 11927–11934, 2013, doi: 10.1021/am4036702.
29. Liqun Ye, Hui Wang, Xiaoli Jin, Yurong Su, Dongqi Wang, Haiquan Xie, Xiaodi Liu, Xinxin Liu. “Synthesis of olive-green few-layered BiOI for efficient photoreduction of CO₂ into solar fuels under visible/near-infrared light,” *Sol. Energy Mater. Sol. Cells*, vol. 144, pp. 732–739, 2016.
 30. J. Jiang, X. Zhang, P. Sun, and L. Zhang, “ZnO/BiOI heterostructures: Photoinduced charge-transfer property and enhanced visible-light photocatalytic activity,” *J. Phys. Chem. C*, vol. 115, no. 42, pp. 20555–20564, 2011.
 31. J. Lyu, Z. Hu, Z. Li, and M. Ge, “Removal of tetracycline by BiOBr microspheres with oxygen vacancies : Combination of adsorption and photocatalysis,” *J. Phys. Chem. Solids*, vol. 129, no. September 2018, pp. 61–70, 2019.
 32. Z. Liu, J. Niu, P. Feng, and Y. Zhu, “Solvothermal synthesis of Bi₂₄O₃₁Cl_xBr_{10-x} solid solutions with enhanced visible-light photocatalytic property,” *Ceram. Int.*, vol. 41, no. 3, pp. 4608–4615, 2015, doi: 10.1016/j.ceramint.2014.12.004.
 33. M. Mousavi, A. Habibi-Yangjeh, and M. Abitorabi, “Fabrication of novel magnetically separable nanocomposites using graphitic carbon nitride, silver phosphate, and silver chloride and their applications in photocatalytic removal of different pollutants using visible-light irradiation,” *J. Colloid Interface Sci.*, vol. 480, pp. 218–231, 2016.
 34. T. Mahmood, M. T. Saddique, A. Naeem, P. Westerhoff, S. Mustafa, and A. Alum, “Comparison of different methods for the point of zero charge determination of NiO,” *Ind. Eng. Chem. Res.*, vol. 50, no. 17, pp. 10017–10023, 2011, doi: 10.1021/ie200271d.
 35. M. Amran, M. Salleh, D. Khalid, W. Azlina, W. Abdul, and A. Idris, “Cationic and anionic dye adsorption by agricultural solid wastes : A comprehensive review,” *DES*, vol. 280, no. 1–3, pp. 1–13, 2011, doi: 10.1016/j.desal.2011.07.019.
 36. P. Raizada, P. Singh, A. Kumar, B. Pare, and S. B. Jonnalagadda, “Zero valent iron-brick grain nanocomposite for enhanced solar-Fenton removal of malachite green,” *Sep. Purif. Technol.*, vol. 133, pp. 429–437, 2014, doi: 10.1016/j.seppur.2014.07.012.
 37. S. Luo, J. Chen, Z. Huang, C. Liu, and M. Fang, “Controllable synthesis of Titania-Supported Bismuth Oxyiodide Heterostructured Nanofibers with Highly Exposed (11 0)

