

**Engineered PPy-g-C₃N₄-MIL88B Z-scheme heterojunction for
visible-light-driven TCPP degradation with improved charge
separation and minimized toxicity**

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Abstract

Engineered PPy-g-C₃N₄-MIL88B Z-scheme heterojunction for visible-light-driven TCPP degradation with improved charge separation and minimized toxicity

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This work introduces a novel photocatalytic methodology that leverages the synergistic action of visible light and H₂O₂ with a green catalyst for the efficient degradation of tris(1-chloro-2-propyl) phosphate (TCPP). A PPy-g-C₃N₄-MIL88B photocatalyst was synthesized with a narrowed bandgap, high structural stability, minimized iron leaching, and enhanced charge transfer properties. Comprehensive characterization using HAADF-FE-SEM, TEM, FTIR, XRD, XPS, BET, PL, and UV-DRS confirmed the successful fabrication of the photo-Fenton catalyst. UV-DRS analysis revealed a 28% bandgap reduction, from 3.2 eV (MIL-88B) to 2.3 eV (PPy-g-C₃N₄-MIL88B). The PPy-g-C₃N₄-MIL88B/H₂O₂/LED system was subsequently synthesized and employed for TCPP degradation, where five by-products (BPs) were detected and quantified, each showing significant elimination within 20 minutes. Toxicity assays demonstrated improved ecological safety, as the LC₅₀ (96 h) for fathead minnows increased from 7.24 mg/L (TCPP) to 19.12 mg/L (BP175) and 58.23 mg/L (BP323) after treatment. Kinetic modelling through response surface methodology and central composite design identified a reduced quartic model with strong significance ($p < 0.0001$). ANOVA-based optimization indicated near-complete TCPP degradation (99.29%) under optimal conditions of 59 min irradiation, 100 mg/L catalyst dosage, pH 5, and 15 L/min airflow. Finally, the applicability of PPy-g-C₃N₄-MIL88B was validated in real water matrices from four Canadian lakes and rivers, achieving over 65% contaminant removal. More, three machine learning models were employed, including KNN (K=5), Random Forest, and linear regression for data modelling and degradation efficiency prediction. Among the applied models, Random Forest showed the best performance in predicting TCPP degradation efficiency

with the least MSE (15.196). These findings highlight the potential of PPy-g-C₃N₄-MIL88B as a sustainable photocatalyst for addressing emerging water pollutants.

Keywords: TCPP; Photo-Fenton catalysts; Z-scheme; degradation; Optimization.

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List of Symbols

English Letters

A	Irradiation time factor	min
C	pH factor	—
EEO	Electrical Energy per Order	kWh·m ⁻³ ·order ⁻¹
k	reaction rate constant	min ⁻¹
K _p	scavenging rate constant of pollutant	L·mg ⁻¹ ·min ⁻¹
K _B	scavenging rate constant of scavenger	L·mg ⁻¹ ·min ⁻¹
P	pollutant concentration	mg·L ⁻¹
B	scavenger concentration	mg·L ⁻¹
t	time	min

Greek Letters

Symbol	Description
Δ	mass error (ppm) in LC-MS
λ	wavelength (UV–vis)

Symbol	Description
η	removal/degradation efficiency
ϕ	photon flux (light input)

List of abbreviations

Abbreviation	Meaning
PPy	Polypyrrole
g-C ₃ N ₄	graphitic carbon nitride
GO	Graphite oxide
MIL-88B	Iron-based Metal–Organic Framework MIL-88B (Materials of Institute Lavoisier)
MIL	Materials of Institute Lavoisier
MOF	Metal–Organic Framework
RSM	Response Surface Methodology
CCD	Central Composite Design
LC-MS	Liquid Chromatography–Mass Spectrometry
XPS	X-ray Photoelectron Spectroscopy
UV-DRS	UV–diffuse reflectance spectroscopy
SEM	Scanning Electron Microscopy
BET	Brunauer–Emmett–Teller surface area
H ₂ O ₂	Hydrogen peroxide
•OH	Hydroxyl radical

Abbreviation	Meaning
$O_2\bullet^-$	Superoxide radical
h^+	photogenerated holes
HA	Humic acid
IPA	Isopropanol alcohol
TCPP	Tris(2-chloro-isopropyl) phosphate
TOC	Total Organic Carbon

1. Chapter 1: Introduction

1.1. Background

With population growth, changing lifestyles, rapid industrialization, and agricultural advances, a diverse group of pollutants at low concentrations and high toxicity are detected in the aquatic environment [1]. In many countries, including China [2] the United States [3], France [4], Japan [5], etc., the recipient water bodies are polluted. The contaminated water generated is owing to the overwhelming discharge of effluents from various sectors. Industrial, agricultural, and municipal effluents might be the significant sources spreading a large volume of contaminants in the environment. Recalcitrant organic pollutants, including pharmaceuticals and personal care products, pesticides, surfactants, and hormones, represent a vast group of contaminants [6]. These persistent pollutants pose harmful risks to terrestrial and aquatic life even at trace concentrations, given their refractory nature. Therefore, sustainable water treatment approaches are required to diminish the potential health risk associated with these chemicals [7,8].

Flame retardants (FRs) are a well-known group of non-degradable emerging contaminants used in consumer products. These pollutants typically migrate from finished products to the environment through processes such as leaching, volatilization, and infiltration. [9]. Even at trace concentrations, FR contaminants exert detrimental effects on marine and land ecosystems. Tris (1-chloro-2-propyl) phosphate (TCPP) is a famous flame retardant representing chlorinated organophosphate flame retardants (OPFRs) group. TCPP exhibited water solubility of 1200 mg L^{-1} at 25°C , with 2.89 octanol-water partition coefficient [10]. TCPP has been recognized as one of the EU high production volume chemicals owing to its huge production and consumption [11,12]. Around 40% of the TCPP in customer products is released to the environment [13].

TCPP concentration in drinking water, surface water, and groundwater is in the range of ng L^{-1} to $\mu\text{g L}^{-1}$ [9,13]. Reported values of TCPP in surface water and in wastewater effluent were as elevated as 200 ng L^{-1} and $24 \mu\text{g L}^{-1}$, respectively [11]. OPFRs could cause neurotoxicity, carcinogenicity, and endocrine distribution [13].

Given the appearance and persistence of flame retardants in Canadian waterways, adopting a feasible and efficient technique is imperative to achieve the Canadian drinking water standard. In Canada, Quebec, 16 flame-retardant compounds were detected in the St. Lawrence River's fish tissue. These deleterious species enter human bodies through contaminated water and accumulate in human tissues. The importance of removing flame retardants lies in the fact that these species could adversely impact thyroid hormone levels, induce immunotoxicity, and cause DNA damage while negatively affecting liver enzyme reactivity [5, 10]. Up to now, some treatment ways have been suggested and explored in the literature [1,10]. An increasing number of investigations have focused on conventional wastewater treatment methods, including adsorption, filtration, coagulation, and biological treatment for the decomposition of organic pollutants [14–18]. These studies showed that the employed methods were ineffective for the complete degradation of recalcitrant organic compounds and highlighted the inherent challenges related to their complete mineralization [19]. The failure of these processes to completely mineralize hazardous pollutants has encouraged the development of photocatalytic advanced oxidation processes (AOPs) [20]. Various techniques have been used for flame retardant removal, such as constructed wetlands [21], photocatalysis [11], reactor membrane [22], adsorption [23], and ozonation [24]. Photocatalysis is a potential candidate in large-scale applications to degrade various contaminants. The attractive features of photocatalysis, such as sustainability, eco-friendliness, and widespread availability, can be pointed out [7,25,26]. However, this method suffers from technical challenges such as low

visible light absorption, agglomeration tendency of catalyst particles, separation, and regeneration difficulties [27,28]. Some of the abovementioned limitations have been investigated, and recommendations such as using heterojunction photocatalysis have been made to enhance photon absorption [29–32]. To date, a variety of photocatalytic materials, including metal-organic frameworks (MOFs), metal oxides [33], graphitic carbon-nitride-based catalysts [34], etc., have been investigated. These materials are selected for photocatalysis owing to their chemical stability, high photocatalytic activity, cost efficiency, and electronic structure [35].

Photocatalysis has also become the most popular technique for the removal of Tris(2-chloroisopropyl) phosphate (TCPP); one of the most famous flame retardants, frequently discovered in waterways, from wastewater. While the constructed wetlands could remove TCPP up to 26%-28% [21] photocatalysis exhibited more than 60% TCPP removal [11]. Liu et al. [10] showed that using mesoporous TiO_2 , 67 to 100% of the TCPP content was eliminated successfully.

1.2. Problem statement and research questions

The increasing detection of Tris(2-chloroisopropyl) phosphate (TCPP), one of the most widely used organophosphate flame retardants, in aquatic environments across Canada has raised significant environmental and public health concerns. As a persistent organic pollutant, TCPP is known for its resistance to natural degradation processes, its potential to bioaccumulate, and its toxicity to aquatic organisms and humans. Despite growing attention to its ecological impacts, conventional water treatment technologies remain largely ineffective in addressing the complete and safe removal of TCPP. Many of these approaches either fail to achieve sufficient degradation or lead to the generation of toxic intermediate compounds, which can be more harmful and persistent than the parent pollutant.

Although photocatalysis has been introduced as a promising approach for degrading various organic pollutants, there remains a substantial gap in the development of novel heterojunction photocatalysts for the degradation of persistent compounds such as TCPP. Besides, limited information is available regarding the optimization of operational parameters, energy efficiency, catalyst reusability, toxicity studies of the degradation by-products and the degradation mechanisms specific to TCPP.

Given these knowledge gaps, this research aims to develop and investigate a novel heterojunction photocatalyst system capable of efficiently degrading TCPP in aqueous environments using LED light as a sustainable energy source. The study also seeks to explore the influence of catalyst morphology, operational parameters, and degradation pathways, with the broader goal of providing a cost-effective, energy-efficient, and environmentally friendly water treatment solution. Particular attention will be given to minimizing the formation of toxic degradation by-products, whose identification remains a significant limitation in the existing literature. By bridging these research gaps, this study aspires to contribute to the development of advanced photocatalytic materials and strategies for the treatment of water contaminated with flame retardants.

To achieve the objectives outlined above, the following research questions guided the investigation:

1. How can a heterojunction MIL-based photocatalyst be synthesized to effectively degrade TCPP under LED light irradiation?

This question explores the baseline performance of the novel catalyst in targeting TCPP removal, focusing on degradation rate, completeness, and repeatability.

2. What are the optimal operational parameters for maximizing the photocatalytic degradation of TCPP?

Key parameters to be examined include catalyst loading, pH, irradiation time, light intensity, and initial pollutant concentration. Understanding these factors is essential for optimizing the system efficiency.

3. How do variations in the catalyst morphology, induced by altering synthesis conditions such as temperature and pressure, impact the photocatalytic morphology and performance of the synthesized photocatalyst toward TCPP degradation?

This question investigates the structural–functional relationship of the catalyst, seeking to determine how physical changes at the nanoscale level affect reactivity and efficiency of the photocatalyst.

4. Can the developed photocatalytic system minimize or prevent the generation of toxic intermediate by-products, and what is the degradation pathway of TCPP under these conditions?

Here, the focus is on analyzing the transformation products formed during degradation, and understanding the associated chemical mechanisms to ensure that the process does not inadvertently produce more hazardous substances.

5. Is the proposed photocatalytic system energy-efficient and cost-effective, and can the catalyst be reused over multiple cycles without significant loss of activity?

This question addresses the long-term feasibility of the proposed system in real-world applications by evaluating the sustainability, economic viability, and operational robustness of the photocatalyst.

1.3. Research objectives

Based on the abovementioned problems and identified research questions, it is crucial to explore and introduce an efficient photocatalysis system as a leading technique for flame retardants' degradation. Introducing a photocatalysis technique suitable for the degradation of flame retardants without generating toxic intermediates or by-products is necessary. This study represents an attempt to assess and investigate the feasibility and effectiveness of using synthesized novel heterojunction MIL-based catalysts under LED light for the removal of flame retardants from water. The first step involved examining catalyst morphology and characteristics. The following steps focused on the optimization of operational parameters during the photocatalysis of TCPP.

In light of the above discussion, the following main objectives were identified in this research:

- Development of an energy-efficient, eco-friendly, and optimized photocatalytic system capable of degrading TCPP and the generated by-products.
- Achievement of optimized operational conditions for the highest degradation efficiency of TCPP through experiments.
- Optimization of the energy efficiency and cost-effectiveness of the developed photocatalytic process through the preparation of a robust, reusable photo-Fenton catalyst.
- Reduction of the overall toxicity of the system through mineralization of the degradation by-products.
- Assessment of the capability and efficiency of the developed photocatalytic system for degradation of TCPP in Canadian waterways.

1.4. Thesis outline and organization

This dissertation is a manuscript-based thesis in which the contents of chapters 2 to 6 are part of the published or submitted journal papers in the area of environmental chemical engineering:

Chapter 2:

- **M. Motamedi**, L. Yerushalmi, F. Haghighat, Z. Chen "A critical review of water contamination by polybrominated diphenyl ethers (PBDE) and main degradation techniques" *Journal of Environmental Chemical Engineering*, 2022, 108196.
- **M. Motamedi**, L. Yerushalmi, F. Haghighat, Z. Chen "Recent developments in photocatalysis of industrial effluents: A review and example of phenolic compounds degradation" *Chemosphere*, 2022, 133688.

Chapter 4:

- **M. Motamedi**, L. Yerushalmi, F. Haghighat, Z. Chen, Y. Zhuang "Comparison of photocatalysis and photolysis of 2,2,4,4-tetrabromodiphenyl ether (BDE-47): Operational parameters, kinetic studies, and data validation using three modern machine learning models", *Chemosphere*, 2023, 138363.

Chapter 5:

- **M. Motamedi**, Z. Chen, L. Yerushalmi, F. Haghighat "Z-scheme PPy-g-C₃N₄-MIL88B heterogeneous photo-Fenton catalyst for tris-(2-chloroisopropyl) phosphate (TCPP) degradation: by-products, RSM optimization, and machine learning models" *Journal of Water Process Engineering*, 2026, 82, 109373.

Chapter 6:

- **M. Motamedi**, L. Yerushalmi, F. Haghighat, Z. Chen " *In-situ* polymerization of Z-scheme PPy-g-C₃N₄-MIL-88B heterogeneous photo-Fenton catalyst for tris-(2-chloroisopropyl) phosphate (TCPP) degradation: morphologies, operational parameters, RSM optimization, and energy efficiency", *Green synthesis* (submitted).

- **M. Motamedi**, L. Yerushalmi, F. Haghighat, Z. Chen, "Development of Three Step Modified MIL-based Heterogeneous Photocatalysts for Tris-(2-chloroisopropyl) Phosphate (TCPP) Degradation" *International Conference on Sustainable Energy and Green Technology*, 2023, Ho Chi Minh, Vietnam.
- **M. Motamedi**, Z. Chen, L. Yerushalmi, F. Haghighat, Z. Asif, "Z-scheme MIL-based Heterogeneous Photo-Fenton Catalysts for Tris-(2-chloroisopropyl) Phosphate (TCPP) Degradation and Possible Application to Risk-based TCPP Control under Field Water Conditions" *PEOPLE 2023 – Collaborative Solutions to Environmental Problems under Climate Change*, 2023, Montreal, Canada.
- **M. Motamedi**, L. Yerushalmi, F. Haghighat, Z. Chen, "Comparison of photocatalytic debromination and photolysis of 2,2,4,4-tetrabromodiphenyl ether (BDE-47)" *72nd Canadian Chemical Engineering Conference*, 2022, Vancouver, Canada.

The subsequent sections of this dissertation are organized as follows:

Chapter 1 (Introduction) - This chapter provides an overview of the background, problem statements, research questions, and main objectives of the research.

Chapter 2 (Literature review) – This chapter presents a comprehensive literature review covering the prior research on the photocatalysts preparation, design and operation of photocatalytic systems used for TCPP degradation. It provides an in-depth discussion of the previously introduced systems, delves into their limitations, and proposes potential research directions in this domain.

Chapter 3 (Methodology)- This chapter provides detailed descriptions of photocatalytic procedures and setups employed at bench scale experiments. Additionally, this chapter focuses on the step-by-step methodology of photocatalyst fabrication. Section 3.1. discusses the preparation of three MIL88B photo-Fenton catalysts, including graphite carbon nitride (g-C₃N₄), and polypyrrole (PPy). It further explores the modification of MIL88B with g-C₃N₄, and then examines the implantation of PPy on the previously prepared photocatalysts (MIL88B-g-C₃N₄).

The characteristic analyses to validate and assess the accuracy of the proposed photo-Fenton catalysts are also discussed in this section. Rigorous characterization analysis, including HAADF-FE-SEM, TEM, FTIR, XRD, XPS, BET, PL, and UV-DRS, confirmed the authenticity of the prepared photo-Fenton catalysts. In section 3.2, the influence of key operational parameters (reaction time, photocatalyst dosage, pH, TCPP initial concentrations, and the effect of radical scavengers) on system performance is discussed. The effect of environmental conditions on TCPP degradation efficiency was investigated by changing one parameter at a time, and also with the interaction of parameters.

Section 3.4. introduces the degradation pathways, by-products detection and quantification, followed by intermediates toxicity assessment. In this part, LC-MS was used to identify and relatively quantify the degradation intermediates of TCPP which were produced during the photo-Fenton reaction of PPy-g-C₃N₄-MIL88B under LED illumination. First, the five main by-products were detected, and second, the relative quantification of the degradation by-products was evaluated. Based on the detected intermediates, three possible degradation pathways were presented.

In section 3.5. experimental data were modelled using three machine learning models. Three machine learning models, including Linear Regression, K-Nearest Neighbours (KNN), and Random Forest, were employed to predict the degradation efficiency of TCPP. Key operational parameters influencing photocatalytic degradation included irradiation time, solution pH, catalyst loading, and initial TCPP concentration. A total of 500 experiments were conducted, and the input data were classified accordingly. The input features comprised irradiation time (min), photocatalyst dose (mg/L), initial TCPP concentration (ppb), and solution pH, while the output variable was the TCPP degradation efficiency (%). Prior to the model development, the dataset

was randomly split into training (80%) and testing (20%) subsets. Model performance was evaluated using the mean square error (MSE) and coefficient of determination (R^2). The feature correlation matrix illustrated the relationships between the experimental variables and highlighted how each one correlates with the degradation efficiency.

Chapter 4 (Comparison of photocatalysis and photolysis of 2,2,4,4-tetrabromodiphenyl ether (BDE-47): Operational parameters, kinetic studies, and data validation using three modern machine learning models)-In this chapter, the photocatalysis and photolysis of BDE-47 have been studied and reported. First, the effect of operational parameters (including time, P25 loading, pH, and methanol/water ratio) on the photocatalysis and photolysis of BDE-47 was reported and compared. Afterwards, the debromination pathway is proposed and discussed. Finally, three machine learning models were proposed and evaluated based on statistical criteria. In the end, kinetic studies, COD and TOC removal, and electrical energy consumption were estimated to further compare BDE-47 photocatalysis and photolysis.

Chapter 5 (Visible light-driven photocatalytic degradation of TCPP by PPy-g-C₃N₄-MIL88B photo-catalyst with Z-scheme heterojunction: Kinetics, degradation pathway, toxicity assessment, and optimization)- In this chapter, the synthesis of MIL-88B photocatalysts with three different morphologies at reaction temperatures of 80 °C, 120 °C, and 145 °C were discussed. The optimized structure was achieved at 120 °C when combined with g-C₃N₄ and PPy. The successful fabrication of the PPy-g-C₃N₄-MIL-88B composite was confirmed by various characterization techniques. Incorporating H₂O₂ into the MIL-based system created a synergistic effect, enhancing hydroxyl radical generation and improving TCPP degradation efficiency.

The performance of the developed PPy-g-C₃N₄-MIL-88B/H₂O₂/LED photo-Fenton system was systematically evaluated under different operational parameters, including catalyst dose, pH, reaction time, initial TCPP concentration, and radical scavengers. Additionally, its energy efficiency, parameter interactions, and reusability were investigated.

Overall, the results revealed that the newly synthesized catalyst provides a sustainable, efficient, and environmentally friendly approach for degrading flame retardants like TCPP in aquatic environments.

Chapter 6 (*In-situ* polymerization of Z-scheme PPy-g-C₃N₄-MIL-88B heterogeneous photo-Fenton catalyst for tris-(2-chloroisopropyl) phosphate (TCPP) degradation: morphologies, operational parameters, RSM optimization, and energy efficiency)- This chapter further studied the PPy-g-C₃N₄-MIL-88B/H₂O₂/LED photo-Fenton system and systematically evaluated its performance in degrading TCPP. The research presented in this chapter focused on enhancing •OH radical generation to improve degradation efficiency. Comprehensive analyses were conducted on reaction kinetics, degradation mechanisms, by-product identification, mineralization extent, toxicity assessment, and process optimization, providing an in-depth understanding of the system's catalytic behaviour and degradation pathways.

Chapter 7 (Conclusions and recommendations)-Finally, Chapter 7 offers a thorough summary of the findings, draws key conclusions, and discusses the limitations of the current study. This chapter also highlights potential directions for future research.

This dissertation primarily follows a manuscript-based format with chapters comprising scientific papers. The included manuscripts have been either published or submitted to peer-reviewed journals and conferences.

2. Chapter 2: Literature review

With population growth, changing lifestyles, rapid industrialization, and agricultural advances, a diverse group of pollutants at low concentrations has been detected in the aquatic environment [1]. In many countries, including China [2], the USA [3], France [4], Japan [5], etc., the receiving water bodies are polluted more than ever, owing to the overwhelming discharge of wastewater. Among many sources, industrial, agricultural, municipal, and pharmaceutical/hospital sectors might be the major roots of contaminants spread in the ecosystem. Recalcitrant organic pollutants, including pharmaceuticals and personal care products, pesticides, surfactants, and hormones, represent a vast group of contaminants [6]. Given their refractory nature, the presence of these persistent pollutants even at trace concentrations poses harmful risks to terrestrial and aquatic life. To diminish the potential health risk associated with these chemicals, sustainable water treatment approaches are required [7,8]. The contamination of our environment with flame retardants poses a serious threat to public health, stemming from their extensive use in consumer products aimed at fire prevention [36–40]. Flame retardants have emerged as a growing concern due to their persistence, carcinogenicity, neurotoxicity, and bioaccumulation [41,42]. In the early 21st century, the production of polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), and brominated flame retardants (BFRs) was phased out, and they were replaced by organophosphate flame retardants (OPFRs) [42–45]. As the primary alternative to PBDEs, the production and use of OPFRs rapidly increased. OPFRs are added to consumer products, which accelerate their release and leach into the environment. In recent years, the production of chlorinated OPFRs has risen significantly, now comprising 52-75% of the OPFR family. The presence of tris (2-chloro-2-propyl) phosphate (TCPP), a highly persistent chlorinated OPFR, in

aquatic environments is particularly notable which has been classified as the 4th substance of high concern by the European Union (EU) [11,46].

Recently, physical, chemical, biological, and combined approaches have been widely used for the removal of flame retardants from the environment. Among them, biological methods using biofilm reactors have been explored to enhance TCPF biodegradation. However, biological treatment is often hindered by the presence of organic contaminants that may inhibit microbial growth, negatively impacting the biodegradation efficiency [47–49]. Similarly, the potential generation of toxic or non-biodegradable byproducts by advanced oxidation processes (AOPs) will have negative impacts on the efficiency of integrated processes that combine AOPs with biodegradation [50,51].

Given these limitations, developing an AOP that optimizes costs while ensuring the complete mineralization of TCPF and the transformation of its toxic byproducts into non-toxic or less harmful compounds will be a more effective solution. Previous studies have indicated that photo-Fenton catalysis is a suitable technique for the degradation of water-soluble flame retardants, including TCPF [41,52–54]. Accordingly, preparing an appropriate photo-Fenton catalyst to remove the concerning contaminants from water and minimize the toxicity of water media, while maintaining cost efficiency, stability, and reusability, is crucial.

The Materials Institute Lavoisier (MILs), recognized as promising materials for environmental remediation due to their stability and unique pore structure, presents a potential base for an effective photo-Fenton catalyst. Several MIL-based photo-Fenton catalysts have been assessed for the removal of emerging contaminants [55–60]. For instance, NH₂-MIL-101 photo-Fenton catalysts were fabricated to shorten the bandgap and improve the degradation rate through

increased surface reactivity and enhanced hydrophilicity by the NH_2 group [61]. In another study, $\text{g-C}_3\text{N}_4@\text{MIL-101}$ was constructed for a higher absorption in visible light and a lower bandgap. In this case, $\text{g-C}_3\text{N}_4$ was selected due to its suitable bandgap (2.65 eV), while the fabrication of $\text{g-C}_3\text{N}_4@\text{MIL-101}$ only reduced the bandgap by 3% (from 2.65 eV to 2.57 eV) [62]. Although the mentioned studies provide valuable insights and enhance treatment efficiency, further investigations are needed to elucidate electron transfer mechanisms. Moreover, most studies focus on a single contaminant without considering the presence of natural ions and mixtures of compounds in real environments. The long-term environmental impact of MIL-based systems also remains understudied. In particular, the potential leakage of Fe^{3+} ions and ligand decomposition products into water systems after photocatalysis requires further investigation [63–65]. Meanwhile, many heterojunctions have been designed in previous research to enhance photocatalytic reactivity, reduce the recombination rate, and improve light energy absorption. Among these, Z-scheme heterojunctions promote photoelectron transfer while maintaining the original oxidation potential. Therefore, constructing a Z-scheme photo-Fenton catalyst that meets electrical requirements and exhibits strong photodegradation capability while addressing the gap in the literature is necessary. This chapter presents a comprehensive review of photocatalytic processes, including mechanisms and components, photocatalytic material, light sources, and major operational parameters. In the end, the limitations and prospects of this study are described and summarized. The present chapter provides a comprehensive study of planning different photocatalytic systems for the decontamination of emerging contaminants. The structure of the present chapter and its subsections are as follows:

- Section 2.1 introduces the photocatalytic mechanism and components. Besides, the fundamental principles and photocatalytic reactions are explained.

- Photocatalytic materials prepared and applied in photocatalytic systems are introduced and explained in Section 2.2.
- Section 2.3 provides details on the light sources in the photocatalysis domain with an overview of their advantages and challenges.
- Section 2.4 elaborates on the operational parameters mainly influencing the photocatalysis reactions. The environmental conditions examined include photocatalyst loading, pH, light intensity, irradiation time, and the effect of oxidizing agents. However, in this case due to fixed geometry of the reactor light intensity has not been investigated.
- Finally, section 2.5 highlights the existing limitations and gaps of previous research.