- Bismuth Oxyiodide Facets for Enhanced Photocatalytic Activity,” no. November 2016, doi: 10.1002/cctc.201601047.
38. A. Dash, S. Sarkar, V. N. K. B. Adusumalli, and V. Mahalingam, “Microwave Synthesis, Photoluminescence, and Photocatalytic Activity of PVA-Functionalized Eu^{3+} -Doped BiOX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) Nano flakes,” *Langmuir*, vol. 30, no. January, pp. 1401–1409, 2014, doi: 10.1021/la403996m.
 39. Y. Nosaka and A. Y. Nosaka, “Generation and Detection of Reactive Oxygen Species in Photocatalysis,” *Chem. Rev.*, vol. 117, no. 17, pp. 11302–11336, 2017, doi: 10.1021/acs.chemrev.7b00161.
 40. M. Chen and W. Chu, “ H_2O_2 assisted degradation of antibiotic norfloxacin over simulated solar light-mediated Bi_2WO_6 : Kinetics and reaction pathway,” *Chem. Eng. J.*, vol. 296, pp. 310–318, 2016.
 41. Y. Y. Chen, Y. L. Ma, J. Yang, L. Q. Wang, J. M. Lv, and C. J. Ren, “Aqueous tetracycline degradation by H_2O_2 alone: Removal and transformation pathway,” *Chem. Eng. J.*, vol. 307, pp. 15–23, 2017.
 42. R. Jain and S. Sikarwar, “Semiconductor-mediated photocatalyzed degradation of erythrosine dye from wastewater using TiO_2 catalyst,” *Environ. Technol.*, vol. 31, no. 12, pp. 1403–1410, 2010.
 43. W. Boyles, “The Science of Chemical Oxygen Demand,” *Tech. Inf. Ser.*, vol. Booklet No, p. 7053, 1997.
 44. F. Azeez¹, E. Al-Hetlani, M. Arafa, Y. Abdelmonem, A. A. Nazeer, M. O. Amin & M. Madkour. “The effect of surface charge on photocatalytic degradation of methylene blue dye using chargeable titania nanoparticles,” *Sci. Rep.*, vol. 8, no. 1, pp. 1–9, 2018.
 45. A. Gnanaprakasam, V. M. Sivakumar, and M. Thirumarimurugan, “Influencing Parameters in the Photocatalytic Degradation of Organic Effluent via Nanometal Oxide Catalyst: A Review,” *Indian J. Mater. Sci.*, vol. 2015, no. September, p. 16, 2015, doi: 10.1155/2015/601827.
 46. Z. Mengting, T. A. Kurniawan, Y. Yanping, R. Avtar, and M. H. D. Othman, “2D Graphene oxide (GO) doped p-n type $\text{BiOI}/\text{Bi}_2\text{WO}_6$ as a novel composite for photodegradation of bisphenol A (BPA) in aqueous solutions under UV-vis irradiation,” *Mater. Sci. Eng. C*, vol. 108, p. 110420, 2020, doi: 10.1016/j.msec.2019.110420.

47. M. H. Habibi, N. Talebian, and J. H. Choi, "Characterization and photocatalytic activity of nanostructured indium tin oxide thin-film electrode for azo-dye degradation," *Thin Solid Films*, vol. 515, no. 4, pp. 1461–1469, 2006.
48. Y. N. Tan, C. L. Wong, and A. R. Mohamed, "An Overview on the Photocatalytic Activity of Nano-Doped- TiO_2 in the Degradation of Organic Pollutants," *ISRN Mater. Sci.*, vol. 2011, pp. 3–18, 2011, doi: 10.5402/2011/261219.
49. L. Andronic, A. Enesca, C. Vladuta, and A. Duta, "Photocatalytic activity of cadmium doped TiO_2 films for photocatalytic degradation of dyes," *Chem. Eng. J.*, vol. 152, no. 1, pp. 64–71, 2009, doi: 10.1016/j.cej.2009.03.031.
50. N. A. Jamalluddin and A. Z. Abdullah, "Reactive dye degradation by combined Fe(III)/TiO_2 catalyst and ultrasonic irradiation: Effect of Fe(III) loading and calcination temperature," *Ultrason. Sonochem.*, vol. 18, no. 2, pp. 669–678, 2011.
51. M. A. Behnajady, B. Alizade, and N. Modirshahla, "Synthesis of Mg-doped TiO_2 nanoparticles under different conditions and its photocatalytic activity," *Photochem. Photobiol.*, vol. 87, no. 6, pp. 1308–1314, 2011.
52. A. Verma, A. K. Bakhshi, and S. A. Agnihotry, "Effect of different precursor sols on the properties of $\text{CeO}_2\text{-TiO}_2$ films for electrochromic window applications," *Electrochim. Acta*, vol. 51, no. 22, pp. 4639–4648, 2006, doi: 10.1016/j.electacta.2005.12.048.
53. N. Venkatachalam, M. Palanichamy, B. Arabindoo, and V. Murugesan, "Enhanced photocatalytic degradation of 4-chlorophenol by Zr^{4+} doped nano TiO_2 ," *J. Mol. Catal. A Chem.*, vol. 266, no. 1–2, pp. 158–165, 2007.
54. R. W. Matthews, "Kinetics of photocatalytic oxidation of organic solutes over titanium dioxide," *J. Catal.*, vol. 111, no. 2, pp. 264–272, 1988, doi: 10.1016/0021-9517(88)90085-1.
55. P. H. Chen and C. H. Jenq, "Kinetics of photocatalytic oxidation of trace organic compounds over titanium dioxide," *Environ. Int.*, vol. 24, no. 8, pp. 871–879, 1998.
56. Y. Huang, H. Hu, S. Wang, M. S. Balogun, H. Ji, and Y. Tong, "Low concentration nitric acid facilitates rapid electron-hole separation in vacancy-rich bismuth oxyiodide for photo-thermo-synergistic oxidation of formaldehyde," *Appl. Catal. B Environ.*, vol. 218, pp. 700–708, 2017.
57. G. P. Azad Kumar, "A Review on the Factors Affecting the Photocatalytic Degradation of