2.1. Mechanisms and components of photocatalytic advanced oxidation processes

The fundamental principles of photocatalysis have been extensively reviewed and reported in the literature [7,31,66]. Photocatalytic reactions are initiated when the photocatalysts absorb photon energy ($h\nu$) equal to or higher than their bandgap energy. This leads to electron excitation from the valence band (VB) to the conduction band (CB), leaving a positively charged hole ($h\nu_{VB}^{+}$) in the valence band and generating electrons (e_{CB}^{-}) in the conduction band (electron-hole pair). The photo-generated electrons and holes are reducing and oxidizing species, respectively. The reaction between photo-excited electrons and dissolved oxygen yields superoxide radicals. Likewise, the reaction of generated holes with water molecules in the aquatic environment produces hydroxyl radicals, which are strong oxidants [7,25,67,68]. The produced oxidizing species on the catalyst surface are highly reactive. Hence, they can degrade refractory micropollutants and convert them to innocuous compounds. The photocatalytic reactions are presented in Equations 2.1 to 2.4:





Where $h\nu$ is the required photon energy for the excitation of electrons from the valence band to the conduction band. $h\nu_{VB}^+$ and e_{CB}^- are the oxidizing and reductive agents, respectively. As shown in Eqs. 1 to 4, the photocatalytic reactions occur in the presence of water molecules and dissolved oxygen. In the absence of water molecules, highly reactive hydroxyl radicals may not be generated. Adequate photon energy to overcome the bandgap energy of TiO_2 photocatalyst corresponds to light wavelengths less than 400 nm [69]. Fig. 2.1 exhibits the schematic diagram of electron-hole pair generation when $TiO_2@ZnFe_2O_4/Pd$ composite is irradiated under sunlight with adequate photon energy for diclofenac photo-oxidation [70]. When $TiO_2@ZnFe_2O_4/Pd$ nanocomposite was illuminated with adequate $h\nu$, electrons and holes were formed. Due to the higher electron accumulation ability of palladium nanoparticles, covalent band electrons are relocated from TiO_2 to Pd. Then, the interaction of electrons with O_2 and interaction of holes with the surface hydroxyl group resulted in the formation of superoxide anion and hydroxyl radical species that mineralized diclofenac [70].

Generally, there are five fundamental steps in photocatalytic processes that can be described as follows: I) micro-pollutants mass transfer from the aqueous media to the surface of photocatalyst, II) activation of photocatalyst surface by photon energy, III) micropollutants adsorption on the photon activated surface of photocatalyst, IV) photocatalysis reaction on the photocatalyst surface,

and finally, V) intermediate compounds departure from the photocatalyst surface and their transfer to the bulk solution [69,71]. Accordingly, the overall reaction rate is controlled by the slowest step.

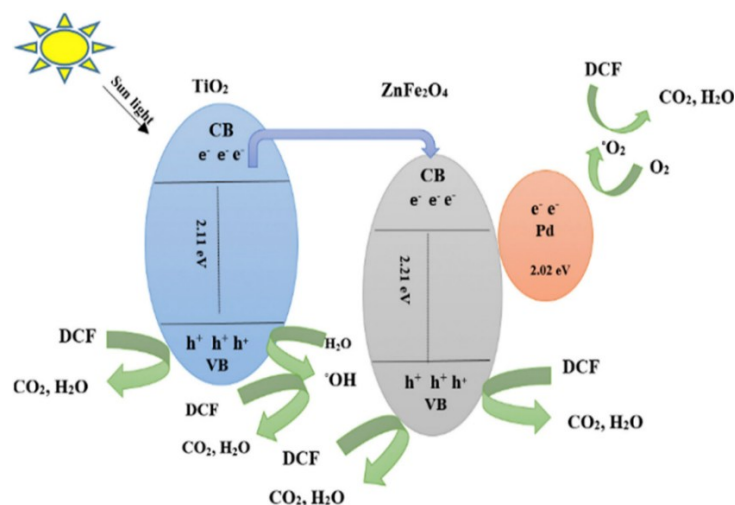


Figure 2.1. Photodegradation mechanism of diclofenac (DCF) by $\text{TiO}_2@\text{ZnFe}_2\text{O}_4/\text{Pd}$ nanocomposite under sunlight according to Ahmadpour et al. [70]. Reprinted and reproduced by permission from the publisher.

Regarding the components, photocatalytic AOPs mostly consist of two main components: a catalyst and a light source, as discussed in the following sections.

2.2. Catalytic materials in photocatalysis

Photocatalysts are materials that can degrade hazardous compounds under light irradiation, either sunlight or UV lamp, without being consumed. These materials promote oxidation reactions by photo-absorption that excite electron and hole pairs [72]. Photocatalytic materials have specific features including high electrical conductivity, large surface area, high photocatalytic efficiency, robustness, and wide photo absorption range [73–75]. Various photocatalysts have been proposed and well-researched, including metal oxides [76], composites [77], metal sulfides [78], oxysulfides [79], metal-organic frameworks [80], hydrogels [81], nano-biomagnetic composites [82], and aerogels [25,83].

The conventional semiconductor photocatalytic materials frequently reported in water decontamination processes are TiO_2 , Fe_2O_3 , CdS , ZnO , and ZrO_2 , which possess specific features including non-toxicity, electronic structure, high surface area, physical and chemical stability. For example, the specific electronic structure of AgAlO_2 facilitated charge separation and induced photocatalytic degradation of alizarin red under visible light up to 70% [84]. Some drawbacks have been reported regarding their reusability and regeneration to satisfy both economic and safety concerns related to their challenging separation after wastewater treatment. Another fundamental challenge is the poor degradation efficiency of bare semiconductors such as ZnO , owing to their wide bandgap and fast recombination rate of electron-hole pairs. For instance, semiconductor BiVO_4 has high chemical stability and narrow band-gap, but it has a low photocatalytic activity because of the fast recombination of electron-hole pairs [85,86]. Furthermore, the nanoparticle aggregation of semiconductors reduces the surface area and inhibits light absorption, thus decreasing the photocatalytic activity [87]. Titanium oxide (TiO_2) is one of the most widely applied semiconductor photocatalysts in photocatalytic treatment processes. Nevertheless, the TiO_2 shortcomings, such as narrow photocatalytic range, insufficient exploitation of visible light, recovery difficulties, and wide bandgap, have limited its application in large-scale operations [88,89]. These shortcomings can be improved by modifying TiO_2 for better visible light usage [90], by producing the second generation of TiO_2 photocatalyst with easy separation [91], and by doping metal or non-metal ions on TiO_2 [92] to enhance its photocatalytic efficiency, reusability, and light absorption. Although these modifications have been frequently achieved, preparing inexpensive and green catalysts with low carbon footprint, high stability, and photocatalytic activity via uncomplicated and economical synthesis methods should be prioritized. In the following sections, recent research direction in the selection and preparation of catalysts is discussed. For example, a

composite made from TiO₂ and graphene oxide was fabricated to overcome the main limitations of TiO₂, such as a wide bandgap and separation challenges [93]. Regarding tetracycline removal, magnetic FeNi₃/SiO₂/CuS was fabricated and employed under ultraviolet light. Under optimum conditions at pH 9, operating time of 200 min, tetracycline initial concentration of 10 mg/L, and catalyst dosage of 0.005 g/L, tetracycline was completely degraded [94]. The fabricated nano-biomagnetic ZNFe₂O₄@methyl cellulose under optimum conditions and UV irradiation oxidized 92.6% and 71.12% Metronidazole in synthesized and real samples, respectively. This study also showed that the synthesized nano-biomagnetic catalyst can be reutilized six times without losing its photocatalytic effects [82].

2.2. 1. Novel catalysts and new trends in catalyst preparation

During the past ten years, much research has focused on a variety of lignin-based composites, carbon nanotube composites, cellulose-based materials, MOFs, hydrogels, aerogels and sponges for photocatalysis [95–99].

2.2.1.1. Photocatalytic composites

Various novel composites have been fabricated, addressing previous shortcomings regarding the degradation efficiency, light absorption, reusability, and preparation difficulties. NiO/red phosphorous (RP) composite was prepared by Chen et al. [100] through a simple roasting method. The analysis of composite characteristics showed that the specific surface areas of both RP and NiO/RP were in the same range (50 m²/g), indicating that the higher NiO/RP photocatalytic activity was not attributed to the catalyst surface area. Based on the diffuse reflectance spectra (DRS) analysis, the enhanced photocatalytic activity of NiO/RP composite may be due to its higher visible light absorption compared to RP. Notably, the significant stability of NiO/RP after recovery

and reuse for ten cycles was verified by XRD and XPS analyses. Munawar et al. [101] prepared the novel ZnO-Yb₂O₃-Pr₂O₃ using the green, economic, and facile co-precipitation technique. The nanocomposite with antibacterial and photocatalytic properties eliminated 99.8% methylene blue under solar irradiation within an hour. Despite the previously mentioned merits, the SEM images of the fabricated nanocomposite demonstrated high particle agglomeration that may hamper its development.

2.2.1.2. Metal-organic frameworks

Metal-organic frameworks (MOF) are three-dimensional porous materials with crystalline networks, organic linkers, metal nodes, high surface area (in the range of 1000-10,000 m²/g), high porosity (3-9.8 nm), and unique photo-electronic features suitable for photocatalytic degradation processes [33,102]. Compared to applying sole semiconductors and metal oxides, MOF- based photocatalysts offer higher surface area as well as porous structure, facilitating pollutant diffusion in their channels and in turn, enhanced photocatalytic conversion. The recyclability of MOFs due to their heterogeneous nature is another advantage of metal-organic frameworks compared to semiconductor nanoparticles [103,104]. Nonetheless, along with the reported specific features, their wide bandgap in the range of 1 to 5.5 eV [105–107], low electronic conductivity, and undesirable stability of MOFs have turned the research direction towards heterojunction formation between semiconductors and MOFs, as well as metal modification [107–111]. Metal nanoparticles can easily load in the MOF framework, promoting electron transfer from metals to MOFs. For example, the CuO/TiO₂@MOF-5 composite was prepared via in-situ incorporation of fabricated CuO/TiO₂ composite onto MOF-5 for organic dyes degradation. Precisely, TiO₂ nanoparticles and CuO nanocomposites were fabricated through TiCl₄ hydrolysis and sol-gel methods, respectively, and were then incorporated into the MOF-5 framework. The SEM images illustrated that the smooth

surface of MOF-5 was preserved after the CuO/TiO₂ implantation, with no aggregates to block the active sites of the synthesized catalyst. The UV-Vis spectra illustrated that embedding the CuO/TiO₂ nanocomposite in MOF-5 had transferred the band gap into a more visible region. Therefore, higher visible light absorption and catalytic activity were observed. Despite the desirable degradation of methylene blue and methyl orange by CuO/TiO₂@MOF-5 nanocomposite, the CuO nanoparticles' toxicity has impeded their application in industrial applications [112].

2.2.1.3. Hydrogels

Hydrogels have lately gained attention in water purification operations as they are non-toxic, inexpensive, and stable with effective light energy absorption. Unlike conventional photocatalytic materials such as semiconductors and metal oxides, hydrogels not only assist easy separation but also prevent nanoparticle aggregation. Recently, various hydrogel photocatalysts including graphene [113–115], polymeric [116], cellulose/GO/TiO₂ [117], Ag₂O/g-C₃N₄ [118], MXene/rGO [119], and chromophore amphiphile-polyelectrolyte hybrid hydrogels [120] have been investigated and prepared for photocatalytic oxidation purposes [121]. Graphene hydrogels facilitate photogenerated electron-hole pairs separation due to their multidimensional electron transfer channels and offer high surface area while being recoverable and recyclable [113,122]. A self-assembled TiO₂-graphene hydrogel (TGH) was prepared via a facile, equipment-free hydrothermal method by Zhang et al. [123]. TGH was synthesized by the addition of TiO₂ nanoparticles to graphene oxide and was dispersed under sonication. The sealing of the mixture in an autoclave and natural cooling were steps before obtaining TGH. SEM images exhibited that the decoration of TiO₂ on graphene oxide prevented the graphene sheets aggregation as no aggregated nanoparticles were observed in the TGH images. This was a positive development since during

the hydrogel formation, graphene sheets have aggregation tendency owing to the loss of oxygen-containing groups by hydrothermal approach. Preventing particle aggregation by anchoring TiO_2 improved surface area and in turn increased degradation efficiency. The specific surface areas of graphene hydrogel and TiO_2 -graphene hydrogel were 148.58 and 267.98 $\text{m}^2 \text{g}^{-1}$, respectively. The fabricated TGH hydrogel offered increased adsorption capacity, desirable electrochemical capacitive performance, and improved photocatalytic activity compared to applying sole titanium dioxide and graphene hydrogel. The maximum adsorption capacity of TGH for methylene blue was reported to be 120 mg g^{-1} which was higher than many available adsorbents. PANI/ TiO_2 composite hydrogel with synergistic effects of adsorption and photocatalytic degradation was fabricated via polymerizing aniline. PANI is a conductive polymer with specific electrochemical features that assist charge recombination prevention and in turn, increases the photocatalytic rate. Another promising aspect of the synthesized hydrogel is its recyclability after oxidation reaction compared to TiO_2 . Moreover, as the UV-vis diffuse reflectance spectra exhibited, the PANI/ TiO_2 -10% hydrogel with a pore diameter of 20-50 nm had a higher pore volume than the PANI hydrogel or TiO_2 , which resulted in a higher degradation capacity [124]. However, hydrogels application may be restricted by their tendency to concentrate contaminants rather than degrading them to harmless species [125]. Table. 2.1 depicts different photocatalysts and their synthesis methodologies for micropollutants degradation [114].

Table 2.1. Overview of the recently reported photocatalytic materials and their fabrication methods.

Photocatalyst	Synthesis methodology	Target pollutant	Operational conditions	Photocatalytic degradation (%)	Ref.
PrVO₄	sonochemical	Eriochrom Black T	[PrVO ₄] ₀ =0.05 g pH 11 UV light t= 90 min	89.61%	[126]
ZnO/CNT nanocomposites	Ball milling-Hydrothermal method	Malachite green	t=60 min CNTs 5 wt. %	79%	[127]
Gd-doped TiO₂	Anodizing method	Methyl orange	t=10 h Gd ³⁺ dosage=0.01 mol/L UV light UV voltage: 60 V	95.8%	[128]
MnO₂/g-C₃N₄	Sol-gel method	Methyl orange Phenol dyes	Catalyst dosage : 100 mg UV absorbance 290 nm	Phenol: 98% MO: 92%	[129]
ZnO/Bi₂WO₆ heterojunction	Solvothermal method	norfloxacin	t=120 min solar illumination ZnO wt.% 0.05	NOR: 97%	[130]
CoP/ZSO	Precipitation-calcination	tetracycline	t= 60 min visible light irradiation ($\lambda > 420$ nm) 2% CoP-ZSO	96.44%	[131]
Nitrogen-and boron-codoped TiO₂	Hydrothermal technique	Bisphenol A	Solar-light driven t=120 min catalyst dosage: 0.8 g/L [bisphenol A] ₀ =0.1 μ M	100%	[132]
Copper doped ZnO nanorods	Chemical growth method	Methyl orange Methylene blue	t=180 min copper content: 20 mg	MO:57.5% MB:60%	[133]

Co₃O₄@CdS double layer hollow spheres	Template-removal method	phenol	Visible light irradiation t=2 h	90%	[134]
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2.3. Light sources

Lighting conditions have shown a profound effect on the photodegradation rate and efficiency [69]. Many studies have investigated the performance of photocatalytic technology under a variety of light sources, including UV lamps [135–137], xenon lamps [138,139], LED [140,141], solar irradiation [142–144], and their combination [145,146]. The choice of the light source is strongly dependent on the type of photocatalyst utilized and its characteristics, especially bandgap threshold and phase. Using a crystalline phase of TiO₂, a light wavelength of up to 400 nm is required which suits the UV-A wavelength range of 315–400 nm. However, UV-B with a wavelength span from 280–315 nm cannot provide the sufficient photon energy required for catalyst activation [147]. The impact of lighting conditions on the rate and efficiency of oxidation has been reported in previous investigations. For example, Rashed and El-Amin [148] studied methyl orange photocatalytic oxidation by TiO₂ under various light sources including halogen lamp at 100 W, solar light, and fluorescent lamp. They reported that sunlight irradiation resulted in a higher degradation rate compared to halogen and fluorescent lamps under the same operating conditions. A similar finding was reported by Abdelrahman and Hegazey [149] where hydrothermally-fabricated HgO nanoparticles were used for crystal violet dye photocatalytic degradation under UV and sunlight. Crystal violet dye was 100% decomposed by HgO nanoparticles within 180 and 120 minutes under UV and sunlight, respectively. Common light sources in photocatalytic AOPs have been compared in Table 2.2.

Sunlight-driven photocatalytic degradation has been reported as a sustainable, clean, low-energy and low-cost process. The exploitation of sunlight for water decontamination by sunlight-

driven catalysts has been presented as a response to energy shortage and the pollution associated with some light sources, such as the atmospheric pollution resulting from mercury vapors emitted from mercury lamps [150–152]. Neelgund and Oki [152] constructed a sunlight-active photocatalyst through the deposition of ZnO nanotrapezoids on the graphene nanosheets' surface. The prepared photocatalyst produced 100% decomposition of organic dyes, including azo, thiazin, and fluorescein-based dyes under solar light illumination. The solar-driven cobalt ferrite nanoparticles photocatalyst degraded 83.41%, 82.76% and 63.62% of methylene blue, rhodamine B, and crystal violet after 90 min, respectively. However, CoFe₂O₄/BiVO₄ photocatalyst oxidized only 72.47% of methylene blue under a halogen lamp after 240 min [153]. These investigations demonstrate the effectiveness of solar illumination for the oxidation of a variety of contaminants.

Regarding UV irradiation, Puga et al. [154] prepared an AgBr/SnO₂ composite for the oxidation of rhodamine B and caffeic acid under UV and visible light. After 45 minutes, both pollutants were degraded by nearly 95% under UV irradiation, whereas they were degraded by only 85% when exposed to visible light. Other light sources have been used in photocatalytic processes as reported before [155–158]. For example, phosphorus-doped TiO₂ was illuminated under a blue light-emitting diode and xenon lamp for benzylamines and phenol oxidation. After 3 hours, phenol was degraded by 100% under xenon lamp irradiation. Even within the first hour when only 75% of phenol was degraded, the generated intermediate compounds, such as hydroquinone, catechol, and benzoquinone were completely decomposed under xenon lamp exposure [138]. Jamali et al. [159] showed that under optimum conditions, 42% of phenol content in a solution was degraded by titanium dioxide under a 90 Mw LED light source and 120° beamwidth. However, the phenol photodegradation efficiency was increased to 87% under the same operating conditions when the beamwidth declined to 40 °.

Table 2.2 Reported light sources in photocatalytic AOPs for degradation of recalcitrant contaminants.

Photocatalyst	Light source	Target pollutant	Operational conditions	Photocatalytic degradation (%)	Ref.
ZrO₂/MWCNT nanocomposite	Solar irradiation	Indigo Carmine	t=180 min alkali pH catalyst dosage= 3 mgL ⁻¹	96%	[160]
TiO₂	UV-LEDs	Microcystin-LR anatoxin-a	t= 30 min [TiO ₂] ₀ =0.05 g L ⁻¹ pH 9	100%	[161]
Chitosan-zinc sulfide	UV lamp	Acid black 234 Acid brown 98	UV lamp wavelength 254 nm t A234= 100 min t A98= 165 min	Acid black 96.7% Acid brown 92.6%	[162]
GO@B-TiO₂ nanocomposite	Solar irradiation	Bisphenol A	t= 240 min GO loading: 2 wt%	47.66%	[163]
PES/CCTO membrane	HF Rhodamine B	UV lamp	UV power 360 W Wavelength 544 t=40 min [RhB]= 5 mg/L	74.66%	[164]
GO/TiO₂ composite	Sunlight illumination	Salicylic acid	t=60 min [COD] ₀ = 63 mg/L	57%	[165]
Bismuth ferrite (BFO)	LED lamp	Particular matter	t=120 min [BFO] ₀ = 10 mg/L	80%	[166]
Vessel-like biochar-based photocatalyst Bi₂S₃/BiOBr/BC	LED light	diclofenac	t=40 min pH 5 catalyst dosage of 0.6 g/L	93.65%	[167]
CuO decorated ZnO nanoflakes	Solar light	Methylene blue, methylene orange	Catalyst dosage 5 mg Initial dyes concentrations= 10 μM t _{MB} =40 min t _{MO} =60 min	100%	[168]
TiO₂-rGO	sunlight	formaldehyde	0.5: TiO ₂ -rGO wt.% 90 min	93.8%	[169]
Ca/TiO₂/NH₂-MIL-125	Solar visible light	Methyl Orange, Rhodamine B	pH 5 photocatalyst dosage 0.4 gL ⁻¹	MO: 86.22% RhB: 82.87%	[170]

Nano flower-like rutile TiO₂	Solar light	Methylene blue	[MB] ₀ = 5 mgL ⁻¹ t=180 min	98.95%	[171]
TiO₂ nanotube	UV light	Orange II	[Orange II] ₀ = 70 mg/L t=2000 min	89.46%	[172]
ZrO₂-TiO₂	LED light	Rhodamin B	pH 9 [RhB] ₀ = 20 mg L ⁻¹	95%	[173]

2.4. Major controlling parameters in photocatalytic degradation

Operating parameters, including the catalyst dosage, pH, temperature, type and concentration of the oxidizing agent, and light intensity, significantly influence the oxidation efficiency and degradation rate of pollutants during photocatalytic processes [25,76,174]. To optimize photocatalytic systems in water reuse applications, the major controlling parameters affecting the performance of photocatalytic processes have been evaluated and discussed in the following subsections.

2.4.1. Catalyst dosage

The catalyst dosage affects the photocatalytic degradation efficiency, reaction rate and operational expenses, as the required photocatalyst concentration up to the optimum catalyst loading is proportional to the overall photocatalytic reaction rate [31]. Optimum catalyst concentration can considerably enhance the extent and rate of photocatalytic oxidation, possibly due to the following reasons: (i) at higher catalyst dosage more surface area and active sites are available in the solution, leading to higher adsorption of pollutants and light; and (ii) higher production of reactive species resulting from higher electrons and holes concentrations that speed up photocatalytic reactions. Nevertheless, when the concentration of the catalyst exceeds the optimum value, catalyst particle aggregation happens, which hinders light penetration and adsorption due to the solution turbidity and light dispersion. Under these conditions, particle

agglomeration reduces the surface area of the photocatalyst exposed to light irradiation, thus lowering the corresponding degradation efficiency [29,70,175,176]. Isari et al. [176] investigated the decomposition of pharmaceuticals under visible light and showed that increasing the catalyst dosage (WO_3/CNT) from 0.1 to 0.7 g/L improved the degradation efficiency from 38.7% to 82%. This observation is most likely due to the higher surface area and active sites and effective light adsorption. Similarly, sulfamethoxazole oxidation efficiency by MgO/ZnO nanoparticles connected to graphene nanosheets under UV-A and US irradiation was highest at an optimum catalyst dosage of 0.8 g/L. In fact, when the catalyst dosage increased from 0.4 to 0.8 g/L, sulfamethoxazole degradation improved and reached 83% within 2 hours [175]. Further increase in the catalyst loading from 0.8 to 1.2 g/L adversely affected sulfamethoxazole photocatalytic degradation associated with nanoparticle aggregation that inhibited photon penetration. A similar trend was observed in the study of furosemide oxidation using zinc oxide supported on clinoptilolite at the concentration of 0.05 to 1.25 g/L under UVA irradiation [177]. The results showed that furosemide degradation was most favored at the catalyst concentration of 0.75 g/L with an oxidation efficiency of 80%, while declining at higher catalyst concentrations, reaching 64.6% degradation at the catalyst concentration of 1.25 g/L. Akbari et al. [178] reported on the mineralization of ciprofloxacin under UV visible light by three photocatalytic materials at pH 5.5 in 150 min and at catalyst concentration in the range of 0.1 to 5 g/L. These investigators reported that ciprofloxacin removal by the examined catalysts including unmodified TiO_2 , N, S- TiO_2 , and commercial TiO_2 was favored as the catalysts dosage reached 2 g/L. It was demonstrated that ciprofloxacin degradation was increased from 42 to 76%, from 52 to 91%, and from 48 to 81% when the concentration of unmodified TiO_2 , N, S- TiO_2 , and commercial TiO_2 (P25) increased from 0.1 to 2 g/L, respectively. This considerable rise in ciprofloxacin degradation was due to the

elevated number of active sites, resulting in the generation of higher reactive species. On the contrary, higher catalyst loading enhanced particle interactions, which resulted in lower efficiency of degradation [178]. Table 2.3 presents the reported optimum catalyst loadings for the photodegradation of selected pollutants.

Table 2.3. Optimum catalyst dosage reported by recent literature for different pollutants and photocatalytic systems.

Photoatalyst type	Catalyst dosage	Pollutant	Operational conditions	Photocatalytic degradation (%)	Ref.
Cellulose based hydrogel (AgCl@Fe-Carboxymethyl Cellulose)	4 g/L	Rhodamine B	[Rhodamine B] = 10 ppm pH 7 visible light irradiation t= 60 min	87%	[179]
LaCu_xFe_{1-x}O₃ (x = 0.2, 0.4, 0.6, 0.8) perovskite-like catalyst (0.6 LCFE)	785.59 mg/L	acrylonitrile butadiene styrene	T=58.9 °C t= 3h pH 7.32	94.06%	[180]
Pd-TiO₂	0.5, 0.75 wt.% Pd-TiO ₂	Methylene blue, methyl orange	t= 120 min visible light	MB: 99.4% MO: 92.6 %	[181]
BiVO₄	0.75 g/L	Methylene blue	Visible light irradiation t= 90 min	91.9%	[182]
ZnO-Yb₂O₃-Pr₂O₃ nanocomposite	1 g/L	Methylene blue	[MB] ₀ = 6 mg/L pH 5 solar illumination t= 60 min	99.8%	[101]
WO₃/CNT nanocomposite	0.7 g/L	tetracycline	pH 9 US power 250 W/m ² Light intensity 120 W/m ² t=60 min	82%	[176]

Iron oxyhydroxide nanostructure	1.25 mg/L	phenazopyridine	t= 40 min [O ₃] = 15 mg/L [PhP] ₀ = 0.2 mM	98.6%	[183]
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2.4.2. *Light intensity*

In the photocatalytic process, light intensity is one of the key parameters that influence the photocatalytic degradation of organic micro-pollutants. The light source produces photons for catalyst activation and consequently the electron-hole pair generation. Higher light intensity has been shown to enhance electron-hole pair formation, resulting in higher production of oxidizing species [176,184,185]. Altering the intensity of light results in different reaction rates as described below: when the intensity of light is below its optimum value, the concentration of electron-hole pairs is below the value required for complete degradation of micro-pollutants, and the electron-hole pairs are rapidly consumed in oxidation reactions, so the reaction rate increases linearly ($n=1$). With the increase of light intensity, the generation rate of electron-hole pairs increases to values higher than their corresponding consumption rate. Under these conditions, the oxidation reactions are controlled by electron-hole recombination, leading to a half order ($n=0.5$) increase in the rate of reaction since less time is needed for decomposing contaminants [186–188]. Further increase in the light intensity will not influence the degradation efficiency and is not recommended since it will result in the waste of energy [189].