- Hazardous Materials,” *Mater. Sci. Eng. Int. J.*, vol. 1, no. 3, pp. 106–114, 2017.
58. N. Daneshvar, D. Salari, and A. R. Khataee, “Photocatalytic degradation of azo dye acid red 14 in the water on ZnO as an alternative catalyst to TiO₂,” *J. Photochem. Photobiol. A Chem.*, vol. 162, no. 2–3, pp. 317–322, 2004.
 59. M. Pérez, F. Torrades, J. A. García-Hortal, X. Domènech, and J. Peral, “Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions,” *Appl. Catal. B Environ.*, vol. 36, no. 1, pp. 63–74, 2002.
 60. S. Liu, H. Sun, S. Liu, and S. Wang, “Graphene facilitated visible light photodegradation of methylene blue over titanium dioxide photocatalysts,” *Chem. Eng. J.*, vol. 214, pp. 298–303, 2013, doi: 10.1016/j.cej.2012.10.058.
 61. O. Ibukun, P. E. Evans, P. A. Dowben, and H. Kyung Jeong, “Titanium dioxide-molybdenum disulfide for photocatalytic degradation of methylene blue,” *Chem. Phys.*, vol. 525, no. June, p. 110419, 2019, doi: 10.1016/j.chemphys.2019.110419.
 62. X. Zhou, L. Wang, X. Liu, M. Xu, and X. Liu, “Organic/inorganic hybrid consisting of supportive poly(arylene ether nitrile) microspheres and photocatalytic titanium dioxide nanoparticles for the adsorption and photocatalysis of methylene blue,” *Compos. Part B Eng.*, vol. 177, no. June, p. 107414, 2019, doi: 10.1016/j.compositesb.2019.107414.
 63. S. M. Tichapondwa, J. P. Newman, and O. Kubheka, “Effect of TiO₂ phase on the photocatalytic degradation of methylene blue dye,” *Phys. Chem. Earth*, vol. 118–119, no. June, p. 102900, 2020, doi: 10.1016/j.pce.2020.102900.
 64. Mustafa K. A. Mohammed, “Sol-gel synthesis of Au-doped TiO₂ supported SWCNT nanohybrid with visible-light-driven photocatalytic for high degradation performance toward methylene blue dye,” *Rev. bíblica*, vol. 13, no. September, pp. 98–99, 2020, doi: 10.1016/j.ijleo.2020.165607.
 65. S. M. Tabrizi Hafez Moghaddas, B. Elahi, M. Darroudi, and V. Javanbakht, “Green synthesis of hexagonal-shaped zinc oxide nanosheets using mucilage from flaxseed for removal of methylene blue from aqueous solution,” *J. Mol. Liq.*, vol. 296, p. 111834, 2019, doi: 10.1016/j.molliq.2019.111834.

66. Z. Han, J. Li, Wentao He, S. Li, Z. Li, J. Chu, Y. Chen “A microfluidic device with integrated ZnO nanowires for photodegradation studies of methylene blue under different conditions,” *Microelectron. Eng.*, vol. 111, pp. 199–203, 2013, doi: 10.1016/j.mee.2013.03.154.
67. A. Mahana, O. I. Guliy, S. C. Momin, R. Lalmuanzeli, and S. K. Mehta, “Sunlight-driven photocatalytic degradation of methylene blue using ZnO nanowires prepared through ultrasonication-assisted biological process using aqueous extract of *Anabaena doliolum*,” *Opt. Mater. (Amst)*., vol. 108, no. June, p. 110205, 2020, doi: 10.1016/j.optmat.2020.110205.
68. I. Fatimah, S. Wang, and D. Wulandari, “ZnO/montmorillonite for photocatalytic and photochemical degradation of methylene blue,” *Appl. Clay Sci.*, vol. 53, no. 4, pp. 553–560, 2011, doi: 10.1016/j.clay.2011.05.001.