An investigation exhibited that when LED current increased from 0.22 to 0.68 amps, the decomposition of blue 15 on Fe-N-Ce-TiO₂ rose from 10 to 98% [190]. The degradation of isopropanol by the TiO₂ nano-tube increased and reached 56% as the light intensity was increased from 0 to 3 mW/cm². Jorfi et al. [191] explained that the lower rate and efficiency

of degradation at low light intensity are due to the electron-hole pair separation difficulties and lower formation of oxidizing species. Higher light intensity accelerates the rate of oxidation reaction and reduces the degradation time. For example, a H_2O_2 -assisted TiO_2 photocatalyst at 400 W lamp irradiation intensity degraded 96% of phenolic content (polyphenols) in 60 minutes. However, using a 250 W lamp, 94% of phenol content was removed under light irradiation after 90 minutes [192]. The light intensity has been reported as one of the three key parameters influencing ammonia oxidation by ZnO/Oak charcoal composite [121]. The ammonia removal efficiency under the optimum conditions, including light intensity of 250 W, pH 9, and 2 g/L catalyst dosage was reported to be 86.7% [121].

2.4.3. Initial pollutant concentration

Industrial wastewater contains a wide range of contaminants at different initial concentrations that often vary in time [193]. It has been reported that the increase of initial pollutant concentration enhances their degradation efficiency due to the desirable collision between the oxidant radicals and pollutant molecules. However, when the initial concentration of pollutants exceeds the optimum value, a higher number of photocatalyst active sites is occupied, which results in a limited formation of oxidative species [194]. Another explanation, especially related to the decolorization of dyes, is the medium turbidity that prevents photon absorption on the catalyst surface and in turn, reduces the oxidation efficiency [195].

Riaz et al. [196] used Cu–Ni/ TiO_2 for methyl orange degradation in the range of 10 to 300 mg L^{-1} under visible light irradiation. They reported that with increasing methyl orange concentration up to 10 mg L^{-1} its removal efficiency reached 100%. However, further increase of the dye concentration had an adverse effect on its degradation efficiency, decreasing from 100% to 22.3%

due to the poor performance of photocatalyst [196]. Similar results have been reported by other investigators [177,194,195,197]. Heidari et al [177] studied the effect of furosemide initial concentration on its degradation by ZnO/ICLT nanophotocatalyst at a constant pH of 7 and at a catalyst dosage of 0.75 mg L^{-1} . They showed that as the furosemide initial concentration rose from 10 to 35 mg L^{-1} , its degradation efficiency declined. These findings were attributed to the formation of a constant concentration of radicals with the increase of initial furosemide concentration that lowered the potential reaction between furosemide and the radicals. Another justification is the inaccessibility of light to the photocatalyst surface due to the turbidity of the solution contaminated with furosemide. Zouhier et al. [198] reported on the effect of methylene blue and remazol brilliant blue concentrations in the range of 10-50 ppm on their respective degradation under UV irradiation and at pH 11, using 1 g/L Fe/ZnO photocatalyst within 60 minutes. Fig. 2.2 illustrates the variations of photocatalytic degradation efficiency for both target dyes under the studied conditions. The results showed that when the concentration of dyes increased from 10 to 50 ppm, the removal efficiencies of methylene blue and remazol brilliant blue decreased from 91% to 70% and from 84% to 44%, respectively. In this study, the reactive species that degrade methylene blue and remazol brilliant blue are OH and O_2^- , and the optimum dye concentration for both target dyes is 10 mg/L [195]. Likewise, [197] reported on the oxidation of 2,4-dinitrophenol by UV/SPS/ Cu^{2+} system over the broad range of 5-50 mg/L, and showed that the removal efficiency of this pollutant decreased from 95% to approximately 89% with the increase of its initial concentration.

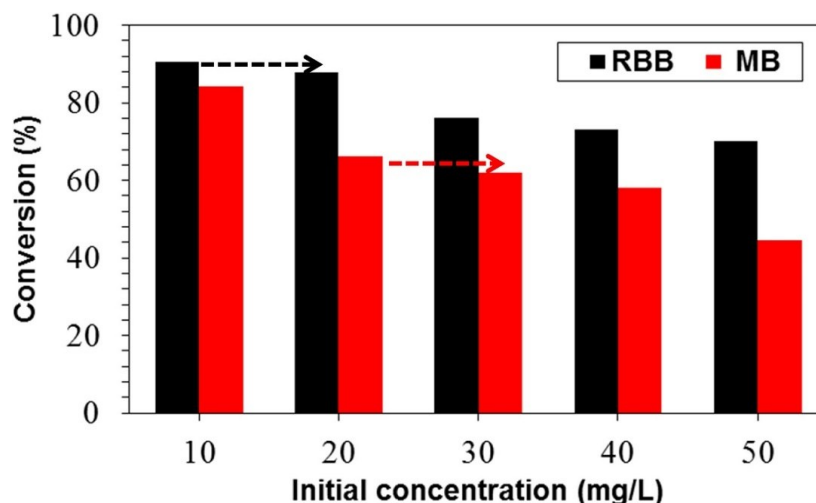


Figure 2.2. The effect of methylene blue (MB) and remazol brilliant blue (RBB) initial concentrations in the range of 10-59 ppm on their photocatalytic degradation by 0.1 g/L Fe/ZnO photocatalyst at pH 11, under UV irradiation after 60 minutes [195].

2.4.4. pH

pH is an important parameter that controls the catalyst surface charge, oxidation potential, ionization degree, band edge position, and size of catalyst aggregates [76,199]. Moreover, the hydroxyl radicals generation is a function of pH, indicating the underlying effect of this operating parameter on the efficiency of the photocatalytic process [200]. The controlling effect of pH on the pathway of degradation and its efficiency has been frequently reported in the literature [70,77,201,202].

The point of zero charge (PZC) is a state where the surface of the photocatalyst has no charge, and a minimum interaction is observed between the target pollutants and the photocatalyst [29]. For the TiO₂ photocatalyst, the PZC lies in the pH range of 4.5-7. Hence, for negatively-charged contaminants, an acidic condition is more suitable to increase their degradation efficiency. Conversely, in a basic environment, the polar repulsion between TiO₂ surface and anionic species reduces the adsorption on negatively charged TiO₂ for subsequent photocatalytic reactions and in turn, decreases the degradation efficiency [199]. It must be stressed that by setting the pH at PZC,

the utilized catalyst could be recovered because neutral pH values intensify particle aggregation and settlement; therefore, facilitating catalyst recovery [69]. Sometimes, the formation of by-products introduces chemical functional groups that may change the initial operating pH [203]. There are numerous reports on the effect of solution pH on photocatalytic degradation of organic contaminants such as aromatic compounds [204], dyes [205], pharmaceuticals [206], and pesticides [207]. Moztahida et al. [114] showed that methylene photocatalytic decomposition on the P25/graphene/polyacrylamide hydrogel is most favorable at pH 9. Another investigation demonstrated that diclofenac absorption and degradation by the $\text{TiO}_2@\text{ZnFe}_2\text{O}_4/\text{Pd}$ catalyst were induced under acidic conditions because the positively charged catalyst adsorbed the negatively charged diclofenac molecules and enhanced the degradation efficiency under acidic condition. This is followed by higher hydroxyl radicals production associated with H^+ and O_2 in aquatic solution [70].

The most favorable pH for the photodegradation of pollutants depends on their properties. For example, while the basic condition (pH 13) was more favorable for the photodegradation of methyl blue by $\text{BaTiO}_3/\text{Bi}_2\text{WO}_6$ (BTO/BWO) heterojunction composite, neutral pH led to a faster methyl orange degradation by this catalyst [208]. Table 2.4 shows the optimal pH values and the corresponding efficiency of organic pollutants oxidation in photocatalytic systems.

Table 2.4. Optimum pH values for photocatalytic degradation of different pollutants.

Pollutant	Optimum pH	Photoatalyst type	Operational conditions	Photocatalytic degradation (%)	Ref.
<i>p</i> -nitroaniline	pH 7	ZnO nanoparticles	[<i>p</i> -nitroaniline] ₀ = 10 mg/L [ZnO] ₀ = 1 g/L t= 105 min	TOC was removed 72.2% <i>p</i> -nitroaniline was eliminated 94.4%.	[209]
Methylene blue	pH 9 (3-9)	BiOI-Silica aerogel	0.5 g: BiOI(80%wt)- SA(20%wt) t= 120 min solar irradiation	96.5%	[210]
Phenol	pH 7.87	Ag/TiO ₂ nanofibers	[Phenol] ₀ = 5.62 ppm Catalyst dosage = 2.06 g/L Visible light	92.91%	[211]
Acridine orange	pH 7 (4-9)	Nitrogen (N) and sulfur (S) codoped graphene aerogels	t= 5 h visible light	88%	[212]
Ciprofloxacin	pH 5.5	Nitrogen and sulfur co-doped TiO ₂ nanomaterials	[Ciprofloxacin] ₀ = 30 mg/L Catalyst dosage= 0.05 g Under UV-Visible light	78.7%	[213]
2-chlorophenol	pH 6	Graphene oxide based TiO ₂	[2-chlorophenol] ₀ = 25 mg/L t=240 min solar light	80%	[214]

Tetracycline	pH 9	WO ₃ /CNT nanocomposites	[WO ₃ /CNTs] ₀ = 0.7 g/L [tetracycline] ₀ = 60 mg/L Ultrasound power= 250 W/m ² Light intensity=120 W/m ² t= 60 min	100%	[176]
Sulfamethoxazole	pH 9	Decorated MgO and ZnO on graphene	[sulfamethoxazole] ₀ = 55 mg/L Catalyst dosage= 0.8 g/L LED power= 90 W US power= 250 W t= 120 min	100%	[175]

2.4.5. Type of oxidants

The effect of oxidizing agents on the photocatalytic degradation of pollutants has been examined and reported by many investigators [215–218]. During the degradation of pollutants in the TiO₂ photocatalytic system, the absence of a proper electron acceptor led to undesirable electron-hole recombination, which was remediated by the addition of an electron acceptor [28,219]. Mohammadzadeh et al. [220] demonstrated that the inclusion of electron acceptors not only reduced the electron-hole recombination potential but also produced reactive species, promoting the degradation rate and efficiency.

Previous studies have exhibited the controlling effect of oxidants in photocatalytic reactions [216,220–222]. Mohammadzadeh et al. [220] explored methylene blue oxidation by ZnO

nanostructures for three cycles with and without H_2O_2 . They showed that in the presence of hydrogen peroxide, methylene blue was completely degraded within 2 hours, while without H_2O_2 , methylene blue was oxidized by only 80% in every cycle. Fig. 2.3a shows the synergic effect of methylene blue photodecomposition when H_2O_2 and ZnO nanostructures were applied together. These findings are in conformity with the findings of Motlagh et al. [222], who studied phenazopyridine hydrochloride (PhP) oxidation by ZnFe-SO₄-LDH/GO catalyst exposed to visible light. These investigators examined the degradation efficiency of PhP (at the initial concentration of 15 mg/L) with the addition of $\text{K}_2\text{S}_2\text{O}_8$ oxidant at two concentrations of 0.5 mmol/L and 1 mmol/L. As Fig. 2.3b illustrates, the introduction of $\text{K}_2\text{S}_2\text{O}_8$ oxidant to the photocatalytic system promoted PhP oxidation rate in 150 min. The addition of $\text{K}_2\text{S}_2\text{O}_8$ oxidant at 0.5 and 1 mmol/L concentrations enhanced PhP decomposition efficiency to 72.41 and 93.95%, respectively, while the removal efficiency by using only $\text{K}_2\text{S}_2\text{O}_8$ oxidant at 1 mmol/L was 10.94%. The higher PhP photocatalytic degradation in the presence of $\text{K}_2\text{S}_2\text{O}_8$ could be explained by the production of sulfate radicals that promoted PhP degradation.

While it is widely accepted that utilizing additional oxidants like H_2O_2 promoted the rate and efficiency of photocatalytic reactions, their effects on photodegradation processes are highly dependent on factors such as the ratio of oxidant to pollutant concentration, contaminant type, and the surface area of the catalyst [223]. For example, congo red oxidation by Al-ZnO-Gr1 photocatalyst at 1h solar illumination in the presence of oxidants (KBrO_3 , KIO_3 , KIO_4 , and H_2O_2) was reported. Compared to using the catalyst alone, the addition of KBrO_3 , KIO_3 , KIO_4 , and H_2O_2 oxidants at similar operating conditions reduced the removal of congo red. This observation was attributed to the removal of holes and hydroxyl radicals by the scavenging effect of additional oxidants [224].

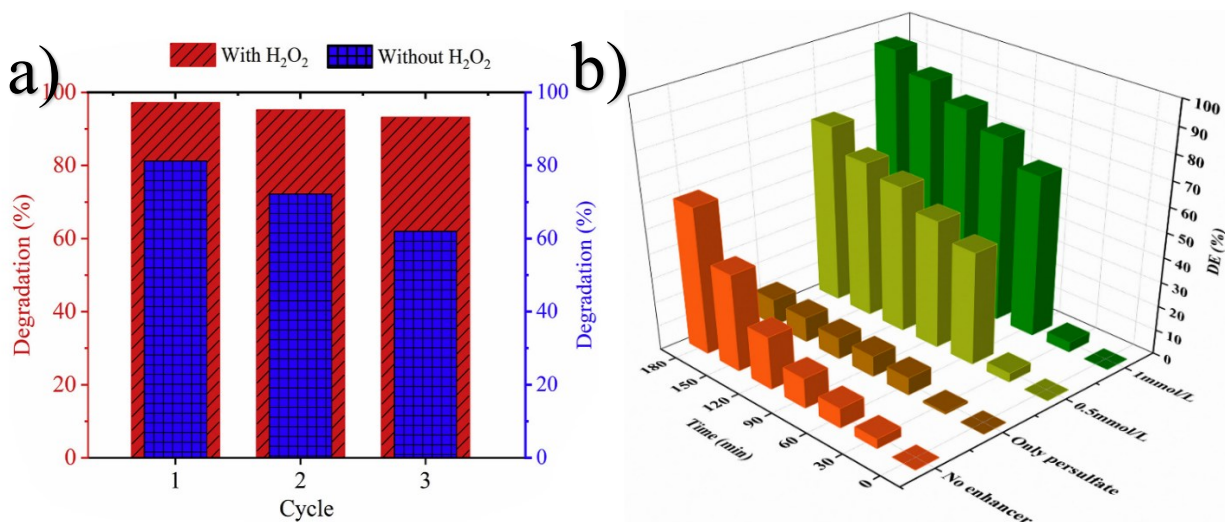


Figure 2.3. a) Comparison of methylene blue degradation efficiency by reused ZnO nanostructures in the presence and absence of H₂O₂ in three cycles [220], b) PhP degradation efficiency (DE%) affected by K₂S₂O₈ under operational conditions of [PhP]₀ = 15 mg/L, three sheets of photocatalyst, and pH 8 [222].

2.5. Existing limitations and research gaps

The field of advanced oxidation processes (AOPs) has seen remarkable developments, particularly through the integration of photocatalysis with Fenton chemistry. Metal-organic frameworks (MOFs), including those from the Materials Institute Lavoisier (MIL) family, have gained considerable attention for their structural tunability, large surface area, and high porosity, which make them attractive candidates for environmental applications. In particular, MIL-based materials such as MIL-88B and MIL-101 have been investigated for their catalytic potential in photo-Fenton processes. However, despite significant advances, the current section presents several important gaps that limit the translation of these systems from laboratory-scale experiments to real-world environmental remediation.

One of the foremost gaps is the lack of studies that address electron transfer mechanisms in MIL-based photo-Fenton systems. While several studies have reported enhanced

photocatalytic activity through the incorporation of functional groups (e.g., NH₂-MIL-101) or hybridization with semiconductors (e.g., g-C₃N₄@MIL-101), few delve into the underlying charge dynamics that govern photocatalytic performance. Understanding how photo-generated electrons and holes behave within these hybrid systems, especially in the context of recombination suppression and interfacial charge migration, is essential for the rational design of more efficient photocatalysts. Furthermore, while the construction of Z-scheme heterojunctions has emerged as a strategy to retain strong redox potential while enhancing charge separation, integration of this architecture within MIL-based systems has been limited. Most Z-scheme research to date has focused on inorganic semiconductors or simple binary composites, leaving a notable gap in the exploration of MIL-based Z-scheme heterojunctions for photo-Fenton reactions.

Another significant limitation of existing studies is the over-reliance on idealized testing conditions which do not reflect the complexity of real environmental systems. Many researchers evaluate catalytic performance using pure water or simple aqueous solutions containing a single pollutant, often at relatively high concentrations. However, real-world water bodies and industrial effluents typically contain a complex mixture of organic and inorganic constituents, including natural organic matter (NOM), anions (e.g., Cl⁻, SO₄²⁻, NO₃⁻), cations (e.g., Ca²⁺, Mg²⁺), and multiple emerging contaminants at trace levels. These matrix components can interfere with the generation of reactive oxygen species (ROS), alter catalyst surface chemistry, and scavenge free radicals, thereby reducing photocatalytic efficiency in practical applications. This gap highlights the necessity to evaluate catalyst behaviour under real or simulated wastewater conditions, including competitive pollutant degradation and ion interference.

A further gap lies in the scope of contaminants investigated. Although many catalysts demonstrate promising results in the degradation of dyes or model pharmaceuticals, these substances do not adequately represent the diversity and persistence of pollutants in the environment. This study addresses this limitation by focusing on tris(1-chloro-2-propyl) phosphate (TCPP), a recalcitrant flame retardant that is persistent in aquatic systems and of growing environmental concern. Yet, more research is needed on diverse and co-occurring contaminants, including industrial solvents, pesticides, PFAS, and microplastics, to develop broadly applicable treatment technologies. Additionally, very few studies explore the synergistic or antagonistic effects that may arise when multiple contaminants are treated simultaneously, which is a common scenario in wastewater treatment.

From the process engineering perspective, the lack of scale-up studies and reactor integration is another critical barrier to real-world application. Most reported systems are evaluated in batch reactors under laboratory conditions using small volumes and controlled irradiation sources. However, transitioning these materials into continuous flow photoreactors or integrating them into existing treatment infrastructure requires special attention to factors such as mass transfer limitations, light distribution, and energy efficiency. The use of LEDs as light sources, as in this study, represents a practical step toward energy-efficient systems, but further work is needed to quantify energy consumption, photonic efficiency, and cost-performance trade-offs in scaled-up settings.

Another weak area involves process modelling and optimization. While some studies investigated fitting experimental data to diverse models, they rarely explored the interaction of multiple operating parameters such as pH, catalyst dosage, time, and light intensity in a systematic way. The incorporation and interaction of these parameters in process modelling is

an important contribution. Moreover, these methods need to be standardized and expanded to better guide operational decisions. Integrating economic and environmental assessments, such as catalyst preparation cost, reuse efficiency, and life-cycle impacts, would provide a more holistic evaluation of technology viability.

Finally, although photocatalysis has shown great potential for the degradation of various organic pollutants, significant research gaps remain regarding the formation intermediate by-products and their inherent toxicity in many reported systems. Most studies prioritize the removal efficiency of the parent contaminant but often neglect the identification and characterization of degradation intermediates, which may exhibit equal or greater toxicity than the original compound. The lack of comprehensive analytical profiling using advanced techniques such as LC-MS/MS or GC-MS limits our understanding of degradation pathways and potential environmental risks. Moreover, toxicity assessment of the treated effluent is frequently overlooked, with only few studies employing bioassays or ecotoxicological evaluations to determine the impact of by-products on aquatic organisms or human health. These gaps highlight the need for integrated studies that combine pollutant removal efficiency with thorough chemical and toxicological evaluations to ensure the safety and sustainability of photocatalytic water treatment processes.

3. Chapter 3: Methodology

3.1. Photo-Fenton catalysts preparation

MIL-88B was prepared by the hydrothermal method. Accordingly, 10 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 8.2 mmol of NaOH, 10 mmol of H_2BDC , and 4.7 mL of CH_3COOH were dissolved in 50 mL of solvent (N,N-dimethylformamide (DMF)) under intense stirring. Subsequently, the solution was sealed in a 50 mL Teflon-lined stainless-steel autoclave. Subsequently, the autoclave was put in an oven at 120°C for 18h. The slurry was then drained after 18h, washed with reagent alcohol, and dried in an oven at 60°C for 8h [225].

G- C_3N_4 material was formulated through the calcination method. Typically, melamine (79.3 mmol) was completely dissolved in Milli-Q water (100 mL). Then, the mixture was subjected to ultrasound for 1 hour and then dried in the oven overnight. The extracted precipitate from the oven was calcinated in a muffle furnace at 550°C [226]. PPy nanoparticles were constructed through an oxidation reaction by lowering the temperature of the cetrimonium bromide solution to 0°C and adding drop wisely 3 mL polypyrrole monomer. After 15 minutes of mixing, 200 g/L ammonium persulfate solution was poured into the previously prepared solution under vigorous mixing. Then, the generated PPy nanoparticles were filtered, washed, and dried [226,227].

The procedure for the preparation of g- C_3N_4 -MIL-88B was the same as MIL-88B preparation, except for the addition of 0.32 mmol g- C_3N_4 to the solvent (DMF) [65]. PPy-g- C_3N_4 -MIL-88B was fabricated via *in-situ* oxidative polymerization by thermal and chemical treatment of MIL-88B. Polypyrrole nanoparticles (0.1g) were completely dissolved in the

solution of treated g-C₃N₄-MIL-88B in HCL. Next, the temperature of the mixture was lowered to 0 °C, followed by the addition of dopant (0.01 M HCL) and oxidant (0.5 g of FeCl₃.6H₂O). Finally, the precipitate was extracted from the solution, washed, and dried.

3.2. Experimental set-up and analysis instrument

Batch experiments were conducted in slurry mode in a 700 mL tabular stainless steel photoreactor. The reactor is equipped with UV and LED lamps with a voltage of 26V installed inside the photoreactor. Fig. 3.1 illustrates the experimental setup and its components. During the experiments, the temperature was set at 25 °C, and pH was adjusted using 0.1 M NaOH and 0.1 M HCL solution. The simulated contaminant solution was prepared at the desired concentration. The solution was poured into the flask, then the prepared photocatalyst was added and stirred using a stirrer and a magnet, and the solution was circulated in the dark for 1h to achieve adsorption/desorption equilibrium. For anaerobic experiments, the reservoir was placed for 15 minutes in vacuum before injecting N₂ into the reactor at the rate of 0.5 L/min also assisted in mixing the solution. The solution was circulated using a pump, and 10 mL of the solution was taken at different time intervals and centrifuged at 8000 rpm for 10 min. The experiments were conducted by varying one variable at a time while other parameters were held constant. The interactions among parameters were also considered through Design Expert.

The selection of 25 °C for the photocatalytic degradation experiments using PPy-g-C₃N₄-MIL-88B for TCPP removal was primarily motivated by the need to simulate environmentally relevant conditions while minimizing thermal artifacts in the reaction system. At this temperature, the process reflects typical ambient aqueous environments, ensuring that the observed degradation is predominantly driven by photocatalytic activity rather than thermally induced reactions. Operating

at 25 °C also preserves catalyst stability, particularly for hybrid materials such as PPy, g-C₃N₄ coupled with MIL-88B, where elevated temperatures may induce structural changes in the polymeric framework or metal–organic framework, potentially affecting charge transfer pathways and active site availability. From a kinetic perspective, temperature plays a critical role in influencing reaction rates, typically described by the Arrhenius equation, where an increase in temperature enhances the apparent rate constant by lowering the activation energy barrier and improving mass transfer and diffusion of TCPP molecules toward catalytic sites. However, in photocatalytic systems, excessive temperature can have competing effects, such as accelerating electron–hole recombination, reducing dissolved oxygen, or destabilizing reactive oxygen species, thereby diminishing overall efficiency. Additionally, adsorption–desorption equilibrium of TCPP on the catalyst surface is temperature-dependent; higher temperatures may weaken adsorption due to increased molecular motion, reducing surface residence time and limiting degradation. Therefore, 25 °C represents an optimal compromise, ensuring stable catalyst performance, environmentally relevant conditions, and reliable kinetic evaluation.

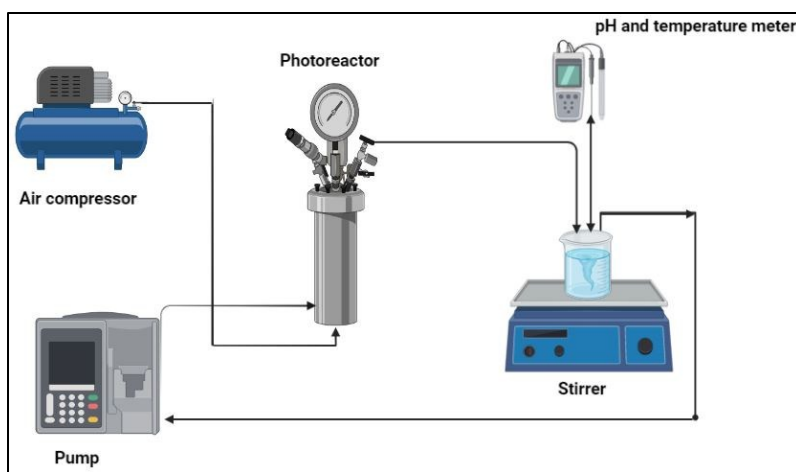


Figure 3.1. Schematic diagram of the setup used for photocatalysis.

3.3. Characterization

Field emission scanning electron microscopy images were collected using FE-SEM, JEOL 35-
cf. Fourier transform infrared spectroscopy and X-ray diffraction analysis were recorded by FTIR,
Thermo Scientific Nicolet 6700 and XRD, and Philips X'Pert Pro Multipurpose X-ray
Diffractometer, respectively. The detailed morphologies and microstructures of as-prepared photo-
Fenton catalysts were examined using transmission electron microscopy (TEM, Talos F200X G2)
with an acceleration voltage of 200 keV. For elemental detection, a high annular dark field detector
(HAADF) coupled with EDX mapping was applied. For sample preparation, the samples were
dispersed in water and ultrasonicated for thinning in order to enhance the quality of TEM images.
A drop of the dispersed sample was deposited onto a TEM grid and left to dry at room temperature.
UV-vis Diffuse reflectance spectroscopy (UV-DRS, UV-Vis-Near IR Cary5000) and
photoluminescence (PL, FLS-920, Edinbourg instruments) were employed to further comprehend
the photocatalytic characteristics. Total organic carbon (TOC, TOC-L Shimadzu) was also
measured to assess the capability of the synthesized photo-Fenton catalysts in the mineralization
of TCPP. X-ray Photoelectron Spectroscopy (XPS, Nexsa G2) was conducted to explore the
surface composition and chemical states of the prepared photocatalysts. X-ray Photoelectron
Spectroscopy (XPS) analysis was carried out with an X-ray source of aluminum- $K\alpha$, spot size of
 $\phi 400\ \mu\text{m}$, survey scan of 200 eV pass energy, and 1.0 eV step size. C1s, O1s, N1s, and Fe2p high-
resolution scans were obtained at 50 eV pass energy and 0.1 eV step size. Thermo Avatage (version
6.6.0) software was used for data processing. High-resolution scans of the PPy-g-C₃N₄-MIL88B
were measured at three locations on a sample surface within 10 nm thickness, and the mean values
were used for data analysis.

3.3.1. FE-SEM

FE-SEM images have been taken from all constructed photocatalysts, including MIL-88B, g-C₃N₄-MIL88-B, and PPy-g-C₃N₄-MIL-88B. As shown in Fig. 3.2a, MIL88-B particles have a hexagonal spindle-like shape. After modification with g-C₃N₄ (Fig. 3.2b), cylindrical-shaped structures were observed with no remarkable change in MIL-88B morphology. In Fig. 3.2c, the FE-SEM images of PPy-g-C₃N₄-MIL-88B consist of PPy sphere-like nanoparticles and layered structure of g-C₃N₄.



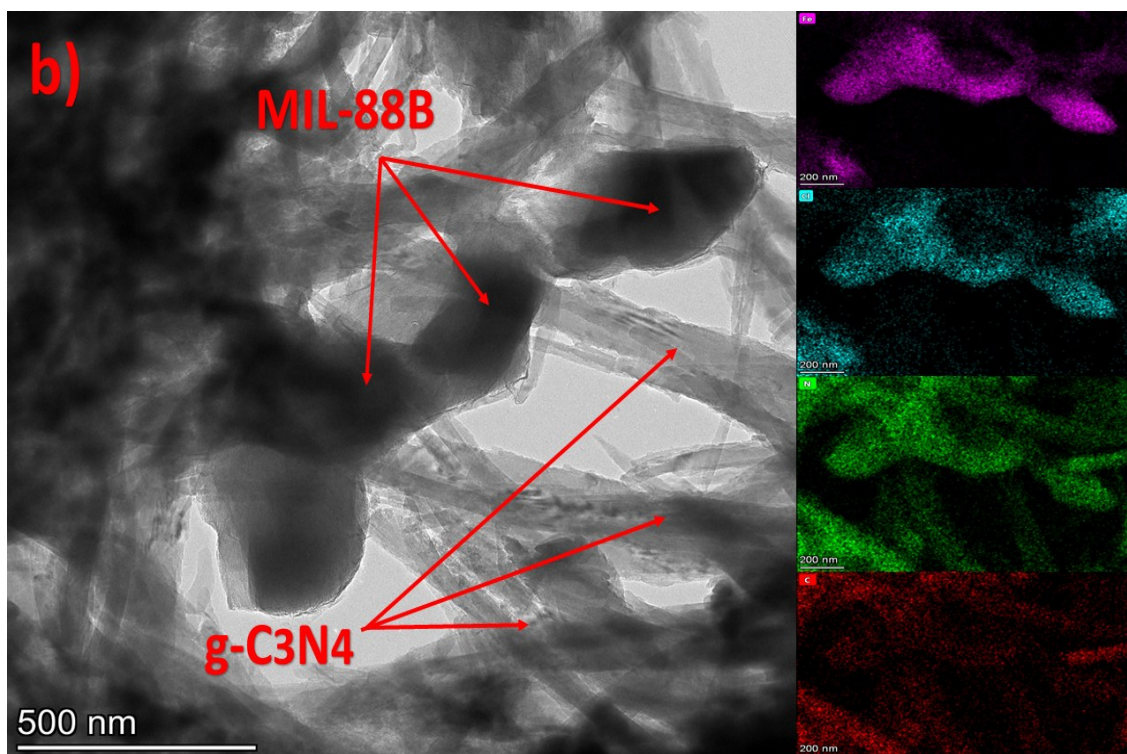
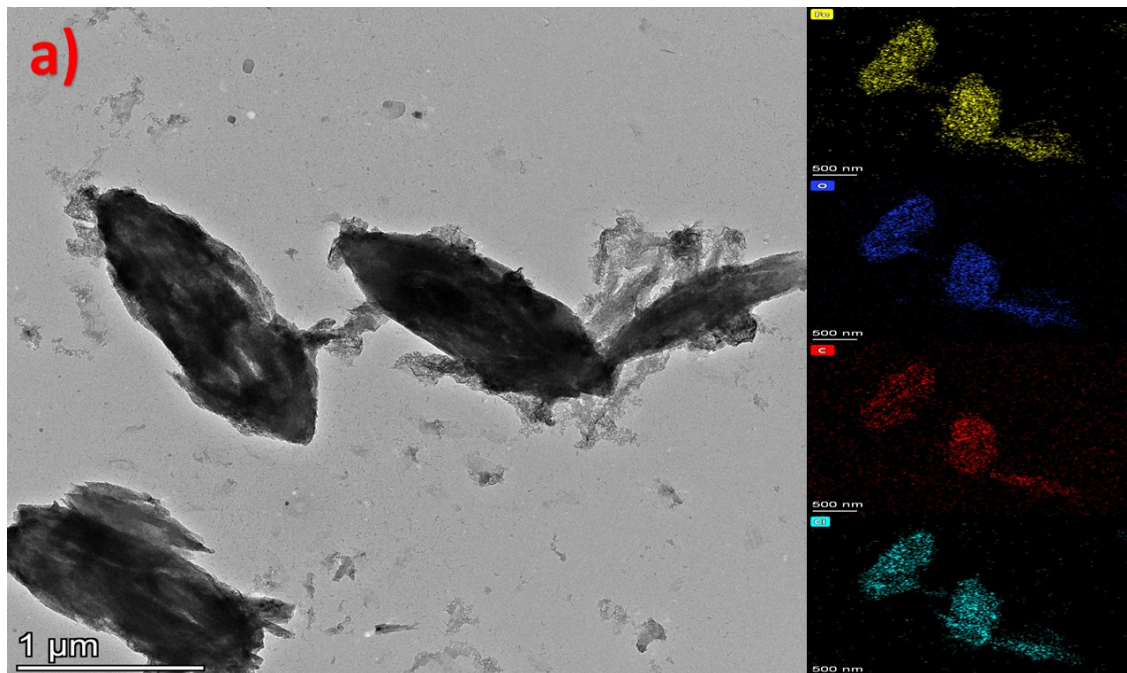
Figure 3.1.FE-SEM images of a) MIL-88B, b) g-C₃N₄-MIL88B, and c) PPy- g-C₃N₄-MIL88B.

3.3.2. TEM analysis

Fig. 3.3a demonstrates the TEM image of hexagonal-shaped MIL-88B particles with some fractured ones, most likely due to the ultrasound-assisted agitation during the preparation. The phenomenon of particle breakage during ultrasonication has been reported in other studies involving water-suspended particles [228,229]. Fig. 3.3a also reveals the presence of Fe, C, O, and Cl elements in MIL-88B mapping.

Fig. 3.3b illustrates TEM images of the g-C₃N₄-MIL88B photocatalyst. The dark hexagonal-shaped areas are attributed to MIL88B, while the surrounding blurred, needle-like structures suggest the presence of g-C₃N₄ wrapped around MIL-88B particles. As shown in Fig. 3.3c, the dispersing distance of the g-C₃N₄-MIL88B photocatalyst is 0.333 nm. The obtained dispersing space aligns well with the range observed for g-C₃N₄ (0.326 nm), with MIL88B layered on top, which reduced the dispersing space. Detected elements of g-C₃N₄-MIL88B photocatalyst verify the presence of a thin layer of g-C₃N₄ through the detection of C and N elements.

The TEM image of the PPy-g-C₃N₄-MIL88B photo-Fenton catalyst is presented in Fig. 3.3d. Elemental mapping discloses that MIL-88B particles are dispersed throughout the entire examined area, which is consistent with the applied physical and chemical modifications to g-C₃N₄-MIL88B. The presence of Fe, C, N, O, Cl, and S elements was confirmed by the elemental mapping, further validating the successful synthesis of the PPy-g-C₃N₄-MIL88B catalyst.



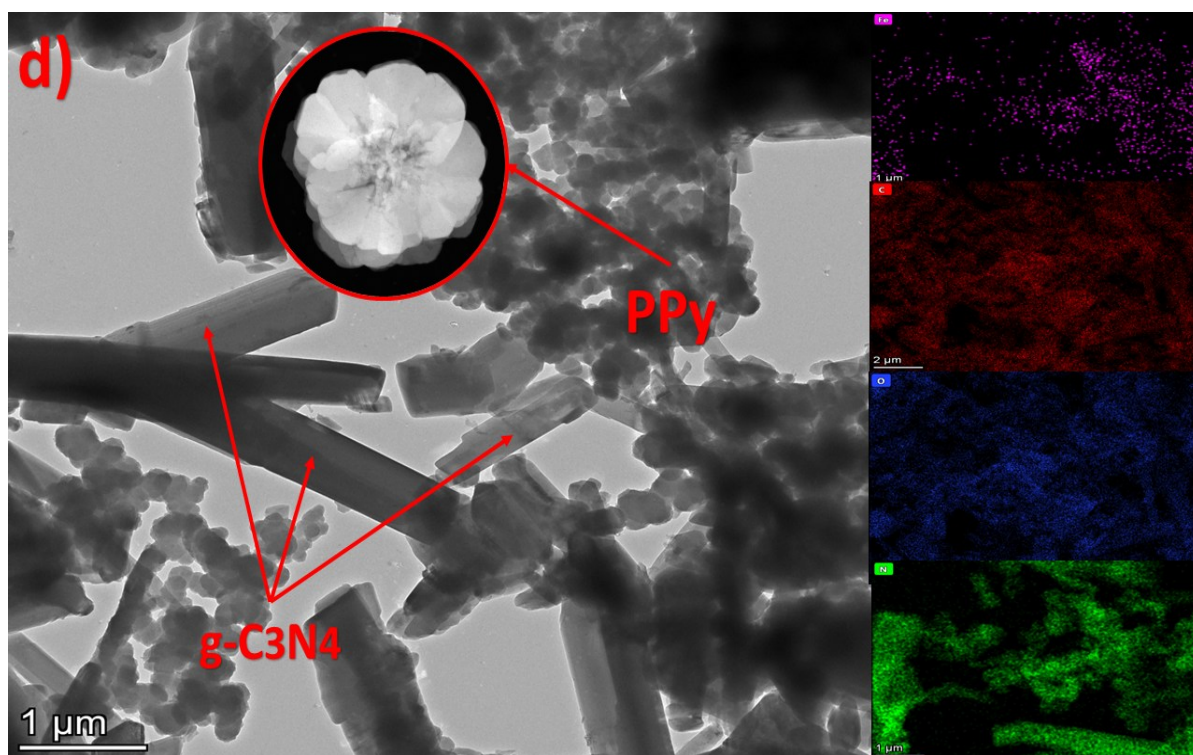
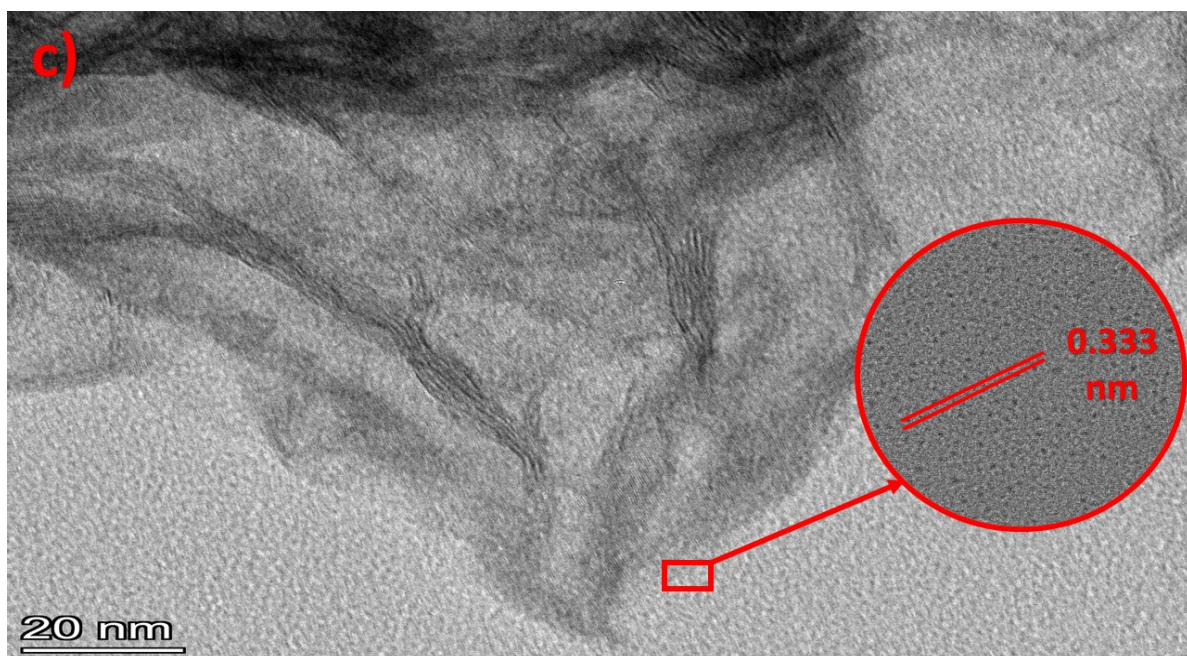


Figure 3.2. TEM images and elemental mapping of a) MIL88B, b) g-C₃N₄-MIL88B, c) dispersing distance of g-C₃N₄-MIL88B sheet, and d) PPy-g-C₃N₄-MIL88B.

3.3.3. FTIR/XRD analyses

To investigate the functional groups and composition phases of catalysts, FTIR and XRD analyses were employed. Fig. 3.4 a presents the FTIR analysis of MIL-88B with the absorption bands of 1590 and 1390 cm^{-1} , associated with asymmetric and symmetric vibrational bands of -COOH groups of MIL-88B. The vibrational band at 570 cm^{-1} was attributed to the Fe-O bond. For g- C_3N_4 , the vibrational bands at 1635 cm^{-1} , 1458 cm^{-1} , and 806 cm^{-1} were assigned to C=N, C-N, and N-H functional groups, respectively. FTIR analysis of PPy revealed that the observed vibrational bands at 1554 cm^{-1} and 1477 cm^{-1} , 811 cm^{-1} and 894 cm^{-1} , were associated with C=C and C-H, respectively.

For the PPy-g- C_3N_4 -MIL88 composite, the interaction between p- π conjugation of the C=C bonds of polypyrrole and the oxygen atom of MIL-88B resulted in a band shift to a higher frequency at 1635 cm^{-1} . Moreover, the detected peaks at 806 cm^{-1} and 1635 cm^{-1} , and those at 894 cm^{-1} and 1477 cm^{-1} (Fig. 3.4a) were attributed to g- C_3N_4 and PPy, respectively. MIL-88B demonstrated distinct peaks at 560 cm^{-1} (Fe-O) and 1590 cm^{-1} (-COOH).

The X-ray diffraction (XRD) analysis of the synthesized photo-Fenton catalysts was performed by using a Philips X'Pert Pro Multipurpose X-ray Diffractometer. MIL-88B diffraction peaks were observed at 11°, 17°, 19°, 22°, 29°, and 32°, as illustrated in Fig. 3.4b. For g- C_3N_4 , three diffraction peaks were observed at 12.2°, 27.5°, and 73°. In the XRD pattern of g- C_3N_4 -MIL88B, peaks around 11°, 19°, and 22° were assigned to MIL-88B, while the peak at 32.5° appeared to be associated with g- C_3N_4 , exhibiting a slight shift from 27.5° to 32.5°. This pattern and the observed shift were also reported in earlier research works [230,231].

Corresponding peaks for PPy nanoparticles were revealed around 21.5° and 25°, when the vibrational peak at 25° was only observed in the PPy-g- C_3N_4 -MIL88B composite (Fig. 3.4b). The other observed peaks at 18° and 28° were attributed to MIL-88B and g- C_3N_4 , respectively.

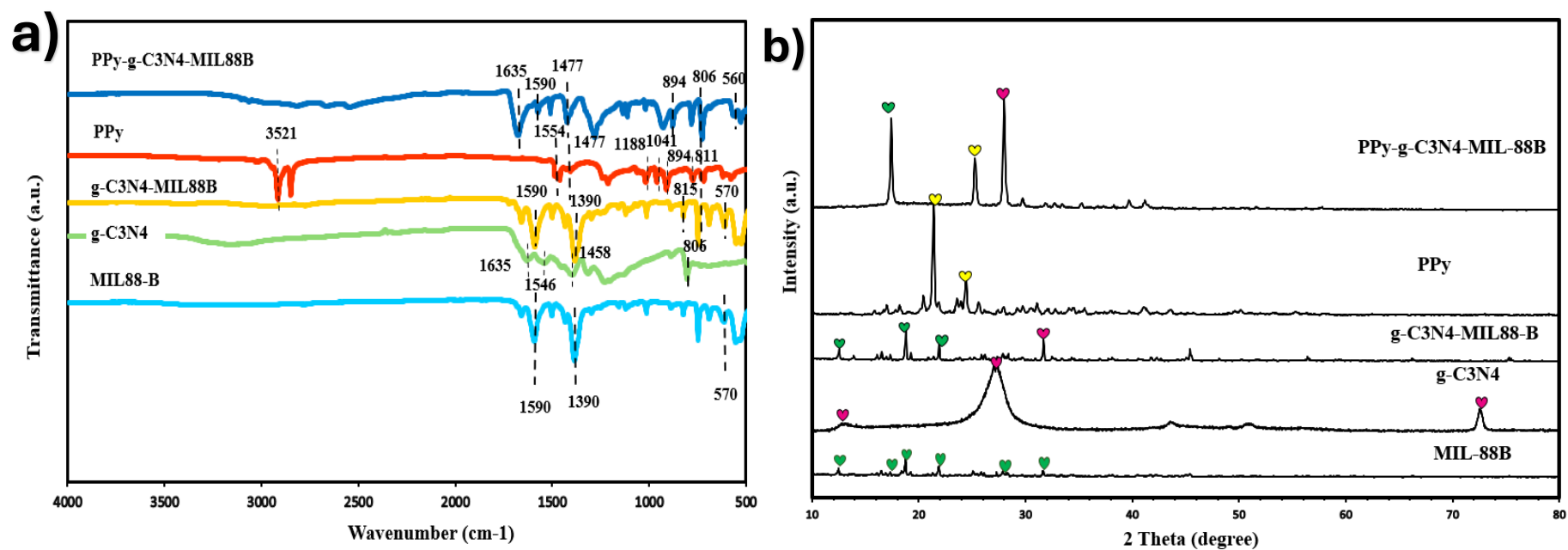


Figure 3.3. a) FTIR and b) XRD analyses of MIL-88B, g-C₃N₄, g-C₃N₄-MIL88B, PPy, and PPy- g-C₃N₄-MIL88B.

3.3.4. BET analysis

BET analysis was carried out to confirm the improvement of MIL-88B for photocatalytic reaction. A desirable photocatalyst typically exhibits two key features: high photocatalytic activity and relatively low BET surface area. This could be explained by higher light absorption through enhanced light trapping and hindered light transmission resulting from blocked pores. Besides that, darker particles pose increased photon absorption due to their lower transmission. Black PPy nanoparticles with a low BET surface area of 4.12 m²/g and pore volume of 0.0724 cm³/g improved the photocatalytic efficiency of the fabricated composite. The results in Table 3.1 show that PPy incorporation enhanced the photocatalytic performance of g-C₃N₄-MIL88B while simultaneously reducing the pore volume.

Table 3.1. BET surface area, pore volume, and pore diameter of the photo-Fenton catalysts fabricated in this work.

Samples	S _{BET} (m ² /g)	V _p (cm ³ /g)	D (nm)
MIL88B	1196	3.8812	12.98
g-C₃N₄	18.58	0.0918	19.77
g-C₃N₄-MIL88B	717.60	2.1346	11.89
PPy	4.12	0.0724	70.29
PPy-g-C₃N₄-MIL88B	308.56	0.8325	10.79

3.3.5. UV-DRS

Comparison of the light absorption capacity of the fabricated photocatalysts was explored using UV-DRS. As expected, due to the dark surfaces of PPy nanoparticles, the light absorption capacity of PPy-g-C₃N₄-MIL88B was enhanced notably, as Fig. 3.5 a presents. Another reason may be the implantation of PPy nanoparticles that produced a lower porosity, confirmed by BET analysis, which enhanced light absorption and photocatalytic activity. With the introduction of g-C₃N₄, a tiny improvement in the absorption capability was observed. The band gap energy was obtained using Tauc plot (Fig. 3.5b) based on the Kubelka-Munk method [230]. The drawn tangents suggest the band gaps of 3.3 eV, 2.7 eV, and 2.6eV corresponding to MIL88B, g-C₃N₄-MIL88B, and PPy-g-C₃N₄-MIL88B, respectively. The bandgap energy (E_g) decreased slightly from 3.2 eV for MIL-88B to 2.6 eV through the formation of g-C₃N₄-MIL88B, and further to 2.3eV by the incorporation of PPy into the previously prepared photoFenton catalyst. The resulting bandgap reduction elevated photon absorption and charge separation of electrons and holes, which in turn enhanced the photocatalytic activity.

The increase in light absorption of photocatalysts achieved through coupling black PPy and g-C₃N₄, forming PPy-g-C₃N₄ with increased photocatalytic activity. Therefore, PPy-g-C₃N₄-MIL88B is expected to have the highest photocatalytic activity among the synthesized photocatalysts.

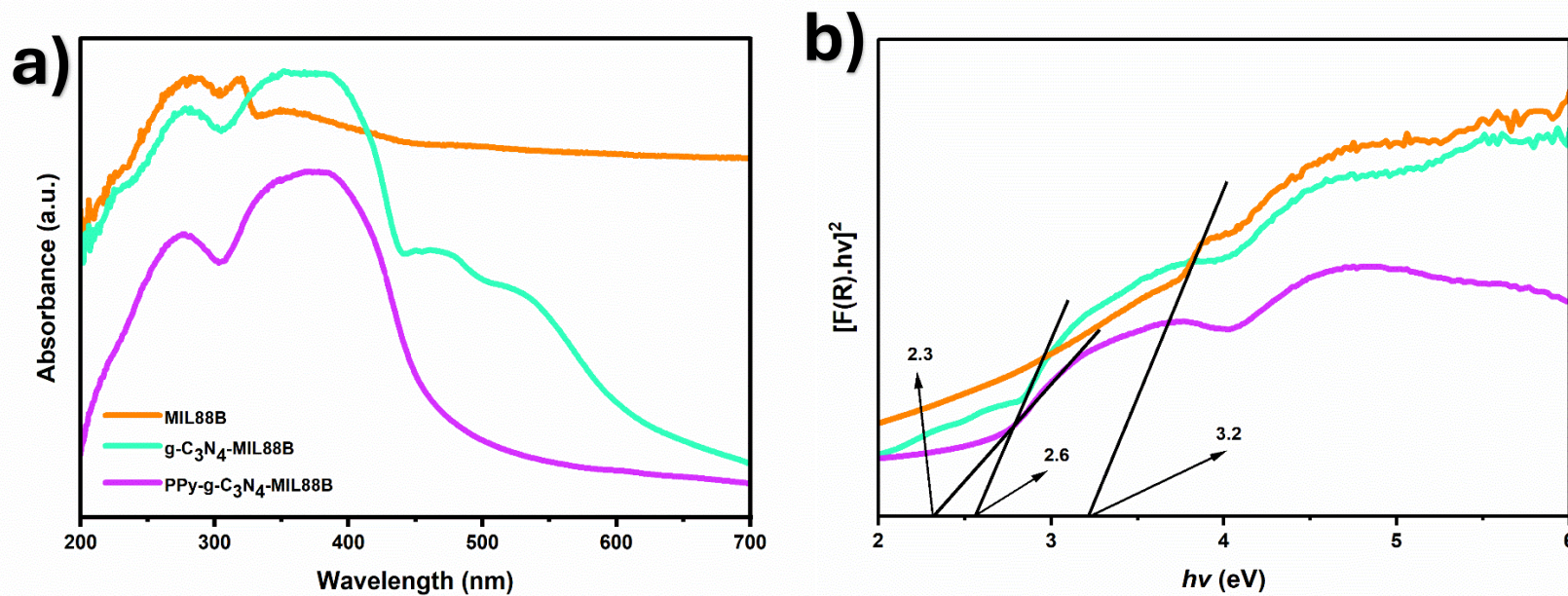


Figure 3.4. a) UV-DRS spectra of MIL-88B, g-C₃N₄-MIL88B, and PPy-g-C₃N₄-MIL88B, b) Tauc plot for direct bandgap calculation.

3.3.6. Photoluminescence analysis

Photoluminescence (PL) results from the recombination of photoexcited charges, and the charge separation efficiency of the samples was evaluated by using photoluminescence emission spectroscopy [232]. Photoluminescence spectra of the synthesized photocatalysts are shown in Fig. 3.6. The results verify the role of g-C₃N₄ and PPy in the reduction of charge recombination of photogenerated electron and hole pairs. Evidently, the photoluminescence signals of PPy-g-C₃N₄-MIL-88B and g-C₃N₄-MIL-88B were lower than those of MIL-88 B. This indicates charge recombination suppression in addition to improved charge separation and extended lifetime of charge carriers in PPy-g-C₃N₄-MIL-88B photo-Fenton catalysts. Obviously, the synthesized Z-scheme photo-Fenton catalyst provides a shortcut for charge transformation, which results in diminished charge recombination. Therefore, the extended lifetime of charge carriers could be associated with the electron shuttling role of PPy in addition to the direct pathway of charge transformation.