CHAPTER 5

5 Conclusion and Recommendations.

5.1 Conclusion

From the series of experiments performed in this study, it can be inferred that $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solution show promising results for applications in textile wastewater treatments. The solid solutions were effectively prepared by simple hydrothermal methods under the same conditions (160°C , 24 h). To understand the morphology, elemental composition, crystallinity, surface area, and absorption edge and bandgap energy of the prepared samples SEM, EDS, XRD, BET, and UV-Vis, respectively, were used for analysis. The degradation efficiencies of the prepared photocatalysts were tested through color removal and COD reduction of a model dye. The photodegradation process was performed under UV-light and solar as the sources of irradiation. UV-light was used as the major source of light in investigating the parameters affecting the degradation process. The best performing photocatalyst was chosen based on degradation efficiency. The degradation reaction was fitted to zero, first, and second-order kinetic models, and the active species responsible for the removal of MB were determined through scavenging experiments. A recyclability test was performed for the $\text{BiOBr}_{0.6}\text{I}_{0.4}$ sample to establish the stability and reusability of the photocatalysts. The main conclusions and findings drawn from this study can be briefly summarized as follows:

- i. A series of bismuth oxy-halides ($\text{BiOBr}_m\text{I}_{(1-m)}$) solid solutions were effectively prepared via a simple hydrothermal method at 160°C for 24 h.
- ii. The SEM analysis showed that the pure BiOBr structures obtained were regular ultrathin plate-like structures. Increase in composition of iodide (I^-) ($M = 0.8, 0.6, 0.4, 0.2$) results into aggregation of microplates to form 3-dimensional flower-like structures. The samples with $M = 0.8$ and 0.6 display a flake-like morphology with average diameters of $2\ \mu\text{m}$. The flake-like structures consist of multi-layered micro sheets that are vertically assembled on the surface. The morphologies of $M = 0.4$ and 0.2 are similar to that of $M = 0.8$ and 0.6 , however, their flake-like structures are slightly different. For the $M = 0.8$ and 0.6 there are more micro sheets assembled within the structure. Bismuth oxy-iodide (BiOI) form flower-like hierarchical micro flowers which consist of loosely packed micro sheets with a thickness of $1 - 2\ \mu\text{m}$ that

intercrossed together to form a 3D structure. The formation of these hierarchical flower-like 3D structures is generally due to the self-assembly process. The TEM pictures also revealed that the BiOBr plate-like morphology and the BiOBr_{0.6}I_{0.4} and BiOI flower-like 3D hierarchical structures were composed of microplates and micro sheets. EDX confirmed the presence of Bi, Br, O, and I in the prepared samples.

- iii. The structural characterization from the XRD analysis revealed that the as-prepared solid solutions consisted of a crystalline tetragonal structure. When the composition of I⁻ increases, the BiOBr_mI_(1-m) peaks broadens and the diffraction peaks change to a lower angle, for example, the (102) plane angle shifts from 31.8 to 29.6 °, this change could be associated with the doping of I⁻ with larger ionic radius of I⁻ (2.2 Å) into Br⁻ (1.96 Å). The high crystallinity improved the photocatalytic activity of the materials
- iv. The BET surface areas of BiOBr, BiOBr_{0.6}I_{0.4}, and BiOI were 0.517, 3.250, and 1.890 m²/g, respectively. The BET surface area of BiOBr_{0.6}I_{0.4} is 6.3 and 3.7 faster than BiOBr and BiOI, respectively hence the higher photocatalytic ability.
- v. The energy band gaps of BiOBr_mI_(1-m) materials changed from 2.59 to 1.96 eV, with the relative changes in the composition of Br and I, thus showing that doping resulted in the tailoring of the bandgap which improved the photodegradation as little energy is required to excite an electron from VB with small bandgap.
- vi. The prepared photocatalysts were poor adsorbent because BiOI, BiOBr_{0.2}I_{0.8}, BiOBr_{0.4}I_{0.6}, BiOBr_{0.6}I_{0.4}, BiOBr_{0.8}I_{0.2}, and BiOBr removed only 14, 15, 16, 19, 17, and 12% of MB, respectively.
- vii. After 3 h of irradiation from solar, the photodegradation efficiencies of BiOI, BiOBr_{0.2}I_{0.8}, BiOBr_{0.4}I_{0.6}, BiOBr_{0.6}I_{0.4}, BiOBr_{0.8}I_{0.2}, and BiOBr solid solutions were determined as 77, 81, 89, 99, 95, and 93%, respectively. The degradation efficiencies of BiOI, BiOBr_{0.2}I_{0.8}, BiOBr_{0.4}I_{0.6}, BiOBr_{0.6}I_{0.4}, BiOBr_{0.8}I_{0.2}, and BiOBr under UV-light were determined to be 33, 71, 78, 88, 83, and 54% respectively. The degradation of efficiencies under solar was higher than UV light. The best performing photocatalyst under solar and UV-light was BiOBr_{0.6}I_{0.4} with degradation efficiency of 99 and 88, respectively. 88% of COD was removed in 3 h of solar radiation. Therefore, the use of a solid solution is effective in the treatment of organic dyes.