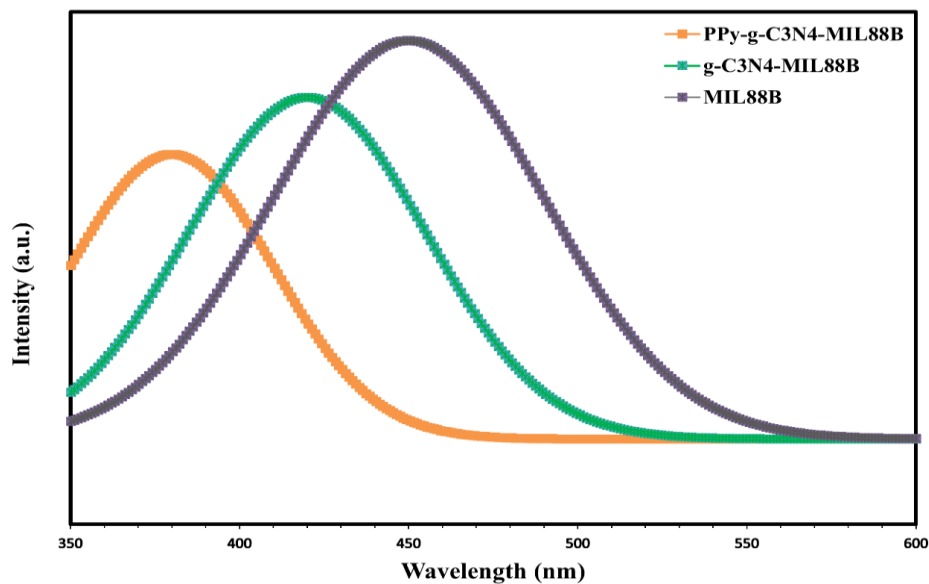
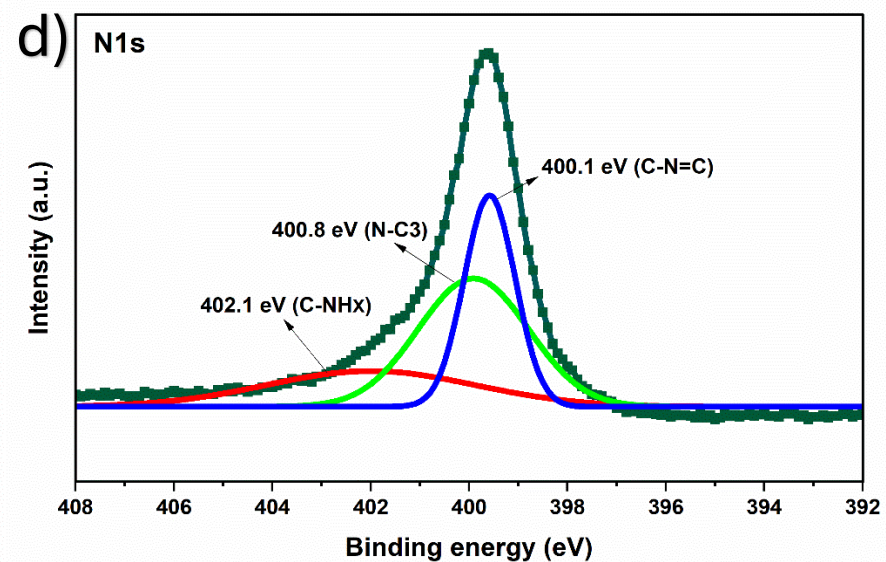
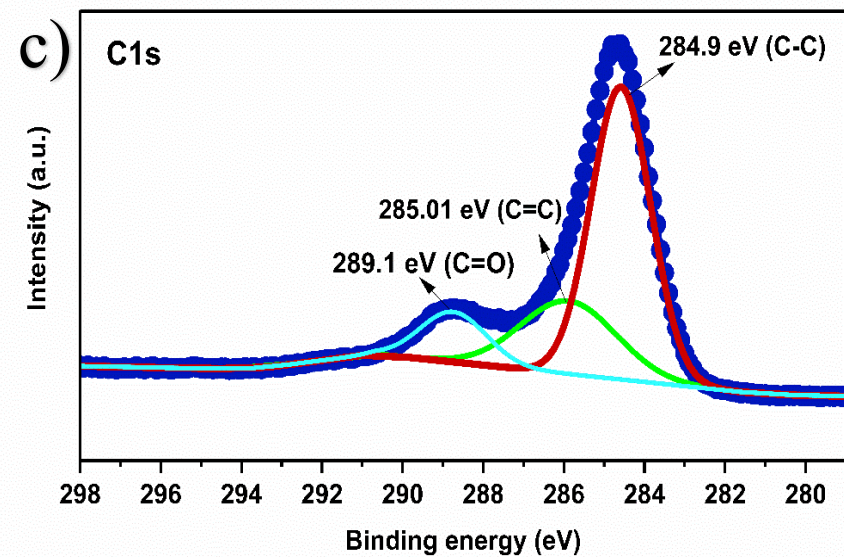
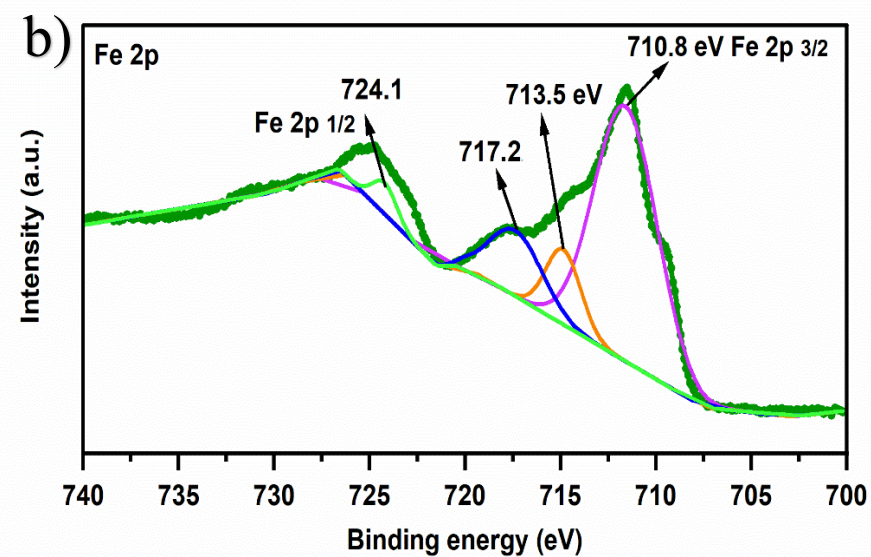
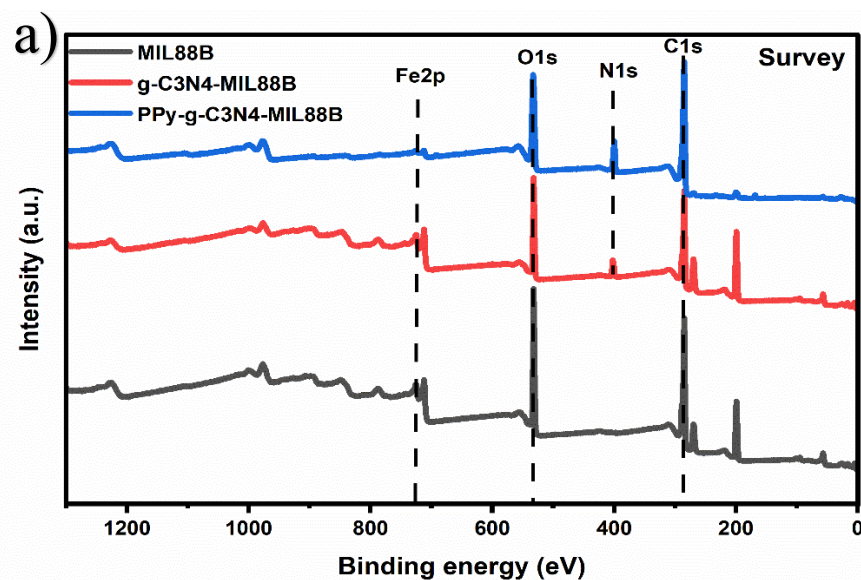


Figure 3.5. Photoluminescence spectra of MIL88B, g-C₃N₄-MIL88B, and PPy-g-C₃N₄-MIL88B, excitation wavelength of 325 nm.

3.3.7. XPS analysis

X-ray Photoelectron Spectroscopy (XPS) analysis was employed on Thermo Scientific Nexsa G2 XPS. The full survey spectra of MIL88B, g-C₃N₄-MIL88B, and PPy-g-C₃N₄-MIL88B are presented in Fig. 3.7a, with intense signals of Fe, O, N, and C for the constructed photocatalysts. MIL88B mainly consisted of Fe, O, and C elements, while the addition of N into the existing elements in g-C₃N₄-MIL88B photocatalyst confirms the successful fabrication of g-C₃N₄-MIL88B. The Fe2p spectrum can be observed in Fig.3.7b with two main peaks of 711 eV and 724 eV assigned to Fe2p_{3/2} and Fe2p_{1/2}, respectively. The expected peaks at 711eV and 724 eV may be deconvoluted into 710.8 eV and 713.5 eV, and 717.2 eV and 724.1 eV, respectively [233–236]. These peaks are normally assigned to Fe^{III}. In Fig. 3.7c, the characteristic peak of C1s was detected at 284.8 which could be divided into three peaks of 285.01, 284.9, and 289.1 eV, associated with C=C, C-C, and C=O, respectively [237,238]. Fig. 3.7d depicts the high-resolution XPS of N1s spectrum with three peaks at 400.1 eV, 400.8 eV, and 402.1 eV associated with C-N=C, N-C₃, and C-NH_x, respectively. [236]. Fig.3.7e demonstrates the high-resolution XPS spectra of O1s, deconvoluted into three peaks with binding energies of 531.42 eV (C=O), 532.55 eV (O-C=O), and 529.3 eV (Fe-O) [239]. The atomic ratios of Fe, C, N, and O elements for MIL88B, g-C₃N₄-MIL88B, and PPy-g-C₃N₄-MIL88B photocatalysts are presented in Table 3.2.



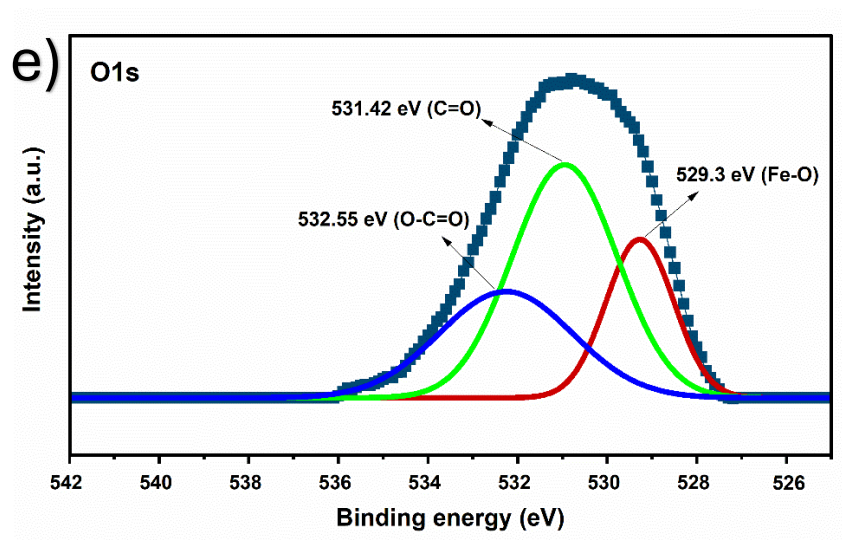


Figure 3.6. High-resolution scanning XPS spectra of a) overall survey, b) Fe 2p, c) C1s, d) N1s, and e) O1s.

Table 3.2. Atomic percentages of each element in MIL88B, g-C₃N₄-MIL88B, and PPy-g-C₃N₄-MIL88B.

Elements	Peak	Atomic % (MIL88B)	Atomic % (g-C ₃ N ₄ -MIL88B)	Atomic % (PPy-g-C ₃ N ₄ -MIL88B)
O1s	531.87	21.59	17.73	23.75
C1s	284.98	62.42	58.42	63.84
Cl2p	199.01	7.26	12.58	1.33
Fe2p	712.03	4.18	5.26	1.28
N1s	401.16	4.55	6.01	7.82

4. Chapter 4: Comparison of photocatalysis and photolysis of 2,2,4,4-tetrabromodiphenyl ether (BDE-47): Operational parameters, kinetic studies, and data validation using three modern machine learning models

Polybrominated diphenyl ethers (PBDEs), banned flame retardants, have been extensively used in electronics, textiles, plastics, building materials, and many other industrial operations. There are 209 congeners of PBDEs with different numbers and positions of bromine atoms on the benzene ring. The most widely used congeners for customer and industrial applications are Penta-BDEs, Octa-BDEs, and Deca-BDEs [240,241]. The abundance of PBDEs in the environment is because of their chemical stability, long half-life, and easy migration as they mix in the water rather than bond chemically. While due to their low water solubility, BDE congeners tend to partition to soil and sediments, their presence in waterways at ng/L poses a critical risk [242,243]. PBDE species exhibit serious health impairments such as cancer, disruption of thyroid function, and neuro-developmental interference [243,244]. The resulting health concerns and environmental issues have resulted in legislating a strict ban against the manufacturing of PBDEs [245]. Consequently, production of PBDEs has been stopped in many countries [246]. In 1977, 15 European countries phased out the production of PentaBDE. In 1989, the sale of PBDEs-containing materials was banned in Germany and Netherlands. In 2008, Canada proposed a restriction on the production of all PBDEs [247]. However, due to their extensive usage in the past and their recalcitrant nature, PBDEs traces are still found in the environment, which necessitates their removal.

Among the PBDE congeners, 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) has attracted special attention due to its abundance in the marine environment, high consumption in customer products, and high persistence. BDE-47 contains two benzene rings with four

bromine atoms at ortho and para positions [248]. The primary source of BDE-47 in the environment is the inappropriate disposal of electronic waste (E-waste)[249]. The bioaccumulation of BDE-47 in humans occurs via seafood consumption as PBDEs have lipophilic characteristics that facilitate their absorption in the fat layers in human bodies [250]. Although the production of this chemical was restricted many years ago, it is still detected in marine creatures. For instance, 5 ng/g lipid weight BDE-47 has been found in benthic species [251]. The usage and bioaccumulation of this toxic chemical promote endocrine disruption, immunotoxicity, neurotoxicity, and many other health hazards [250].

In recent years, an increasing number of investigations have been conducted to probe an effective technique for the decomposition of BDE-47 and its removal from the aquatic environment [252–255]. Treatment methods include physical and chemical techniques [256] such as adsorption [257], ozonation [258], membrane separation [259], chemical precipitation [257], Fenton process [260], photocatalysis [261], biodegradation [262], photolysis [263], and phytoremediation [264]. Among these techniques, photocatalysis has been reported as the most widely applied technique in the literature [243,265]. TiO₂-based photocatalysts have exhibited great removal efficiencies toward PBDEs [266–269]. Despite their wide band-gap, particle agglomerations, and recovery difficulties, their effectiveness was demonstrated for the decomposition of PBDEs [270]. For instance, in a study using RGO/TiO₂-Ar-H₂O system under UV light for 14h, BDE-47 went through both photocatalytic oxidation and reduction, resulting in complete degradation [271]. Furthermore, using Ag/TiO₂, complete degradation of BDE-47 was achieved after 16 min [272]. However, Wang et al. [268] reported that BDE-47 was not degraded, and its concentration did not change in the aerobic system using pristine TiO₂ after 40 minutes of UV irradiation. This may be due to the capture of electrons and hydrogen atom

species by O₂ in air, inhibiting BDE-47 degradation. Furthermore, metal-doped photocatalysts such as Pd/TiO₂ and Pt/TiO₂ showed no reactivity toward BDE-47 under UV light when O₂ was present [272].

Another attractive remediation technique for the treatment of water contaminated with PBDEs is photolysis [273–275]. Photolysis is the primary process in the natural degradation of PBDEs in the environment. The critical parameter in the photolysis of BDE congeners is the compatibility of the wavelength that a BDE congener can absorb with the light source emission spectrum [276]. PBDE compounds absorb light wavelengths in the range of 280–400 nm. Therefore, photodegradation of PBDEs is feasible upon exposure to sunlight, UVA, and UVB lights. The controlling parameters in PBDEs photolysis are their molecular structure and the type and concentration of utilized solvent. Strong hydrogen donating solvents exhibit better degradation efficiency than poor hydrogen donating solvents. For this reason, some previous works added surfactant not only to promote PBDEs solubility but also to assist photolysis by acting as a hydrogen donor [243]. Numerous studies noticed the formation of polybrominated dibenzofurans (PBDFs) during the photodegradation of PBDEs with ortho bromo substitution under UV lights [277–279]. Direct photolysis of PBDEs has been reported frequently before [19,273,274,280]. Rayne et al. [279] investigated photolysis of BDE-153 in acetonitrile matrix under a 6W UV-lamp radiation. After only one minute, BDE-99, BDE-101, BDE-118, and penta-BDEs, along with five BDF congeners, were generated. One study demonstrated that the photodegradation rate of BDE-47 increased by 30% in the presence of surfactants [281]. However, photodegradation has been shown to be mostly suitable for the PBDE compounds without ortho-bromine substitution. This is mainly due to the formation of PBDFs and PBDEs

if ortho-bromine substitution is present [19]. Hence, due to the limited absorbance ability of BDE congeners, direct photolysis is an effective technique only in the UV regions [273].

In this study, 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) is used as the target contaminant to represent the PBDEs family. This compound is a low-brominated BDE congener that has exhibited difficult degradation. However, due to the low solubility of BDE-47, which is 1-15 µg/L, a mixture of methanol/water is used as a solvent. There are several reports on the degradation of BDE-47 by sole TiO₂ or metal-doped TiO₂. Although degradation was enhanced with the doping of noble metals, the cost also increased [282]. For these reasons, two common, facile, and cost-effective remediation methods for BDE-47 elimination, namely photocatalysis and photolysis, were investigated and compared in this study. The photocatalytic and direct photolysis systems applied in this study are TiO₂/UVB/N₂ and UVB/N₂, respectively. The effect of operational parameters, including irradiation time, catalyst loading, pH, and solvent condition, as well as the kinetic studies of BDE-47 decomposition by both phototransformation and photodegradation were investigated and are reported in this paper. Three modern machine learning models were used for data validation and modeling, including Gradient Boosted Decision Tree (GBDT), Artificial Neural Network (ANN), and Symbolic Regression (SBR). Additionally, electrical energy consumption was calculated as a cost indicator. The degradation efficiency, energy consumption, and optimum conditions for BDE-47 degradation removal using two feasible methods have been compared. Despite previous studies on the photocatalytic degradation of BDE-47 [24,25,38], no study has been reported in recent years on the BDE-47 abatement using direct photolysis. Liu et al. [248] reported on the biological effect (e.g., BDE-47 bioaccumulation in organisms, production of intermediates with severe toxicity) of PBDE species under UVB. However, these authors did

not investigate the degradation of BDE-47 by UVB since the toxicity change was the main goal of their research. The present study provides an overview of the direct photolysis of BDE-47 and compares the decomposition of BDE-47 by direct photolysis and photocatalytic processes.

4.1. Materials and methods

The remaining concentration of BDE-47 in samples was quantified by using an Agilent 1260 high-performance liquid chromatography system equipped with DAD detector (HPLC-DAD). The set wavelength was 226 nm, and a C18 reversed column (3 × 100 mm, 2.5 µm particle size) was used for separation. The mobile phase was acetonitrile/water (85:15), and the applied flow rate was 0.6 mL/min. The injected volume was 10 µL for both calibration samples and test samples. The solution's total organic carbon (TOC) was measured by a TOC analyzer (TOC-L shimadzu). COD vials kits in the range of 0 to 1500 ppm were purchased from Fisher Scientific. The degradation efficiencies of BDE-47, COD, and TOC were calculated based on the following equations:

$$DE\% = \left(1 - \frac{C}{C_0}\right) \times 100 \quad (4.1)$$

$$CR\% = \left(1 - \frac{COD}{COD_0}\right) \times 100 \quad (4.2)$$

$$TR\% = \left(1 - \frac{TOC}{TOC_0}\right) \times 100 \quad (4.3)$$

Where DE (CR and TR) is the degradation efficiency (%) of BDE-47. C_0 (COD_0/TOC_0) and C (COD/TOC) are the initial concentration (initial COD/TOC) and the concentration at time t (COD/TOC at time t) in ppm, respectively.

4.2. Results and discussion

4.2.1. Operation parameters affecting BDE-47 degradation

4.2.1.1. Effect of irradiation time

The effect of irradiation time in the range of 0 to 120 min on the efficiency of BDE-47 photodegradation was investigated while keeping the other parameters constant (pH = 6.8; T = 23°C; p25 = 0.5 mg/L; BDE-47 = 5mg/L; solution volume = 300 mL; methanol: water ratio = 70:30). Fig.4.1 (a) presents the overall results of these experiments. The efficiency of BDE-47 degradation reached 46% and 36% by photocatalysis and photolysis, respectively, after 20 minutes of irradiation, while exhibiting a higher rate during the first 10 minutes. After 20 minutes, the degradation of BDE-47 drastically slowed down in both systems and completely stopped after 100 minutes.

The results showed that photolysis required more time (40 min) to remove BDE-47 compared to photocatalysis, which presented a faster reaction rate. Therefore, the irradiation times for photocatalysis and photolysis used in the following experiments were set at 20 and 40 min, respectively. The obtained results are consistent with the findings of other investigators [283–285]. More than 50% BDE-47 debromination in MPSi/Gr system under N₂ atmosphere was observed after 30 min, reaching complete debromination after 150 min [261]. Huang and coworkers [286] demonstrated rapid photodegradation of BDE-47 in UV/TiO₂ system in the first 20 min. From 20 to 60 min, BDE-47 was degraded at a slower pace, with almost complete mineralization after 60 min. The shorter reaction time in the present study compared to similar systems reported in the literature may be due to the presence of anaerobic condition. In previous works, bubbling N₂ or Ar enhanced BDE-47 mineralization in TiO₂-based systems, suggesting that O₂ has an inhibiting

effect on the degradation of BDE-47. This happens because BDE-47 photodegradation is achieved mainly through electrons, and the presence of O₂ molecules in the air may capture these electrons, thus inhibiting BDE degradation [286].

4.2.1.2. Effect of photocatalyst loading

The effect of catalyst loading at 0.5, 0.6, 0.7, 0.8, 1, 1.2, and 1.5 g/L was explored on the photodegradation of BDE-47 by TiO₂. Other operational parameters such as pH, T, time, BDE-47 initial concentration, solution volume, and solvent ratio were set at 6.8, 23 °C, 20 min, 5 mg/L, 300 mL, and 70:30, respectively. Fig. 4.1 (b) shows that with the increase of Degussa P25 catalyst dosage from 0.5 g/L to 0.8 g/L, the degradation efficiency of BDE-47 rose from 55% to 61%. This increase could be due to the high number of active sites and reactive species such as .OH radicals, .O₂⁻, etc., on the surface of the catalyst. However, further increase of the photocatalyst dose had an adverse effect on BDE-47 degradation due to particle agglomeration and higher solution turbidity that inhibited light penetration and suppressed TiO₂ excitation. The monitoring of UV irradiation showed that with the increase of TiO₂ concentration from 0.025 to 1 g/L, the transmitted light fell from 11 to 0.028 mW/cm² [287]. Exceeding the catalyst dosage to 1 g/L resulted in lowering the degradation efficiency to 58.8% and further to 58.4% when the dose rose to 1.5 g/L. The reason for this phenomenon could be the short irradiation penetration depth that negatively affected TiO₂ photoexcitation [247].

Similar results were obtained in previous studies [288–290]. For instance, a study investigated the effect of Cu/Ni/TiO₂ catalyst dosage (10-20-30 mg) on BDE-47 photocatalysis [291]. .OH radicals played the main role in BDE-47 degradation by the developed system. The highest BDE-47 degradation of 65.8% was obtained by using 20 mg catalyst. When the dosage increased to 30

mg, the degradation efficiency declined to 60%. Therefore, by increasing the catalyst dosage from 10 mg to 20 mg and then to 30 mg, BDE-47 degradation increased from 30% to 65.8% and then decreased to 60% [289].

4.2.1.3. Effect of pH

Photocatalytic degradation mostly happens on the surface of the photocatalyst. Thus, the pH of solution plays an underlying role in the degradation efficiency of photocatalysis process as it changes the surface charge of the photocatalyst. Based on previous works, photodegradation of BDE-47 in slightly acidic media, around pH 6.8, is favourable. In the present work, the influence of pH on the photocatalytic reaction of BDE-47 was studied in the pH range of 1-10. When pH increased from 1 to 6.8, BDE-47 degradation rose from 38% to 62.4%. With further increase of pH from acidic to near neutral, OH^- ions become more abundant, resulting in more hydroxyl radical ($\cdot\text{OH}$) and $\cdot\text{O}_2$ generation. At the acidic pH range of 2-3, the degradation of BDE-47 was not efficient due to the low generation of $\cdot\text{OH}$ radicals. In the alkali environment, the photocatalytic degradation of BDE-47 decreased due to two reasons. First, BDE-47 is in an ionized form at high pH values, and the excess OH^- ions may compete with brominated anions compounds for vacant sites. Second, the surface charge of TiO_2 in the basic environment is negative, so the repulsion force between TiO_2 (TiO^-) and OH^- ions inhibits hydroxyl radical generation, which is the main species for BDE-47 degradation. A similar trend was observed by Azri et al. [289], who reported degradation efficiencies of BDE-47 by Cu/Ni/ TiO_2 -PVC (5:10:85) at pH 3, 6.8, and 9 to be 43.1%, 65.8%, and 42.1%, respectively. Fig.4.1 (c) illustrates the overall trends observed for PCR and PL biodegradation of BDE-47. In direct photolysis, the lowest remaining concentration of BDE-47 (2.01 mg/L) was observed at pH 5. This could be due to the presence of more H^+ in acidic conditions, facilitating the degradation of BDE-47. The obtained optimum pH is in agreement with

a study on phototransformation of BDE-47 at ng/L under arc lamp carried out by Zhao and coworkers [292].

4.2.1.4. Effect of solvent ratio

Due to the hydrophobic nature of PBDEs, anoxic solvents with sacrificial organic agents are required in the photocatalysis of PBDEs in aqueous solutions. Besides, during the photocatalytic reduction of BDE-47, the presence of an organic solvent to serve as the electron donor is necessary [285]. On the other hand, water is needed in the solution to facilitate PBDEs oxidation because water content was correlated positively with $\cdot\text{OH}$ radicals generation that were used for oxidation. Besides, water addition inhibited reactive radicals' scavenging while simultaneously promoting PBDEs adsorption on TiO_2 [293]. Huang et al. [293] presented the effect of water on BDE-209 degradation in a water-acetonitrile mixture. They showed that with the increase in water content, higher $\cdot\text{OH}$ radicals were generated. With increasing water volume percent from 0 to 100%, the debromination efficiency rose from 15.4 to 95.6%. However, the amount of water in the mixture does not affect the generated electrons. This is the reason that increasing the water percentage enhances PBDEs oxidation but does not positively influence their reduction [293,294]. Additionally, increasing the water content not only inhibits the scavenging of reactive radicals by organic solvents but also assists in the adsorption of BDE congeners on TiO_2 [295].

Previous investigations confirmed that methanol is the best electron donor that produces hydrogen [296]. Therefore, in this study, methanol was used as the solvent for the preparation of water solutions. To further explore the solvent effect on BDE-47 degradation efficiency, different volumetric methanol/water ratios (30:70; 40:60; 50:50; 60:40; 70:30; 80:20) were examined. It was observed that with the increase of the methanol: water ratio in the solution, the photocatalytic

degradation efficiency constantly increased. As Fig. 4.1(d) shows, the highest photocatalytic degradation rate of BDE-47 (68.4%) was achieved at the methanol: water ratio of 80:20. However, when the methanol: water ratio decreased to 50:50, the degradation efficiency declined to 55.46%. This trend is also consistent with results reported in the literature [285]. Hu and coworkers [285] used different methanol: water ratios to probe the solvent effect on BDE-47 degradation by $\text{TiO}_2\text{-Cu}_2\text{O}$. The results revealed that with the elevation of methanol percentage in the solution, both hydrogen production and BDE-47 degradation were enhanced. Successfully, 97% of BDE-47 was mineralized by using a solution with a methanol percentage of 80% after 150 min, with 14.7 mmol/L hydrogen produced [285]. However, unlike photocatalysis, despite the predominant effect of solvent condition, direct photolysis of BDE-47 was not significantly affected when the solvent percentage in the solution varied. The highest degradation efficiency (61.3%) and lowest Ce (1.93) were obtained at methanol:water ratio of 80:20.