- viii. The experimental data obtained under the effects of change in time were subjected to zero, first, and pseudo-second-order models. The degradation followed the first-order kinetic model.
- ix. The scavenging experiment showed that superoxide radicals and hole were the dominant active species in this degradation reaction system.
- x. The efficiency of $\text{BiOBr}_{0.6}\text{I}_{0.4}$ for the removal of MB showed a slight reduction from 88 to 82% after five cycles. This signifies that the $\text{BiOBr}_m\text{I}_{(1-m)}$ solid solutions showed remarkable good stability and efficiency.

5.2 Recommendations

- a. In this study, a fixed temperature (160 °C) and reaction time were the key parameters used during the synthesis of the solid solutions. However, it is recommended that the influence of changing the hydrothermal temperature and the reaction time should be studied.
- b. Different precursors should be explored to determine their effects on the morphology, surface areas, and the photocatalytic efficiencies.
- c. There are very few reports on the PZC of the bismuth oxyhalide solid solutions, therefore, for a real-life application, it is necessary to determine the pH_{PZC} .
- d. We recommend that the intermediates formed as a result of breaking down MB dye should be identified.

Appendix A: Energy-dispersive X-ray spectroscopy

The elemental analysis of the materials was performed by EDX. The atomic structure of each element is unique and in each discrete energy level or electron shells bonded to the nucleus contains unexcited electrons. When the X-ray is focussed on the sample, the electron will be excited to the inner shell of an atom, thus promoting its ejection hence creating an electron-hole. The EDX confirmed the presence of Bi, Br, O, and I in the prepared materials was confirmed by EDX.