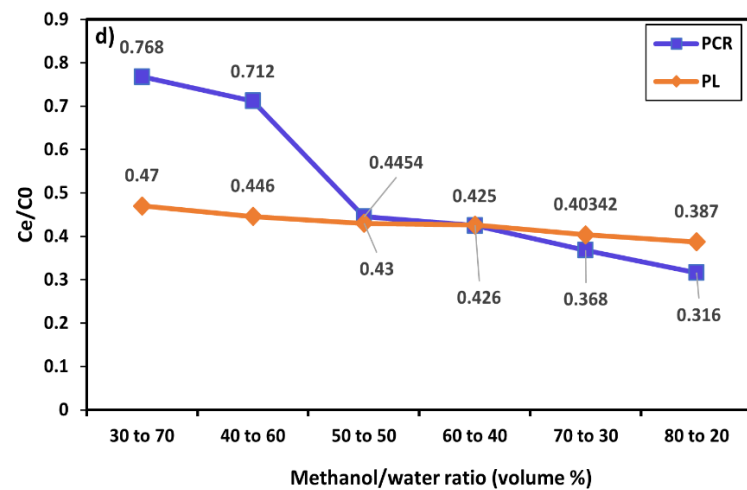
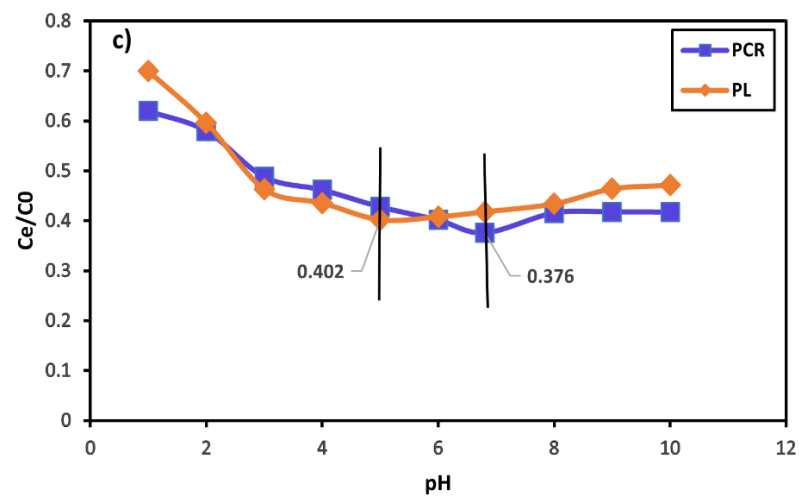
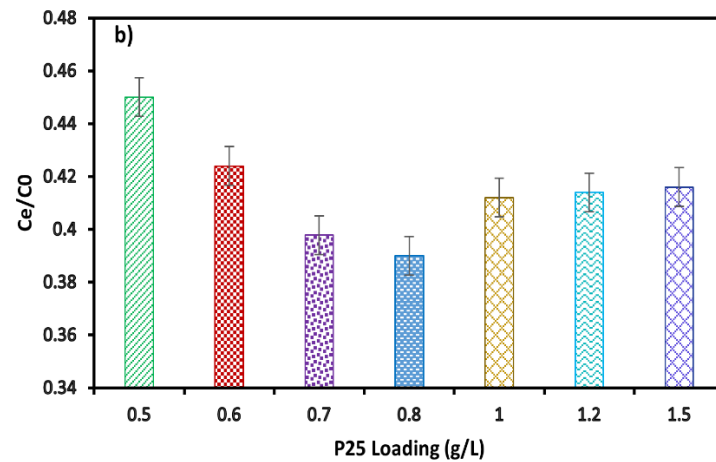
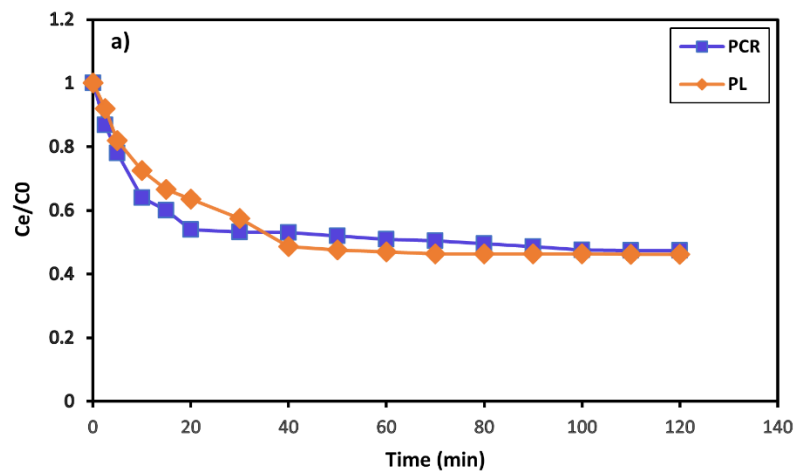


Figure 4.1. Photocatalytic reaction (PCR) and direct photolysis (PL) of BDE-47 (a) at different irradiation times with other operational conditions set as follows: pH, 6.8; T, 23 °C; TiO₂ dosage, 0.5 mg/L; BDE-47 initial concentration, 5 mg/L; and solvent condition, methanol/water=70:30; atmosphere, N₂. (d) At various solvent portions; conditions (PCR): catalyst loading (g/L), 0.8 g/L; temperature, 23 °C; pH, 6.8; time, 20 min; BDE-47 initial concentration, 5 mg/L; solution volume, 300 mL; and atmosphere, N₂; conditions (PL): temperature, 23 °C; pH, 5; time, 40 min; BDE-47 initial concentration, 5 mg/L; solution volume, 300 mL; and atmosphere, N₂.

4.2.2. Machine learning model development

4.2.2.1. Data assembling

In this work, three machine learning models that operated based on supervised learning were used. Constructed models predicted the output data, i.e., the remaining concentration (Ce) of BDE-47, based on the relation between the input and output data. The input data bank (controlling parameters) during the BDE-47 degradation efficiency are irradiation time (min), photocatalyst loading (g/L), pH, and solvent ratio (%). Table.4.1 shows the range of input variables. The methodology and the developed models applied to predict the remaining BDE-47 concentration by PCR and PL are exhibited in Fig. 4.2.

Table. 4.1. Range of input controlling parameters.

Variables	Min. range	Max. range
Time (min)	0	120
Catalyst loading (g/L)	0.5	1.5
pH	1	10
Solvent ratio (%)	30	80

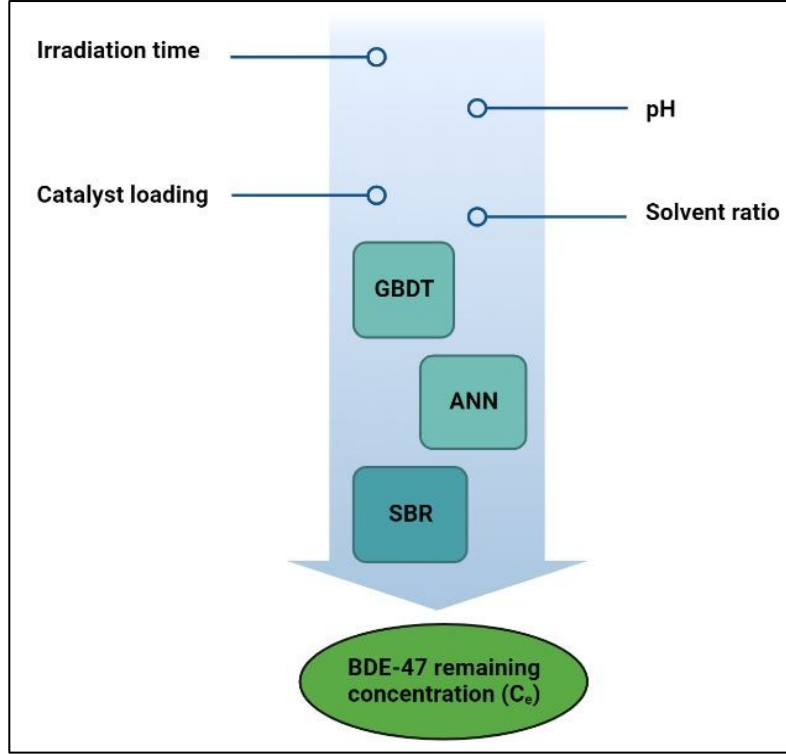


Figure 4.2. Methodology and machine learning models used in this work.

4.2.2.2. Model comparison and accuracy

The input data is the determining factor in reflecting the reliability and exactness of the applied models. For model validation and assessment, four statistical criteria were calculated for the developed models, including R-squared (R^2), root mean square error (RMSE), average relative error (ARER), and absolute error (ABER). These statistical techniques are introduced below:

- I. The coefficient of determination (R^2) reflects how the applied model predicts the outcome variable. The more the outcome variables obtained from the models match the experimental results, the closer becomes R^2 to unity [297].

$$R^2 = 1 - \frac{\sum_{i=1}^n (D_{iP} - D_{iE})^2}{\sum_{i=1}^n (D_{iP} - D_{iE})^2} \quad (4.4)$$

- II. Root Mean Square Error (RMSE) is the standard deviation of errors in the data set. RMSE indicates the level of data concentration around the best fit line [297].

$$\text{RMSE} = \left(\frac{\sum_{i=1}^n (D_{iP} - D_{iE})^2}{n} \right)^{1/2} \quad (4.5)$$

- III. Average Relative Error (ARER) shows the discrepancy between the data obtained experimentally and the data predicted by the ML models [297].

$$\text{ARER (\%)} = \frac{1}{n} \sum_{i=1}^n \left(\frac{D_{iP} - D_{iE}}{D_{iE}} \right) \times 100 \quad (4.6)$$

- IV. Absolute error (ABER) is the difference between the outcome of models and the experimental data.

$$\text{ABER} = \sum_{i=1}^n \left| \frac{D_{iP} - D_{iE}}{D_{iE}} \right| \quad (4.7)$$

Where n is the number of data, D_{iP} and D_{iE} are results obtained from model prediction and experiments, respectively.

4.2.2.3. Machine learning models development

The ability of machine learning models to derive advanced mathematical expressions along with their simplicity, have resulted in their extensive usage [297–300]. Three machine learning models, namely Gradient Boosted Decision Tree (GBDT), Artificial Neural Network (ANN), and Symbolic Regression (SBR) were adopted to assess the capacity of different types of machine learning models in predicting the remaining concentrations of BDE-47 after the PCR and PL treatment processes. ANN is based on neural network, while GBDT and SBR are ensemble models by decision tree and non-linear regression, respectively. These models were generated using Python software; all input data were randomly divided into train and validation

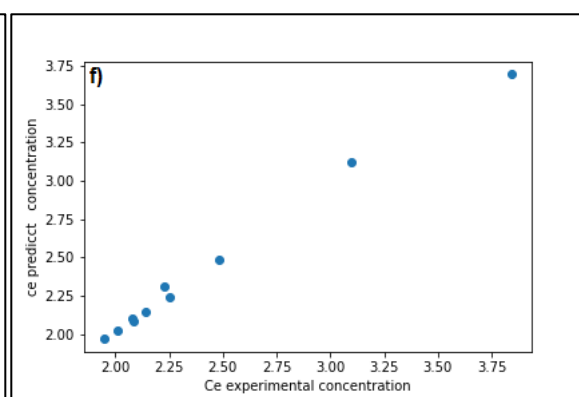
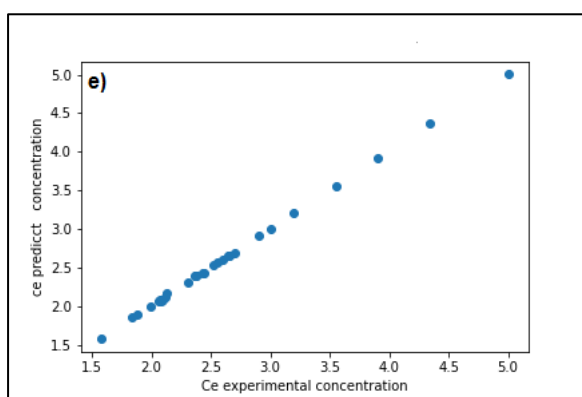
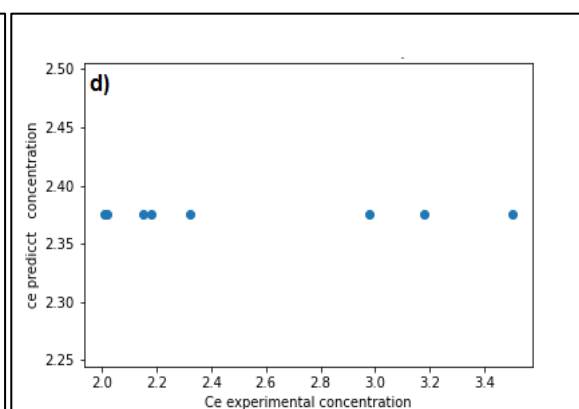
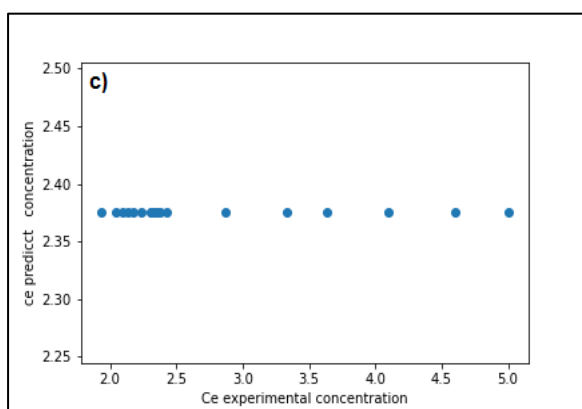
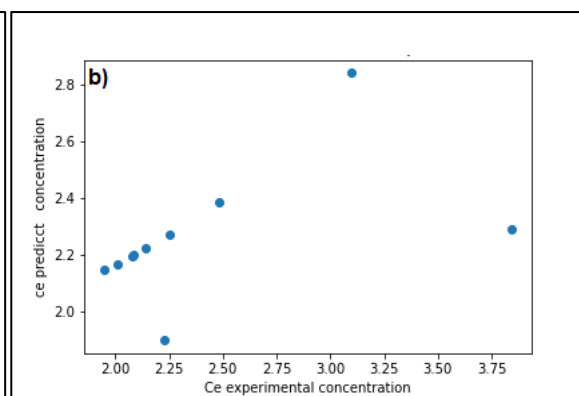
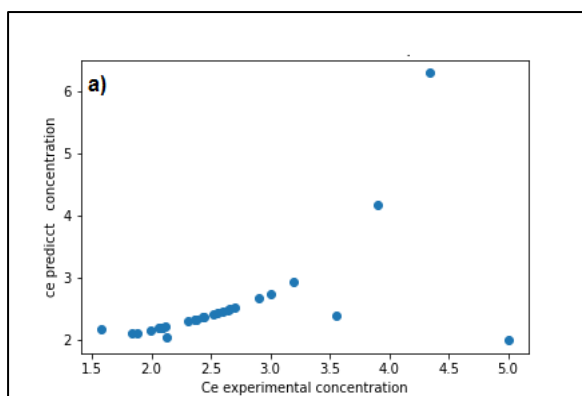
data sets. 80% and 20% of the whole data set was used for train and test, respectively. The highest conformity with experimental results makes a constructed model the most reliable in predicting the remaining BDE-47 concentration. The fitting results of GBDT, ANN, and SBR were compared for BDE-47 degradation by PCR and PL. Table.4.2 demonstrates the statistical criteria of both training and validation steps for all developed models. GBDT exhibited the best accuracy in data validation of PCR, with R^2 , RMSE, ARER, and ABER values of 0.9826, 0.0549, 0.0207, and 0.0549 for the validation phase. Therefore, it was concluded that GBDT is the most reliable model in representing and predicting experimental data owing to its highest R^2 and lowest RMSE value.

Table.4.2. Calculated accuracy evaluators for the applied ML models.

ML model	Treatment process	Train/Test	R^2	RMSE	ARER	ABER
SBR	PCR	Train	0.0718	0.35300	0.1102	0.3530
		Validation	0.1757	0.2919	0.1011	0.2919
	PL	Train	-0.1358	0.4780	0.1361	0.4780
		Validation	-0.0920	0.4666	0.1693	0.4666
ANN	PCR	Train	0.9993	0.0152	0.0064	0.0152
		Validation	0.9905	0.0331	0.0121	0.0331
	PL	Train	0.8196	0.3360	0.1334	0.3360
		Validation	0.5581	0.3605	0.1505	0.3605
GBDT	PCR	Train	1.0000	9.8305e ⁻⁰⁹	3.9968e ⁻⁰⁹	9.8305e ⁻⁰⁹
		Validation	0.9826	0.0549	0.0207	0.0549

PL	Train	0.9999	0.0050	0.0017	0.0050
	Validation	0.8474	0.1245	0.0389	0.1245

The predicted concentrations of remaining BDE-47 versus the experimental C_e values are presented in Fig. 4.3. Contrary to the SBR model, the ANN and GBDT models proved to be reliable for modeling the PL and PCR processes. The GBDT showed excellent predictions, with the highest proximity to the $x=y$ line. The ANN model presented a desirable accuracy in predicting the output data for both PCR and PL. For 20% of the data set, the RMSE was less than 0.04 for PCR and less than 0.4 for PL. The coefficient of determination (R^2) was between -1 to 1. Minus value of R^2 (-0.0920) calculated from the validation data set of PL represent the unsuitability of SBR in modeling the PL process.



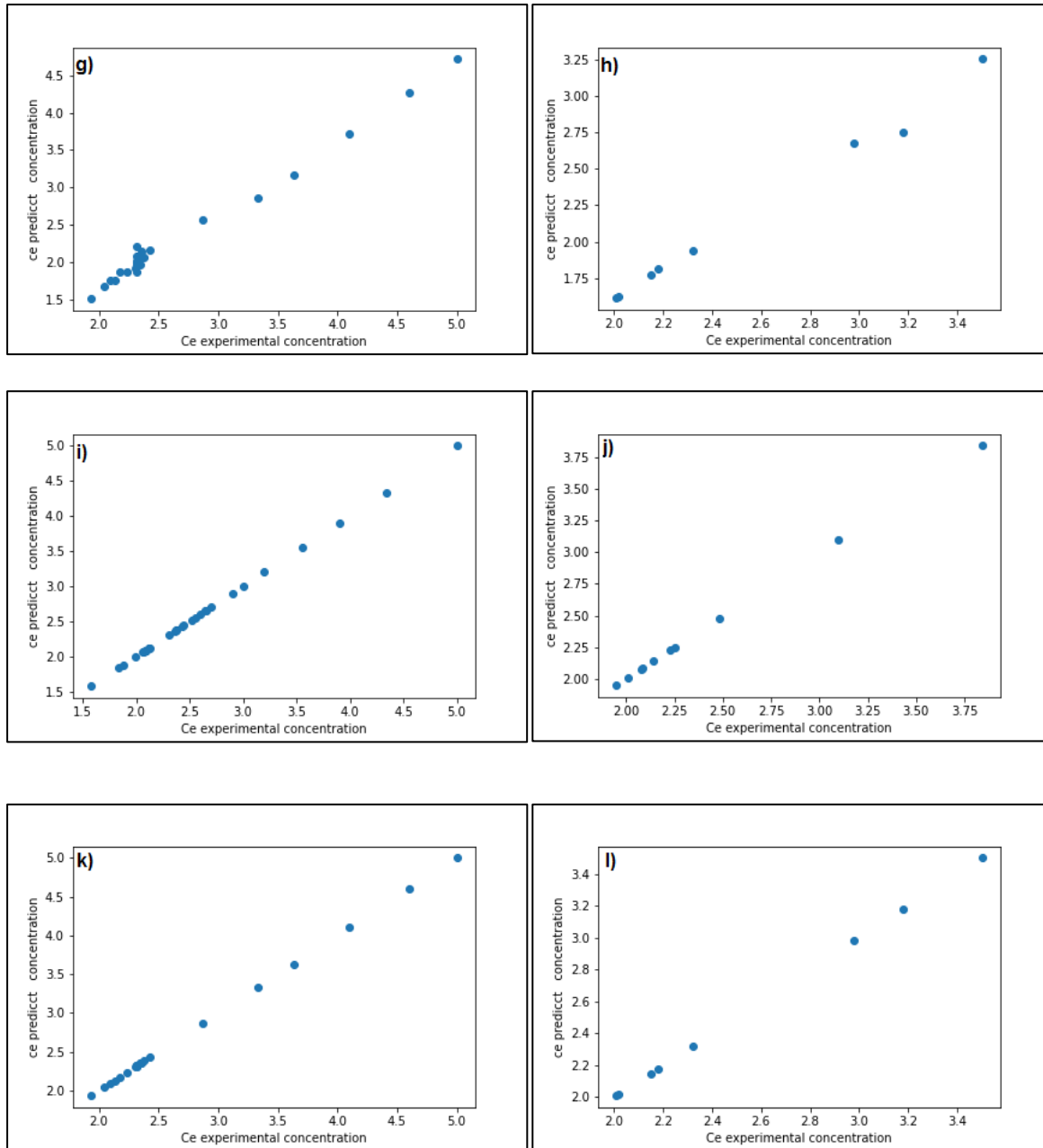


Figure 4.3. Scatter plots of fitting results obtained from three machine learning models (SBR, ANN, and GBDT) for the train and validation datasets of the PCR and PL processes. a) SBR fitting results for the train data set part of PCR. b) SBR fitting results for the validation phase of PCR. c) SBR fitting results for the train set of PL. d) SBR fitting results for the test set of PL. e) ANN fitting results for the train data set part of PCR. f) ANN fitting results for the validation phase of PCR. g) ANN fitting results for the train set of PL. h) ANN fitting results for the test set of PL. i) GBDT fitting results for the train data set part of PCR. j) GBDT fitting results for the validation phase of PCR. k) GBDT fitting results for the train set of PL. l) GBDT fitting results for the test set of PL.

Additionally, the statistical and fitting results for the full data set was investigated, as shown in Table 4.3 and Figure 4.4. Similar to the trends observed for PCR and PL, for the whole data set (combining PCR and PL data), the highest R^2 value was observed for GBDT model (training: 0.9999, validation: 0.9849). In contrast, the negative value (-0.7774) of the coefficient of determination obtained from the training data set of SBR model represents the inaccuracy of SBR in modeling. For 20% of the whole data set, lower RMSE, ARER, and ABER values were obtained for GBDT than ANN and SBR. Beyond that, as Fig. 4.4 indicates, the highest vicinity of data to the $x=y$ axis was achieved with GBDT model, consistent with the obtained results from calculating statistical criteria. Accordingly, SBR and ANN models showed less accuracy than the GBDT predictive model in modeling the whole dataset.

Table 4.3. Statistical criteria calculated for the whole dataset of applied ML models.

ML	Train/Test	R^2	RMSE	ARER	ABER
models					
SBR	Train	-0.7774	0.3361	0.1037	0.3361
	Validation	0.0216	0.47137	0.1321	0.4713
ANN	Train	0.9686	0.0884	0.0336	0.0884
	Validation	0.9580	0.1308	0.0429	0.1308
GBDT	Train	0.9999	0.0031	0.0011	0.0031
	Validation	0.9849	0.0714	0.0213	0.0714

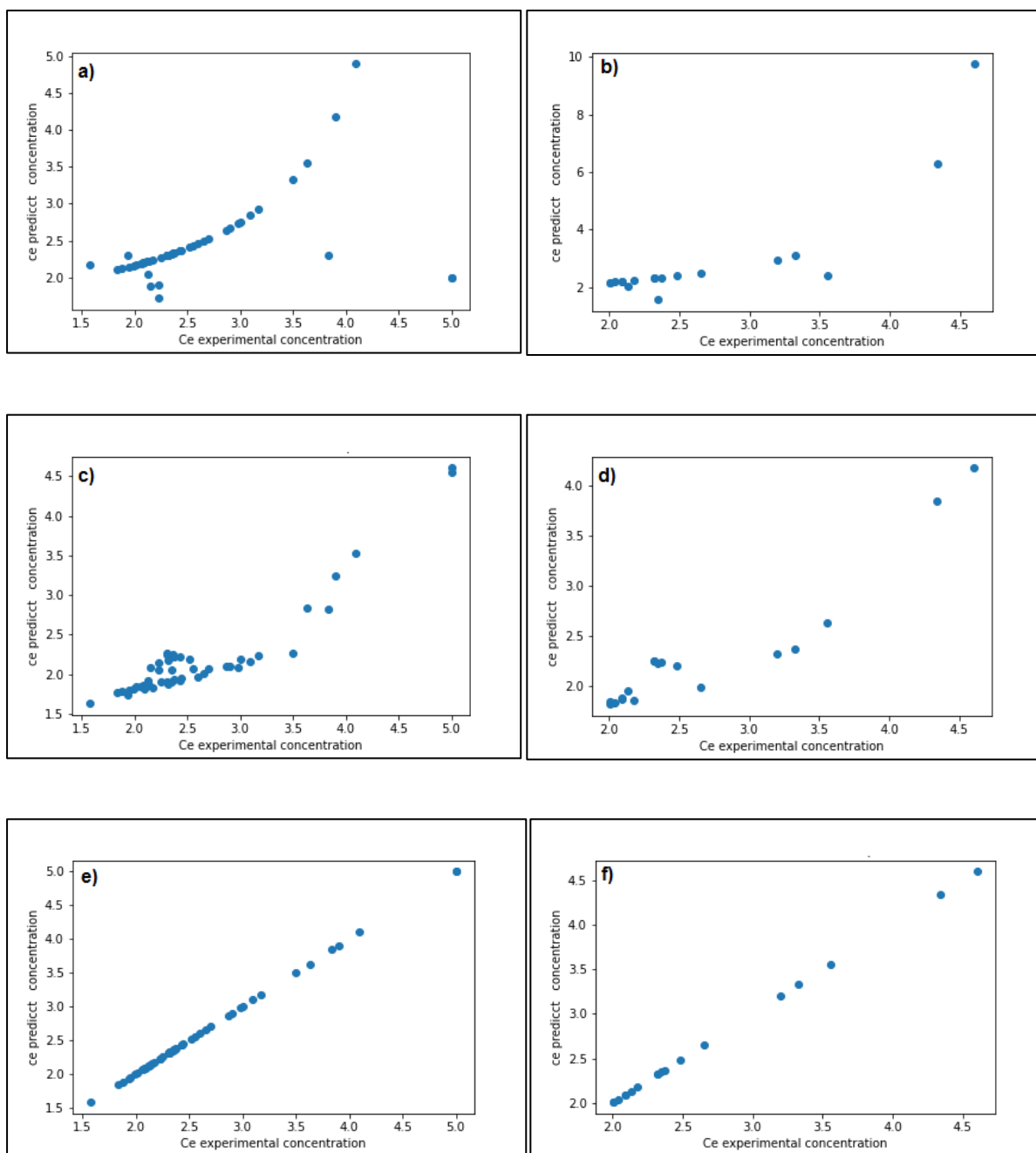


Figure 4.4. Scatter plots of the fitting results obtained from three machine learning models (SBR, ANN, and GBDT) for the whole data set. a) SBR fitting results for the train data set. b) SBR fitting results for the validation phase. c) ANN fitting results for the train data set. d) ANN fitting results for the test data set. e) GBDT fitting results for the train data set. f) GBDT fitting results for the validation phase.