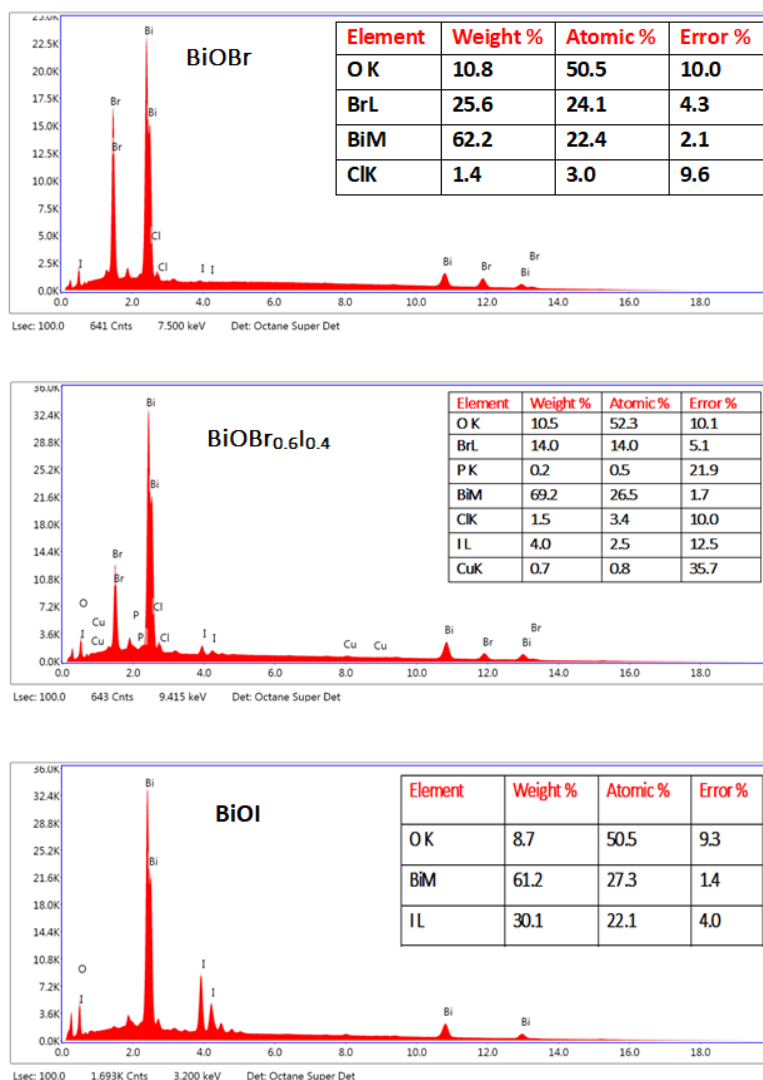
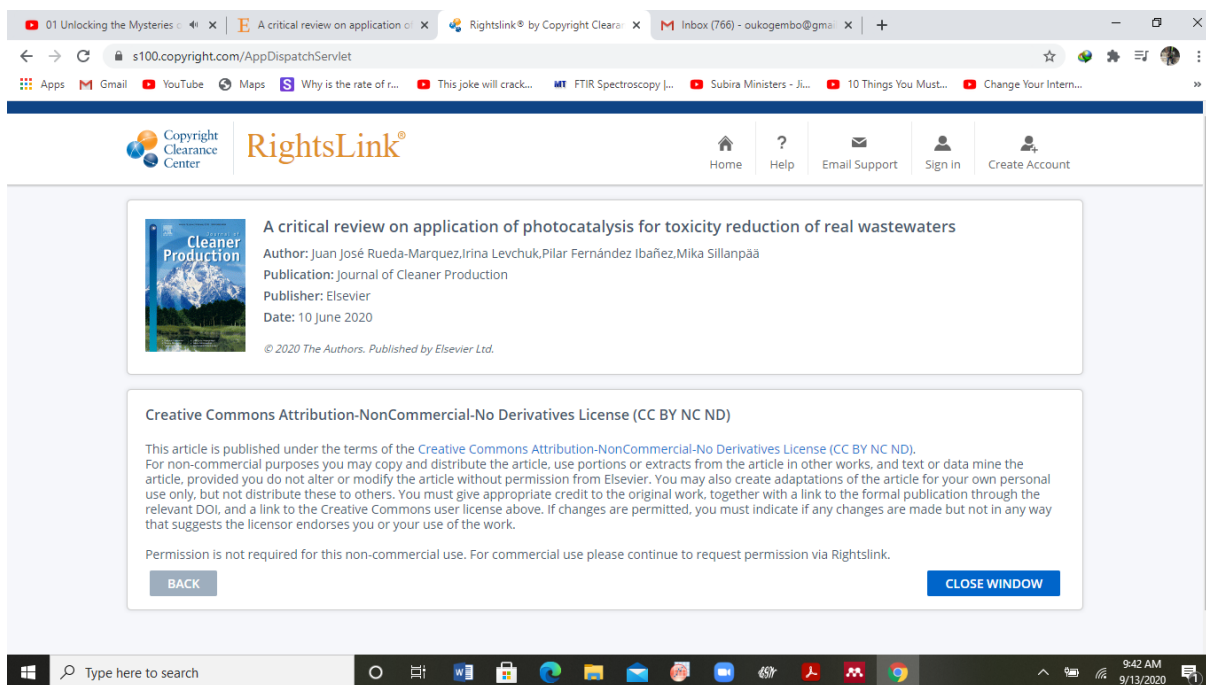


Figure A. EDX of BiOBr, BiOBr_{0.6}I_{0.4}, and BiOI

Appendix B: Yearly scientific publications showing the use of photocatalysis in purification and detoxification of wastewaters.

Reprinted with permission from A critical review on application of photocatalysis for toxicity reduction of real wastewaters, Copyright (2020) Elsevier.



Appendix C: Yearly publications on bismuth-based photocatalysts, BiOCl, BiOBr, and BiOI photocatalysts.