4.2.3. Kinetic studies

The kinetics of photocatalytic degradation and photodegradation of BDE-47 is explained through a commonly applied Langmuir-Hinshelwood (L-H) kinetic model. The linear form of the L-H kinetic equation is presented below (Eq. 4.8):

$$\frac{1}{r_0} = \frac{1}{K_r K_{ad}} \frac{1}{C_0} + \frac{1}{K} \quad (4.8)$$

Where C_0 (mg/L) is the initial concentration of the BDE-47. K_r (mg L⁻¹ min⁻¹) and K_{ad} (L mg⁻¹) are the apparent reaction rate and adsorption equilibrium constants, respectively. r_0 (mg L⁻¹ min⁻¹) is the initial degradation rate [301]. $K_r K_{ad}$ (K_{app} , min⁻¹) is commonly mentioned in previous works as the apparent reaction rate obtained by plotting $\ln (C_0/C)$ vs. t . At low concentrations ($K_{ad} C \ll 1$), Eq. (4.8) could be simplified to the famous first-order equation:

$$\ln \left(\frac{C}{C_0} \right) = - K_r K_{ad} t = - K_{app} t \quad (4.9)$$

Where C (mg/L) is the concentration at time t . In this study, t is considered as the illumination time, not the reaction time. Reaction time is the illumination time plus the time needed for the adsorption-desorption equilibrium [302,303]. Also, the half-life is estimated from:

$$t_{1/2} = \frac{\ln 2}{K_{app}} \quad (4.10)$$

Experiments were conducted at the optimum operating conditions to explore the kinetics of PCR and PL processes during the degradation of BDE-47. As Fig. 4.5 indicates, both PCR and PL of BDE-47 follow first-order kinetics, which is in agreement with previous research [304]. Fig. 4.5 also compares the kinetic constants for the abatement of BDE-47 by PCR and PL. During the first 10 minutes, as exhibited in Fig. 4.1 (a), the reaction rates were high (0.0492 min⁻¹ for PCR and 0.0487 min⁻¹ for PL) for both PCR and PL, while after 20 minutes, with the progress of reactions, the rates considerably

diminished. This is mainly due to the formation of intermediates, including BDE-28, BDE-17, BDE-15, and BDE-3, during the reaction that may compete with BDE-47 for the catalyst's active sites, photon absorption, and reaction with electrons and $\cdot\text{OH}$ [286,302,303]. The highest apparent rate constant (0.0027 min^{-1}) for BDE-47 degradation was obtained by PCR. The apparent reaction rate and half-life of degradation for both photocatalysis and photolysis are presented in Table. 4.4.

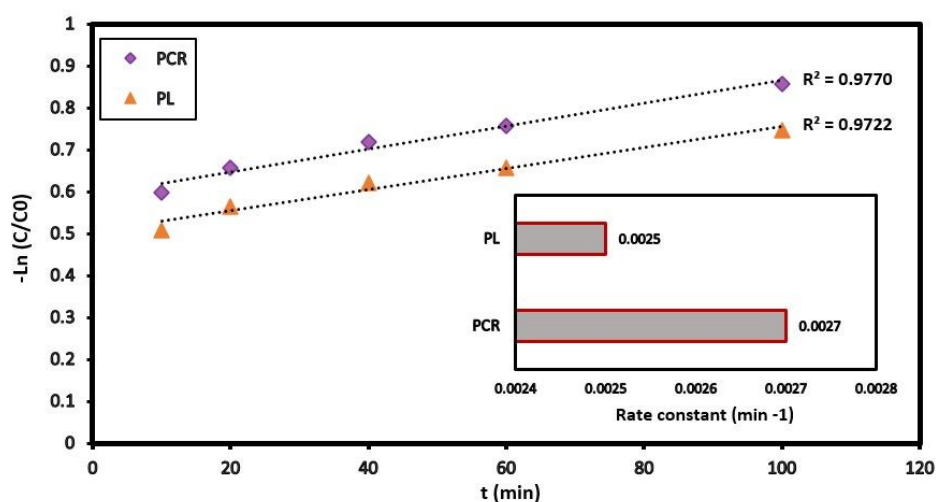


Figure 4.5. Photocatalytic and photolysis BDE-47 degradation rates; pH 6.8, T: 23 °C, P25 loading: 0.5 mg/L, [BDE-47]₀: 5 mg/L, 300 mL solution with methanol: water ratio of 70:30.

Table.4.4. Parameters obtained from first-order reaction kinetics of PCR and PL.

Kinetic parameters	PCR	PL
Apparent reaction rate	0.0027	0.0025
(K_{app} , min^{-1})		
Half-life ($t_{1/2}$, h)	4.27	4.62

4.2.4. COD and TOC removal

Chemical oxygen demand (COD) was measured at different time intervals for both photolysis (PL) and photocatalysis (PCR) of BDE-47. Fig. 4.6 demonstrates the general trends for COD removal by PCR

and PL. As Fig. 4.6 indicates, although 46% of the initial content of BDE-47 was degraded after 20 min, the COD removal was only 4.83%. This is mainly due to the generation of persistence intermediates that are hardly degradable. Therefore, the recalcitrance of BDE-47 congeners and the generated by-products was assessed at the following conditions: pH 6.8, T 23 °C, p25 loading 0.5 mg/L, [BDE-47]₀: 5 mg/L, 300 mL solution with methanol: water ratio of 70:30. COD gradually decreased to 41% and 32% after 60 minutes by photocatalysis and photolysis, respectively. Compared to photolysis, an enhancement in the COD removal efficiencies was observed in the photocatalytic system. The results showed that photocatalysis had a better performance in the degradation of BDE-47 by-products. This could justify the advantage of photocatalysis for the abatement of flame retardants compared to photolysis.

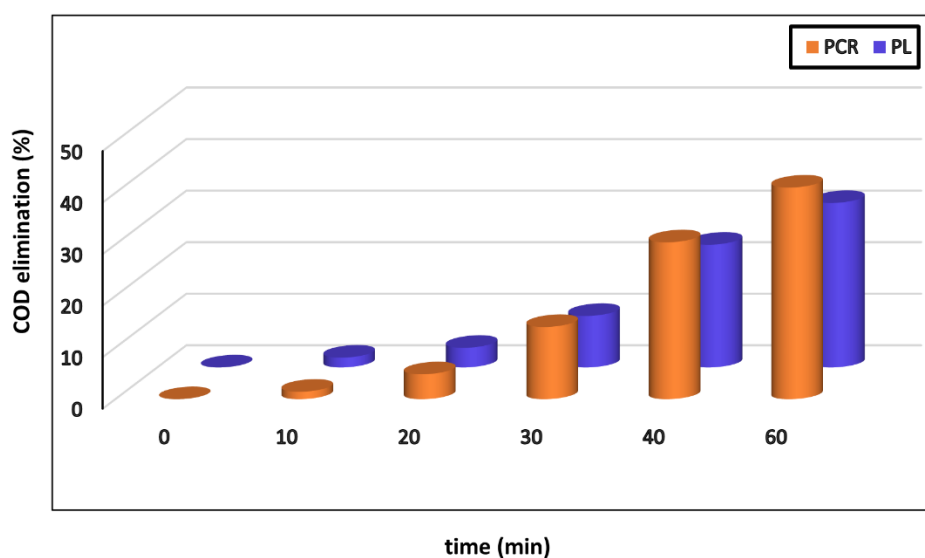


Figure 4.6. Comparison of COD reduction (%) at different time intervals by photocatalysis and photolysis at pH 6.8, T 23°C, p25 loading 0.5 mg/L, [BDE-47]₀: 5 mg/L, 300 mL solution with methanol: water ratio of 70:30.

In addition to COD analysis, TOC measurements were also conducted in order to verify the results obtained through COD analysis. TOC indicates the mineralization extent, and as Fig. 4.7 illustrates, TOC removal increased for both systems as time advanced. When irradiation time increased from 20 to 120 minutes, TOC degradation rose from 13% to 84.97% in PCR and from 4% to 60% in PL. This proves the capability of photocatalysis in the mineralization of generated intermediates. In direct photolysis,

BDE-47 degradation efficiency was 36.44% after 20 minutes of irradiation, while under the same operating conditions, TOC removal was only 4%. This finding suggests that direct photolysis may fail to abate aliphatic intermediates and Br^- ions [305]. However, upon the removal of a fraction of aliphatic species, TOC gradually diminished to 32.51% after 180 min. In the presence of Degussa p25 TiO_2 photocatalyst, the removal efficiency of TOC increased from 13% to 60% with the increase of irradiation time from 20 to 180 minutes. The rapid TOC removal suggested the fast mineralization of the less-brominated intermediates that were generated during the process, possibly as a result of high interaction with $\cdot\text{OH}$ radicals and holes on TiO_2 . This finding is consistent with those reported by Lei et al. [305].

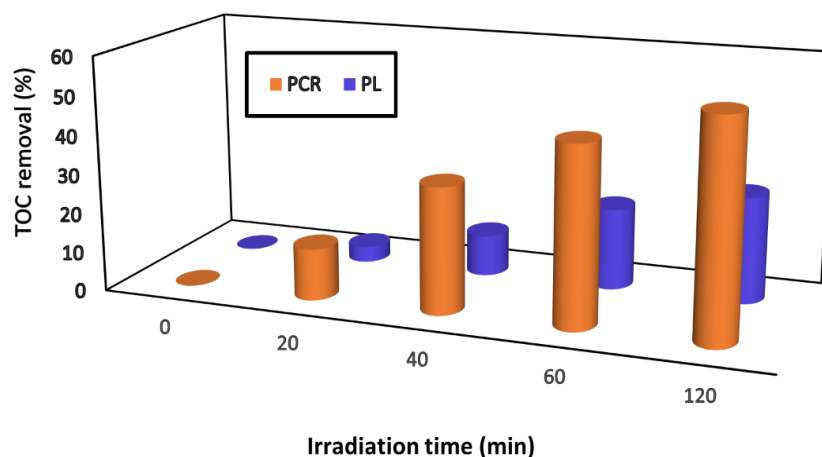


Figure 4.7. Comparison of TOC elimination (%) at different time intervals by photocatalysis and photolysis at pH 6.8, T 23°C, p25 loading 0.5 mg/L, [BDE-47]₀: 5 mg/L, 300 mL solution with methanol: water ratio of 70:30.

4.2.5. Electrical energy consumption

Electrical energy per order (E_{E0}) is the required electrical energy to reduce the concentration of the target contaminant by one order of magnitude (90% reduction) in 1 m^3 of polluted water [306]. In this

work, E_{E0} was used to compare energy consumption in photocatalysis and photolysis processes. E_{E0} was calculated based on the following equation (Eq. 4.11):

$$E_{E0} = \frac{P \times t \times 1000 \times (C_i - C_e)}{V \times 60 \times (C_i - C_e)} \quad (4.11)$$

Where P (kW) is the UV lamp power and, t (min) is the irradiation time, V (L) is the volume, C_i and C_e (mg L⁻¹) are the initial and final concentrations of BDE-47, respectively.

Fig. 4.8 shows E_{E0} at different time intervals for photolysis and photocatalysis under the same operating conditions. Direct photolysis consumes more electrical energy compared to photocatalysis during irradiation, from 10 to nearly 78 minutes. During the PCR process, the E_{E0} was 69.87 MW h m⁻³, and DE was 46% in the first 20 minutes. The difference between the E_{E0} values of PCR and PL under the same operational conditions continued during the first 40 minutes. The difference between E_{E0} values of PL and PCR at 10 and 20 mins are 25.94 and 33.94 MW h m⁻³, respectively. This indicates that at the beginning of the reaction, PCR required less electrical energy to degrade BDE-47 due to the presence of p25. P25 increases energy efficiency, especially in the first 40 minutes, by adsorbing BDE-47 molecules and promoting electron and hole generation. Besides, the faster rate of reaction observed in the photocatalysis process compared to the reaction rate of BDE-47 in phototransformation leads to lower energy consumption. The reason for greater electrical energy consumption of PCR compared to PL after 78 min is the higher BDE-47 remaining concentration. Overall, 10% less energy consumption of photocatalysis compared to photolysis for the whole period proved the cost-effectiveness and energy-saving properties of photocatalysis for PBDEs diminution.

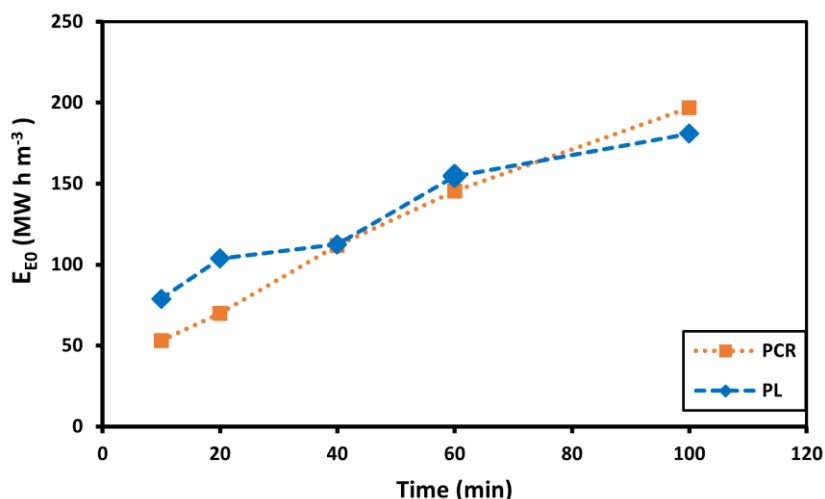


Figure 4.8. E_{EO} change in the first 100 min of irradiation while other parameters are set at pH 6.8, T 23°, $p25=0.5$ mg/L, BDE-47: 5 mg/L, solution volume: 300 mL, methanol: water ratio 70:30.

4.3. Summary

This chapter explored the anaerobic degradation of BDE-47 through photocatalysis and direct photolysis under UVB light and nitrogen atmosphere. Titanium dioxide (TiO_2), one of the most widely used photocatalysts for the decomposition of halogenated organic pollutants, was employed in this study. The effects of key process parameters on the degradation efficiency and residual concentration of BDE-47 were systematically examined.

In the TiO_2 /UVB/ N_2 system, 68.4% of BDE-47 was debrominated under optimal conditions (irradiation time = 20 min; pH = 6.8; catalyst loading = 0.8 g/L; methanol: water ratio = 80:20). Under similar solvent conditions but with optimized parameters for photolysis (irradiation time = 40 min; pH = 5), the degradation efficiency reached 61.3%.

To validate the experimental results, four state-of-the-art machine learning (ML) models were applied. Among them, the Gradient Boosted Decision Trees (GBDT) model demonstrated the best performance across the dataset, showing the highest R^2 and lowest RMSE, ARER, and ABER values. For the

validation set (20% of the data), the GBDT model yielded an R^2 of 0.9849, RMSE of 0.0714, ARER of 0.0213, and ABER of 0.0714, confirming its reliability in predicting the residual concentration (C_e) of BDE-47 in both photocatalytic reduction (PCR) and photolysis (PL) systems.

The degradation kinetics of BDE-47 for both PL and PCR followed the Langmuir-Hinshelwood (L-H) first-order model. Due to the low initial concentration of BDE-47 used in the study, the L-H model simplifies to its first-order form. The estimated half-life for both processes was approximately 4 hours, attributed to the high availability of hydrogen donors provided by methanol as the solvent.

Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) analyses revealed that while photolysis could partially degrade BDE-47, it was significantly less effective at mineralizing the intermediate compounds compared to photocatalysis. PCR achieved an 85% TOC removal, whereas PL removed only 60%, indicating a 25% higher mineralization efficiency for PCR.

Considering the formation and persistence of by-products as critical challenges in the degradation of PBDEs in water, photocatalysis emerged as the more desirable technique due to its enhanced breakdown of BDE congeners. Additionally, energy consumption analysis showed that PL had a higher electrical energy demand, with an EE_0 of $103.82 \text{ MW}\cdot\text{h}\cdot\text{m}^{-3}$ after 20 minutes of irradiation, compared to $69.87 \text{ MW}\cdot\text{h}\cdot\text{m}^{-3}$ for PCR. This higher energy requirement directly affects operational costs, which are crucial in selecting an efficient treatment method. The elevated EE_0 for PL is likely due to the longer irradiation time needed to achieve similar degradation levels as PCR.

The relatively low degradation efficiency of BDE-47 observed in this work can be attributed to a combination of intrinsic molecular stability and process-related limitations. BDE-47 is highly recalcitrant due to its brominated diphenyl ether structure, where strong C–Br bonds and resonance-stabilized aromatic rings hinder both oxidative and reductive transformation pathways; additionally, as a lower-brominated congener, it is less susceptible to stepwise debromination compared to highly brominated

PBDEs. BDE-47's extremely low aqueous solubility further limits mass transfer and reduces effective contact between the pollutant and reactive sites on the catalyst surface, thereby constraining degradation kinetics. Moreover, in photocatalytic systems, insufficient generation and utilization of reactive species due to factors such as limited light absorption, rapid electron–hole recombination, and suboptimal band structure can significantly reduce degradation efficiency. Catalyst surface properties, including agglomeration and limited active sites, may also restrict adsorption and interfacial electron transfer. Another critical factor is the formation of stable intermediates, including lower-brominated congeners or partially debrominated products, which can accumulate and slow down overall mineralization, leading to an apparent plateau in degradation.

To enhance the degradation of BDE-47, strategies should focus on improving charge separation and reactive species generation through the design of advanced photocatalysts such as heterojunctions, doped semiconductors, or conductive polymer–based composites. Enhancing pollutant availability via surfactants or co-solvents can improve interfacial interactions, while coupling photocatalysis with advanced oxidation processes such as persulfate activation can generate highly reactive sulfate radicals ($\text{SO}_4^{\bullet-}$) capable of cleaving C–Br and ether bonds more efficiently. Overall, integrating optimized catalyst design with hybrid treatment approaches is essential to overcome the persistence of PBDEs and achieve deeper degradation and eventual mineralization.

5. Chapter 5: Z-scheme PPy-g-C₃N₄-MIL-88B heterogeneous photo-Fenton catalyst for tris-(2-chloroisopropyl) phosphate (TCPP) degradation: morphologies, RSM optimization, and machine learning models

Flame retardants (FR) are persistent emerging contaminants typically found in consumer products. These pollutants reach the environment through leaching, volatilization, and infiltration. [9,19,307]. Tris (1-chloro-2-propyl) phosphate (TCPP) stands out as a prevalent flame retardant within the chlorinated organophosphate flame retardants (OPFRs) group. TCPP has a water solubility of 1200 mg L⁻¹ at 25°C, with a 2.89 octanol-water partition coefficient [10–13]. These properties result in noticeable concentrations of TCPP in surface water and wastewater effluent as high as 200 ng L⁻¹ and 24 µg L⁻¹, respectively [11]. Such levels of TCPP may lead to neurotoxicity, carcinogenicity, and endocrine disruption [13].

Various techniques have been employed for TCPP degradation, including constructed wetlands [21], photocatalysis [11], membrane reactors [22], adsorption [23], and ozonation [24]. Among these methods, photocatalysis has gained significant popularity, evidenced by the increasing number of research studies dedicated to TCPP degradation using photocatalysis. While constructed wetlands demonstrate a degradation efficiency of 26%-28% [21], photocatalysis surpasses these values with over 60% TCPP degradation [11].

The Materials Institute Lavoisier (MILs) comprise metal carboxylate salts possessing hydrothermal stability, symmetrical porous structure, and high surface area [308–311]. Despite the mentioned advantages, MIL-based catalysts encounter challenges during photocatalysis, such as high electron-hole pair recombination and limited light absorption that commonly diminish the photocatalysis efficiency. To overcome these issues, various modification techniques have been applied, including coupling MILs with materials such as graphitic carbon nitride (g-C₃N₄) and graphene oxide (GO) [312,313].

Graphitic carbon nitride (g-C₃N₄) possesses desirable electronic properties while being restricted by photoexcited carrier separation, which limits its sole use. [314–316]. Improvements such as heterojunction formation, noble metal introduction, and doping have been applied to enhance the performance of g-C₃N₄ [316–319]. Polypyrrole (PPy), a conductive polymer, exhibited favourable redox potential and high electrical conductivity [320] while demonstrating limitations such as low surface area and particle agglomeration. He and coworkers [321] anchored PPy into MIL-88B, which improved light absorption and electron transfer properties of the resulting photocatalyst. Furthermore, the coupling of PPy with g-C₃N₄ improved photocatalytic efficiency by impeding the electron-hole recombination [322]

Herein, a novel Z-scheme PPy-C₃N₄-MIL-88B photo-Fenton catalyst was synthesized via an *in-situ* polymerization technique for TCPP degradation. Anchoring polypyrrole (PPy) in the composite serves for electron shuttling between C₃N₄ and MIL-88B, reducing and delaying charge recombination. Compared to alternatives, such as reduced graphene oxide (RGO), PPy is more cost-efficient, stable, and environmentally friendly [323]. Moreover, PPy enhances the electron shuttling between MIL88B and g-C₃N₄, limiting charge recombination, which is a critical limitation in previously reported photo-Fenton catalysts [324–326]. Unlike many previous works that focused only on photocatalytic efficiency, this study considers energy efficiency, non-toxicity, and tailored synthesis strategies, which provide material optimization for catalytic applications [327–330]. The synthesized Z-scheme PPy-C₃N₄-MIL-88B photo-Fenton catalyst demonstrated great performance in TCPP degradation in the presence of radical scavengers, which has not been observed in similar research works [330–332]. Regarding the methodology, this study introduces a new synthesis technique for implanting PPy on the surface of C₃N₄-MIL-88B photocatalyst. The applied technique provides more uniform coating and a stronger interaction with the polymer interface. Additionally, compared to other methods, this technique does not require large amounts of organic solvent, enhancing its environmental

friendliness [333]. Therefore, the novelty of this work lies in the application of a new synthesis technique that resulted in the unique dispersion of PPy nanoparticles, as verified by TEM analysis. Furthermore, the effect of reaction temperature on the morphology of photocatalyst was investigated and is reported.

Three morphologies of MIL-88B were prepared at different reaction temperatures (80 °C, 120 °C, 145 °C). Subsequently, the MIL-88B structure was improved by combining g-C₃N₄ and PPy at 120 °C. The successful fabrication of the PPy-C₃N₄-MIL-88B photocatalyst was confirmed through several characterization techniques. As shown before, incorporating H₂O₂ into MIL-based systems presents a synergistic effect on TCPP degradation as it results in higher generation of .OH radicals [334–336]. The performance of PPy-g-C₃N₄-MIL-88B/H₂O₂/LED¹ photo-Fenton system was evaluated by investigating its efficiency in the degradation of TCPP under different operating conditions, including the catalyst dose, pH, reaction time, TCPP initial dosage, and radical scavengers. In addition, the system's energy efficiency, the interplay between operational parameters, and the reusability of the PPy-C₃N₄-MIL-88B Photo-Fenton catalyst were evaluated. The results demonstrated that the developed system offers a sustainable, efficient solution to address flame retardant pollution in aquatic environments.

5.1. Material and methods

The methodology involves photocatalyst preparation (presented in the following 5.1.1) and characterization (presented in 3.3). The developed photocatalysts' fabrication is presented as follows.

5.1.1. MIL-88 B-based photocatalysts preparation

¹ Light-emitting diode

Three morphologies of MIL-88B were prepared through the hydrothermal technique at reaction temperatures of 80 °C to 120 °C and 145 °C. For all the synthesized samples, the reaction time was set at 18h. MIL-88B was synthesized by adding 10 mmol terephthalic acid, 10 mmol FeCl₃ · 6H₂O, 8.2 mmol NaOH, and 4.7 mL acetic acid to 50 mL *N,N*-dimethylformamide (DMF). The mixture was under vigorous stirring for 6 h at room temperature, and then it was sealed in a 50 mL teflon-lined stainless-steel autoclave. The autoclave was subsequently placed in an oven at 80 °C for 18h. The mixture was then washed with ethyl alcohol and the resulting precipitate was dried in an oven at 70 °C for 18h. Other MIL-88B morphologies were prepared by the same procedure while changing the reaction temperature from 80 °C to 120 °C, and 145 °C [337,338].

G-C₃N₄ was fabricated through the calcination method by dissolving 79.3 mmol melamine in 100 mL MilliQ water and applying ultrasound for 1h. Next, it was dried in an oven at 70 °C for 14h. The precipitate was calcinated at 550°C in a furnace, resulting in a yellow powder of g-C₃N₄ [339]. In the next step, g-C₃N₄-MIL-88 was fabricated through solvothermal reaction. At first, 0.32 mmol g-C₃N₄ was dissolved in 10 mL DMF and ultrasound was applied for 60 min. Then, 10 mmol terephthalic acid, 4.7 mL acetic acid, 8.2 mmol NaOH, and 10 mmol FeCl₃ · 6H₂O were added to 50 mL DMF. In the next step, the previously prepared solution, including g-C₃N₄ in DMF, was added to the MIL-88B solution while undergoing rapid stirring. After 12h, it was sealed in an autoclave and placed in an oven at 120 °C for 18h. The slurry taken from the autoclave was dried in an oven at 70 °C for 12h and was washed several times with pure ethanol [65].

PPy nanoparticles were fabricated through pyrrole oxidation. First, 1 g cetrimonium bromide was dissolved in 40 mL deionized water at 0 °C followed by the drop-wise addition of 3 mL pyrrole monomer and mixing for 15 min. In the next step, 0.2 g ammonium persulfate ((NH₄)₂S₂O₈) dissolved in 1 mL of deionized water was used as an oxidant and was added to

the previous solution with vigorous stirring for 4h to react. The produced black PPy nanoparticles were washed with ethanol and were dried in an oven at 60 °C for 10h [340].

In the last step, PPy-g-C₃N₄-MIL-88B was prepared; first by thermal treatment of g-C₃N₄-MIL-88B at 100 °C, and then by chemical treatment with 0.01 M hydrochloric acid. After these treatment processes, the surface of g-C₃N₄-MIL-88B was activated and ready for the deposition of polypyrrole nanoparticles. PPy nanoparticles were then deposited through a technique similar to the *in situ* oxidative polymerization method. At first, 0.5 g of g-C₃N₄-MIL-88 was sonicated in 50 mL HCL of 0.01 M. After that, 0.1 g (1.5 mmol) of pyrrole nanoparticles were added to the previously prepared solution and underwent vigorous stirring and sonication. Next, the solution was cooled to 0 °C at low-speed stirring. 45 mL of 0.01 M HCL as the dopant and 0.5 g of FeCl₃.6H₂O as an oxidant were added in a dropwise manner, and the solution was stirred for 15 h. The resulting precipitate was collected, washed, and dried in an oven for 12h at 70 °C. Fig. 5.1 shows MIL88B fabrication steps.