Reprinted with permission from BiOX (X = Cl, Br, I) photocatalytic nanomaterials : Applications for fuels and environmental management, Copyright (2018) Elsevier

ELSEVIER LICENSE
TERMS AND CONDITIONS
Sep 28, 2020

This Agreement between Mr. Robert Gembo ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4905810612102
License date	Sep 11, 2020
Licensed Content Publisher	Elsevier
Licensed Content Publication	Advances in Colloid and Interface Science
Licensed Content Title	BiOX (X = Cl, Br, I) photocatalytic nanomaterials: Applications for fuels and environmental management
Licensed Content Author	Yang Yang, Chen Zhang, Cui Lai, Guangming Zeng, Danlian Huang, Min Cheng, Jiajia Wang, Fei Chen, Chengyun Zhou, Weiping Xiong
Licensed Content Date	Apr 1, 2018
Licensed Content Volume	254
Licensed Content Issue	n/a
Licensed Content Pages	18

Start Page	76
End Page	93
Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Title	Bismuth Oxy-halide (BiOBr _m I _(1-m)) Solid Solutions for the Photodegradation of Methylene Blue Dye under Solar and UV-Light Irradiation
Institution name	Botswana International University of Science and technology
Expected presentation date	Sep 2020
Order reference number	NIL
Portions	Figure 1
	Mr. Robert Gembo
	Private Bag 16, Palapye
Requestor Location	Palapye, 420
	Botswana
	Attn: Mr. Robert Gembo
Publisher Tax ID	GB 494 6272 12
Total	0.00 USD

Appendix D: Schematic illustration of the degradation of methyl orange over modified BiOI

Reprinted (adapted) from Visible light photocatalysis of BiOI and its photocatalytic activity enhancement by in situ ionic liquid modification copyright (2011), with permission from the American Chemical Society

The screenshot shows a web browser window with multiple tabs. The active tab is titled "Rightslink® by Co..." and the address bar shows "s100.copyright.com/AppDispatchServlet". The main content area displays a permission notice for ACS Publications. The notice includes the title "Visible Light Photocatalysis of BiOI and Its Photocatalytic Activity Enhancement by in Situ Ionic Liquid Modification", the author "Yunan Wang, Kejian Deng, Lizhi Zhang", the publication "The Journal of Physical Chemistry C", the publisher "American Chemical Society", and the date "Jul 1, 2011". Below this, a section titled "PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE" explains that this type of permission is granted instead of standard terms and conditions. It lists several conditions: permission is granted for print and electronic formats; figures and tables may be adapted; appropriate credit must be given; and one-time permission is granted for the specified use. At the bottom of the notice are "BACK" and "CLOSE WINDOW" buttons. The footer of the page includes copyright information for 2020 and links to the Copyright Clearance Center, Inc., Privacy statement, and Terms and Conditions. The Windows taskbar at the bottom shows the time as 10:40 AM on 9/11/2020.

Visible Light Photocatalysis of BiOI and Its Photocatalytic Activity Enhancement by in Situ Ionic Liquid Modification

Author: Yunan Wang, Kejian Deng, Lizhi Zhang
Publication: The Journal of Physical Chemistry C
Publisher: American Chemical Society
Date: Jul 1, 2011
Copyright © 2011, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.

BACK CLOSE WINDOW

© 2020 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions

Appendix E: The suggested oxidation mechanism for cyclohexane over TiO₂ and BiOM photocatalysts

Reprinted with permission from Selective oxofunctionalization of cyclohexane over titanium dioxide-based and bismuth oxyhalide (BiOX, X= Cl⁻, Br⁻, I⁻) photocatalysts by visible light irradiation, Copyright (2017) Elsevier

ELSEVIER LICENSE
TERMS AND CONDITIONS

Sep 28, 2020

This Agreement between Mr. Robert Gembo ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4917010390365
License date	Sep 27, 2020
Licensed Content Publisher	Elsevier
Licensed Content Publication	Applied Catalysis B: Environmental
Licensed Content Title	Selective oxofunctionalization of cyclohexane over titanium dioxide-based and bismuth oxyhalide (BiOX, X=Cl ⁻ , Br ⁻ , I ⁻) photocatalysts by visible light irradiation
Licensed Content Author	Adolfo Henríquez,Héctor D. Mansilla,Azael Martínez Martínez-de la Cruz,Juanita Freer,David Contreras
Licensed Content Date	Jun 5, 2017
Licensed Content Volume	206
Licensed Content Issue	n/a
Licensed Content Pages	11

Start Page	252
End Page	262
Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Title	Bismuth Oxy-halide (BiOBr _m I _(1-m)) Solid Solutions for the Photodegradation of Methylene Blue Dye under Solar and UV-Light Irradiation
Institution name	Botswana International University of Science and technology
Expected presentation date	Sep 2020
Portions	Scheme 1
	Mr. Robert Gembo Private Bag 16, Palapye
Requestor Location	Palapye, 420 Botswana Attn: Mr. Robert Gembo
Publisher Tax ID	GB 494 6272 12
Total	0.00 USD