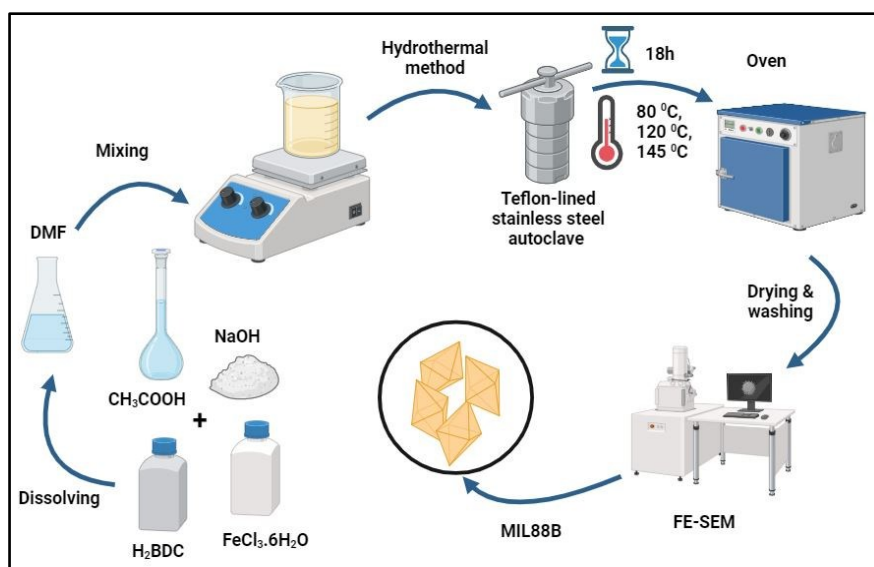


Figure 5.1. The overall procedure and main steps in MIL88B fabrication.

5.1.2. Analytical procedure

The remaining concentrations of TCP in the samples were measured using Gas Chromatography coupled with Mass Spectrometry (GC-MS) with an electron impact ion source (Agilent technologies 6890N (GC), 5975B (MSD)). The column was 5-MS (30m x 0.25mm x 0.25 μ m). 0.4 μ L of the filtered sample containing TCP dissolved in Milli-Q water was injected through an automatic sampler with splitless injection mode. The oven temperature was set at 50 $^{\circ}$ C in the first minute and increased to 200 $^{\circ}$ C at a rate of 15 $^{\circ}$ C/min. After staying at 200 $^{\circ}$ C for one minute, the temperature was further increased to 220 $^{\circ}$ C at a rate of 4 $^{\circ}$ C/min and stayed for one minute. The carrier gas was ultra-high purity helium with a flow rate of 1 mL/min. The temperatures of the injector, ion source, and interface were 280 $^{\circ}$ C, 230 $^{\circ}$ C, and 280 $^{\circ}$ C, respectively. This technique was adopted from Yu and coworkers [12] which works well for TCP detection and quantification.

The injected volume was estimated using the GC-MS vapour volume calculator to ensure that the inlet linear capacity was not exceeded. Due to injecting water, the maximum amount of 0.4 μ L was allowed for both calibration samples and test samples. The pressure, GC run time, and inlet flow rate were 7.626 psi, 10 min, and 18.83 mL/min, respectively. NIST library was used to detect TCP at an acquisition time of 7.916 min and mass-to-charge (m/z) ratios of 98, 125, and 277. The degradation efficiency was calculated based on the remaining concentration with 277 m/z value.

For concentrations lower than 10 ppm, the solid phase extraction (SPE) technique was used to concentrate, minimize pollution, and change the matrix (from water to organic solvent) to inject 1 μ L for more accurate results. Oasis WAX 6 cc Vac cartridge with 150 mg sorbent (copolymer) with a pore size of 80 $\text{\AA}$ and ion exchange capacity of 0.6 meq/g was provided from Waters. The SPE procedure began by reducing the sample pH to 3 using 0.1% (V/V)

formic acid. A 6cc WAX cartridge was then conditioned with 3 mL methanol and equilibrated with 3 mL of MilliQ water. Subsequently, 5 mL of sample was loaded at a flow rate of 2 mL/min and washed with 4 mL of 2% formic acid (V/V) in water. The elution was carried out with 4 mL of methanol and 4 mL of 5% NH₄OH in methanol. The sample was completely dried in a vacuum oven and redissolved in 0.25 mL of MilliQ water. Finally, the sample was centrifuged and injected into GC-MS. To assess the reliability of the SPE process, a 100 ppb TCPP standard was compared with 100 ppb SPE-treated TCPP, showing a 96% recovery rate. All experiments were conducted three times to ensure reliability, and the average results are reported.

1 µL of concentrated samples was injected into GC-MS using splitless injection mode with an inlet temperature of 280 °C. The column was 5- MS (30m x 0.25mm x 0.25 µm) with helium as the carrier gas (1.2 mL/min flow rate). The initial oven temperature was 50 °C (held 1 min) and then it rose to 200 °C (20 °C/min) and later to 280 °C (35 °C/min). The oven temperature was kept at 280 °C for 2 min and the total analysis run was 15.29 min. The inlet pressure and carrier gas flow rate were set at 7.642 psi and 18.83 mL/min, respectively. TCPP was detected at the retention time of 11 min and mass-to-charge (*m/z*) ratios of 98, 125, and 277. The degradation efficiency was calculated based on the remaining concentration at 277 *m/z* value. All experiments were repeated three times with fresh photo-Fenton catalysts and samples with a total error of less than 5%.

The degradation efficiency of TCPP was estimated by using the following Equation:

$$DE\% = (1 - C/C_0) \times 100 \quad (5.1)$$

Where DE is the degradation efficiency (%) of TCPP, *C*₀ and *C* are the initial TCPP concentration and the TCPP concentration at time *t* in ppb, respectively.

5.2. Results and discussion

5.2.1. Energy efficiency and cost evaluation based on E_{EO}

Energy consumption and cost evaluation are two important factors in choosing a suitable water treatment technique. Photocatalysis is normally one of the most energy-intensive methods since energy consumption constitutes the major fraction of operating cost [341]. To assess the energy efficiency of the developed photocatalytic process, electrical energy per order (E_{EO}), which is the kilowatt hours of electrical energy needed to diminish TCPP concentration by one order of magnitude (90%) in a unit volume of aqueous solution, was estimated. This parameter has been applied as a criterion to assess electrical energy consumption based on the removal efficiency of a given process [302]. E_{EO} was calculated based on equation (5.2) [342]:

$$E_{EO} = \frac{p \times t \times 1000}{V \times 60 \times \log(C_i/C_f)} \quad (5.2)$$

Where p (kW) is the power of LED lamp, t (min) is the irradiation time, and V (m^3) is the volume of solution. C_i and C_f (mg/L) are the initial and final concentrations of TCPP in water, respectively. The required electrical energy per order for TCPP degradation using PPy-g- C_3N_4 -MIL-88B/ H_2O_2 /LED system developed in this study was compared with the UV/ TiO_2 catalytic system [343]. The TiO_2 photocatalyst under UV light with 10 kW lighting power has an E_{EO} of 17 kWh/ m^3 order. On the other hand, the PPy-g- C_3N_4 -MIL-88B photo-Fenton catalyst is coupled with an LED light source with 2W power, resulting in E_{EO} of 6.66 kWh/ m^3 order (representative E_{EO} values are calculated using only the lighting source energy output at the optimum operating conditions).

Several reasons can justify the lower electrical energy per order for the developed photocatalytic system compared to the findings in other studies [22,344,345]. They include the use of less energy-consuming LED lamps compared to UV lamps and the synergic effect of

combining MIL88B-based catalysts with LED lamp and H₂O₂ for TCPP degradation [346]. Furthermore, accelerating the TCPP degradation rate through decreasing the recombination rate of electrons and holes by fabricating z-scheme PPy-g-C₃N₄-MIL-88B photocatalysts diminished the irradiation time and, in turn, led to a more pronounced energy efficiency. Additionally, the emitted light was completely consumed by designing a narrow photoreactor which optimized photon harvesting from the catalyst and prevented the waste of energy. Friedmann et al. [347] specified the factors that control energy consumption in a system. They included pH, temperature, photocatalyst type, type of mixing, reactor geometry, and concentration of radical scavengers. The farther a photocatalytic system is from its optimum environmental conditions, the higher the electrical energy per order [348]. This encourages careful design of the photocatalytic reactor and optimization of the operating and process parameters during the operation of photocatalytic systems.

5.2.2. Experimental design and data analysis

The impacts of four key operating parameters, i.e. irradiation time (A) ranging from -2 to +2, photocatalyst dosage (B) from 50 to 200 mg/L, pH (C) from 3 to 11, and initial TCPP concentration (D) from 1 µg/L to 20 µg/L on TCPP degradation were investigated. The selected parameters had a significant effect on TCPP degradation efficiency in previous works [12,349]. The experimental design concentrated on the degradation efficiency of TCPP by the PPy-g-C₃N₄-MIL-88B photocatalyst. For each experimental variable, the five applied levels were high and low axial (+2 to -2), high and low cubic (-1 to +1), and central (with 0 value). Central Composite Design (CCD) was applied, followed by the least squares regression technique to minimize the variations. The coded and actual levels of the operating parameters are presented in Table. 2. The ranges of effective variables applied in the central composite design (CCD) were specified in a previous study [350–352]. 30 experimental runs were designed, including

8 axial (2k), 16 factorial (2⁴), and 6 central points with alpha 2 (rotatable (k<6)) suggested by Design Expert 12.0.3.0 software with quadratic design mode. From the data provided in Table 2, a second-order polynomial equation (Eq. 5.3) was suggested to reflect the TCPP degradation efficiency (Deg%) based on the selected four key parameters:

$$\text{Deg\%} = 86.1 + 3.2875 A + 4.1875 B - 13.4875 C - 4.02083 D + 1.50625 A B + 1.68125 A C - 0.74375 A D - 1.60625 B C + 1.06875 B D + 3.91875 C D - 2.71146 A^2 - 2.47396 B^2 - 5.08646 C^2 - 3.96146 D^2 \quad (5.3)$$

Where Deg% is the degradation efficiency of TCPP, and A, B, C, and D are the coded parameters (Table 5.1).

Table 5.1. Coded and actual values of four variables considered in the Central Composite Design (CCD).

Effective variables	Symbol	Unit	Ranges and levels				
			-2(-α)	-1	0	+1	+2(+α)
Irradiation time	A	min	10	20	40	50	60
Photocatalyst dosage	B	mg/L	50	100	150	200	250
pH	C	-	3	5	7	9	11
Initial TCPP concentration	D	ppb	1	5	10	15	20

Large F-value and small *p-value* (less than 0.05) indicated the statistical significance of the presented model and the estimated parameters [353,354]. The actual regression (R²) of the model was 0.98 with the model *F-value* of 5.74, 0.09% noise, and *p-value* of 0.0009, which showed the statistical significance of the developed model. *P-value* < 0.05 indicates that the model terms were significant. The significant model terms were B, C, C², and D². The numerical optimization showed the highest degradation of 98.1%, and desirability of 1, which were

achieved at 47.55 min reaction time (A), catalyst dosage (B) of 128.6 mg/L, pH (C) value of 4, and initial TCPP concentration (D) of 5 ppb.

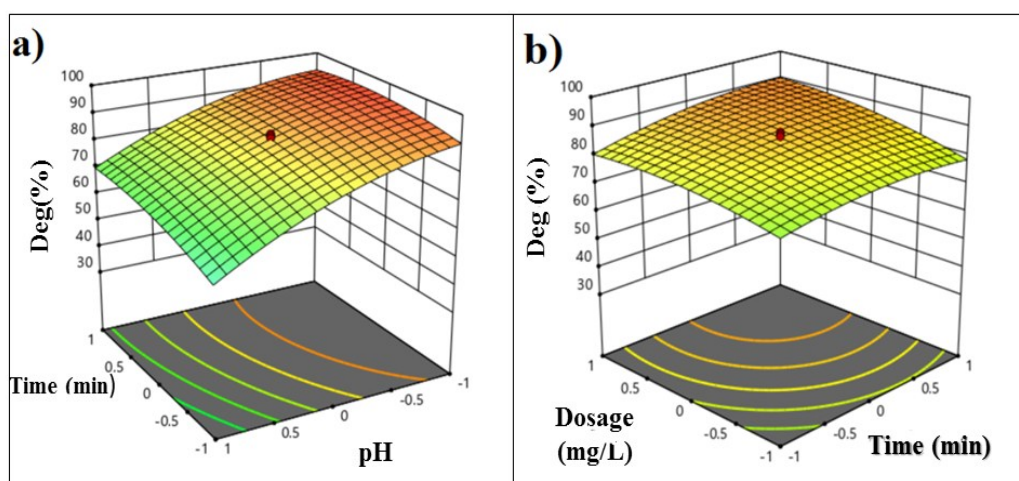
5.2.3. Effect of operating parameters on TCPP degradation

Fig. 5.2a presents the 3D surface model graph of the TCPP degradation efficiency variations corresponding to irradiation time (A) and solution pH (C). As the figure indicates, with decreasing pH level from basic (11) to acidic (3), the degradation efficiency of TCPP changed from the middle level of 70% to the highest level of 96.8% at pH 3. Similar results pertaining to favourable degradation of TCPP under acidic conditions were reported before [346,355,356]. The increase of irradiation time did not show a significant impact on the degradation efficiency of TCPP compared to the effect of pH. This demonstrated that pH (C) was indeed a significant model parameter, as verified by the *P-value* of less than 0.05. Fig. 5.2 b exhibits the interaction of catalyst dosage (B) and irradiation time (A) and their impact on the TCPP degradation efficiency. Increasing the catalyst dosage from 50 to 200 mg/L and the irradiation time from 10 to 50 min resulted in the optimum degradation efficiency of 90% (200 mg/L, 50 min). However, further increase of the catalyst dosage from 200 mg/L to 250 mg/L reduced the degradation efficiency due to the shielding effect of the catalyst.

The interaction of initial TCPP concentration (D) and irradiation time (A) (Fig. 5.2c) shows that at 50 min irradiation time, the increase of initial TCPP concentration from 1 ppb to 5 ppb increased the degradation efficiency to 88%. Higher initial TCPP concentrations were disadvantageous to its degradation because the TCPP isomers competed for the photocatalysts active sites and reactive species. TCPP degradation efficiency as a function of the catalyst dosage (B) and pH (C) exhibited unfavorable degradation when the catalyst dosage and pH values were between 50 to 100 mg/L and 7 to 11, respectively (Fig. 5.2d). This happens because a higher catalyst dosage provides more active sites, higher photon absorption and in turn more

reactive species [357]. Increasing the catalyst dosage up to 200 mg/L when the solution pH was between 3.5 and 4, showed 98% degradation efficiency.

The interaction effects of catalyst dosage (B) and initial TCPP concentration (D) on the degradation efficiency are demonstrated in Fig. 5.2e. It can be seen that the PPy-g-C₃N₄-MIL-88B catalyst dosage revealed a higher effect on TCPP degradation compared to the initial TCPP concentration. At the initial TCPP concentration of 5 ppb, the variations in catalyst dosage from 50 mg/L to 250 mg/L increased the degradation efficiency from 70% to 88.3% (optimum degradation at 200 mg/L and 6 ppb). On the other hand, at 50 mg/L catalyst loading, the change of initial TCPP concentration from 1 to 20 ppb reduced the degradation efficiency slightly from 70% to 60%. Fig. 5.2f depicts the variations of TCPP degradation as a function of pH (C) and initial TCPP concentration (D). The highest degradation efficiency (90%) was achieved at pH 4 and initial TCPP concentration of 5 ppb. The significant effect of the initial TCPP concentration on the degradation efficiency is also illustrated in this graph.



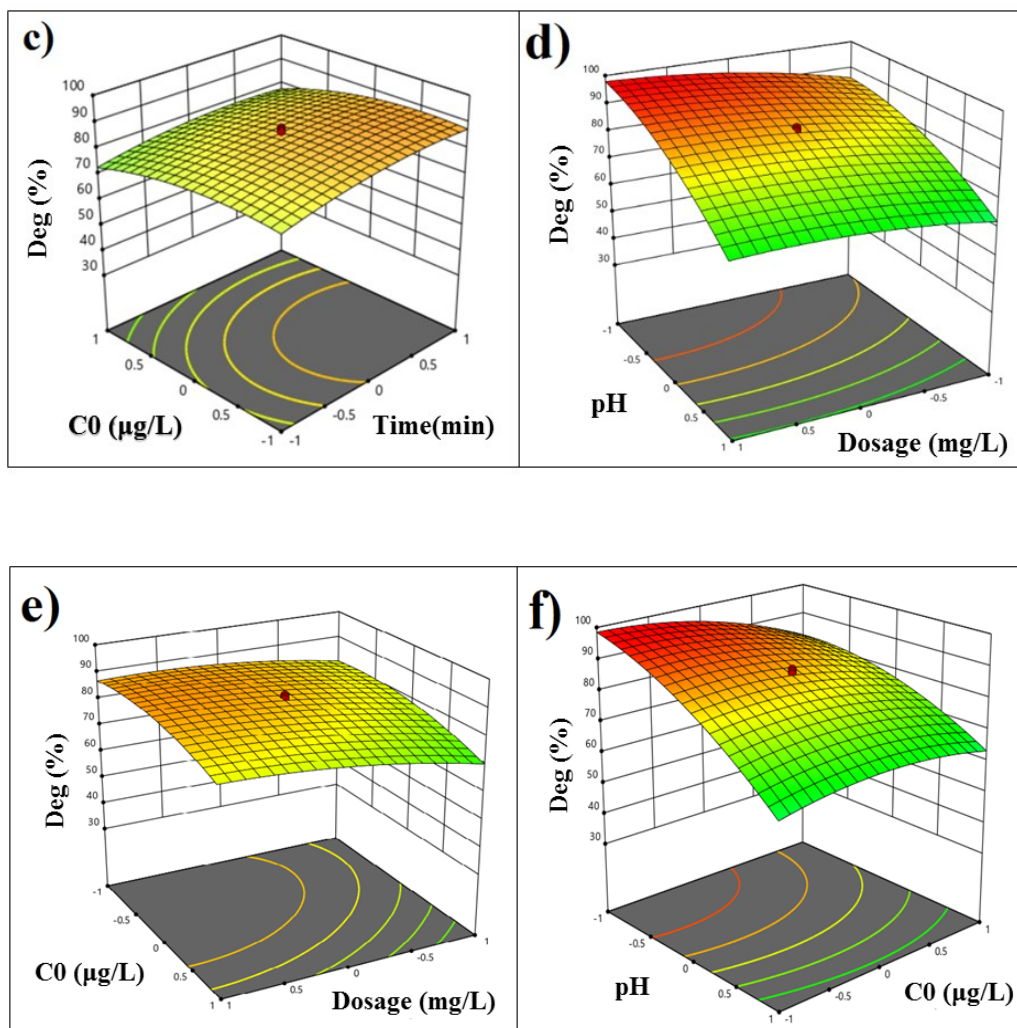


Figure 5.2. 3D surface model graphs of TCPP degradation efficiency (%) for (a) irradiation time vs pH, (b) PPy-g-C₃N₄-MIL-88B dosage vs irradiation time, (c) Initial TCPP concentration vs irradiation time, (d) pH vs PPy-g-C₃N₄-MIL-88B dosage, (e) Initial TCPP concentration vs pH.

5.2.4. Effect of environmental factors on TCPP degradation

TCPP degradation was investigated using LED light as a visible light source. It had previously been demonstrated that the photolysis of TCPP under UV light hardly happened because of its limited light absorption [355]. However, with the addition of H₂O₂, TCPP became degradable under UV light, and the combination of LED light and H₂O₂ showed a synergistic effect towards TCPP degradation [355]. Accordingly, the effect of environmental conditions, including irradiation time, pH, photocatalyst dosage, and initial concentration, on TCPP degradation for the three fabricated photo-Fenton catalysts was explored. The impacts of four

radical scavengers (HA, Cl^- , NO_3^- , and IPA) in the water matrix on TCPP degradation were also explored and compared to the TCPP degradation efficiency of PPy-g- C_3N_4 -MIL-88B/ H_2O_2 /LED system with no scavenger. Besides, to assess the stability of the PPy-g- C_3N_4 -MIL88B photo-Fenton catalyst, TCPP degradation efficiency over five consecutive cycles was investigated. The influence of environmental parameters on TCPP degradation was investigated by changing one parameter at a time while keeping other parameters constant.

5.2.4.1. Irradiation time

The variations in TCPP degradation efficiency with the increase of irradiation time are presented in Fig. 5.3a. Despite the low degradation of TCPP during the first 10 min of irradiation, degradation efficiencies reached up to 75.5%, 82.1%, and 96.86% for MIL-88B, g- C_3N_4 -MIL88B, and PPy-g- C_3N_4 -MIL88B photo-Fenton photocatalysts, respectively. A high degradation efficiency (96.86%) was observed in the PPy-g- C_3N_4 -MIL-88B/ H_2O_2 /LED system at pH 7 and at photocatalyst dosage of 150 mg/L. This is attributed to the synergetic effect of components in the PPy-g- C_3N_4 -MIL-88B/ H_2O_2 /LED photo-Fenton system. The observed synergetic effect originated from favourable photodegradation of H_2O_2 under LED light compared to UV sources, which shortened the irradiation time [358]. It has been shown that without the addition of H_2O_2 , negligible $\cdot\text{OH}$ radicals are generated in MIL-88B photocatalytic systems under visible light [359–361].

5.2.4.2. pH

Fig. 5.3b shows the photocatalytic performance of the three fabricated photo-Fenton catalysts at pH values of 3–11. The acidic environment proved to be more effective for TCPP degradation in all systems in comparison to the alkali environment. The highest degradation efficiency (98.3%) was observed at pH 3 after 60 min using the PPy-g- C_3N_4 -MIL-88B/ H_2O_2 /LED photo-Fenton system.

5.2.4.3. Photocatalyst loading

The change of photocatalyst dosage produced ascending-descending patterns in TCPP degradation. From the dose of 50 mg/L to 150 mg/L at pH 3, 90 min irradiation time for MIL88B/H₂O₂/LED, and 60 min for g-C₃N₄-MIL88B /H₂O₂/ LED and PPy-g-C₃N₄-MIL-88B/H₂O₂/LED systems the degradation efficiency vividly rose from 78.34% to 98.30%. An elevated photocatalyst dose is associated with a higher availability of electrons, holes, and reactive species for photo-Fenton reactions. Increasing the dosage further to 200 mg/L showed a negative effect on the degradation efficiency of TCPP, which was caused by the development of turbidity, inhibiting light penetration. TCPP was 100% removed at the initial TCPP concentration of 1 ppb, pH 3, and 150 mg/L photocatalysts (Fig. 5.3c).

5.2.4.4. TCPP initial concentration

As shown in Fig. 5.3d, increasing the initial TCPP concentration from 1 ppb to 25 ppb had an adverse effect on its degradation efficiency. One reason could be the competition for reactive species ($\cdot\text{OH}$ and H^+) between TCPP and the generated by-products at higher TCPP concentrations. Moreover, at constant photocatalyst loading and light intensity, higher pollutant concentration required more time to degrade as the ratio of existing reactive species to TCPP concentration diminished [362,363]. The obtained results agree with the results of previous research works [362,364–366].

5.2.4.5. Radical scavengers

Fig. 5.3e illustrates the effect of radical scavengers on TCPP degradation using PPy-g-C₃N₄-MIL88B photo-Fenton catalysts. Normally, in real water matrices, many different compounds and ions exist, which may affect the degradation efficiency of target contaminants. Additionally, the investigation of radical scavengers has the advantage of exploring the

mechanism of degradation process. For example, humic acid (HA) and isopropyl alcohol (IPA) are holes and $\cdot\text{OH}$ scavengers, respectively. Therefore, studying the effects of HA and IPA on the TCPP degradation process could assist in identifying the reactive species that make the highest contribution to TCPP degradation.

The results in Figs. 5.3e show that the addition of NO_3^- noticeably disturbed the photo-Fenton reactions and diminished the efficiency of TCPP degradation compared to the addition of Cl^- at similar doses. The nitrate radicals reduced the efficiency of photodegradation due to their photo competitor and radical scavenger nature [367]. The addition of NO_3^- at 50 mg/L reduced the degradation efficiency of TCPP from 98% to 72%, while the degradation efficiency remained higher than 80% by adding the same concentration of Cl^- . The increase of Cl^- radical concentration to 100 mg/L diminished the degradation efficiency by 30% during the examined period, suggesting that at higher Cl^- concentrations, H^+ reactive species were captured by Cl^- ions. On the other hand, with the addition of 100 mg/L NO_3^- radical scavengers, the TCPP degradation efficiency dropped by more than 50% (from 100% to 45.3%), possibly due to the generation of nitrate from the photodegradation of NO_3^- radicals, consuming free $\cdot\text{OH}$ radicals. This effect is noticeable at all examined NO_3^- concentrations: after 100 min of irradiation, the degradation efficiency fell from 100% (no scavenger) to 72% at 50 mg/L NO_3^- , and further to 45.3% at 100 mg/L NO_3^- .

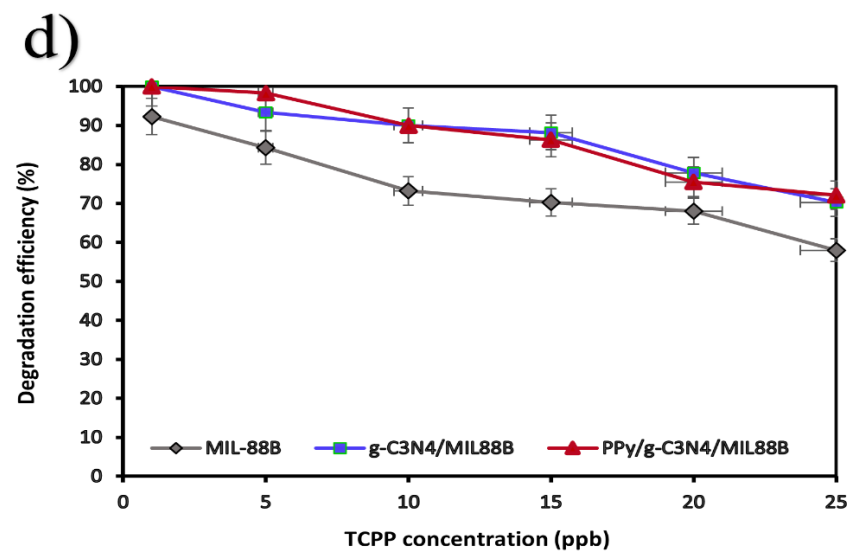
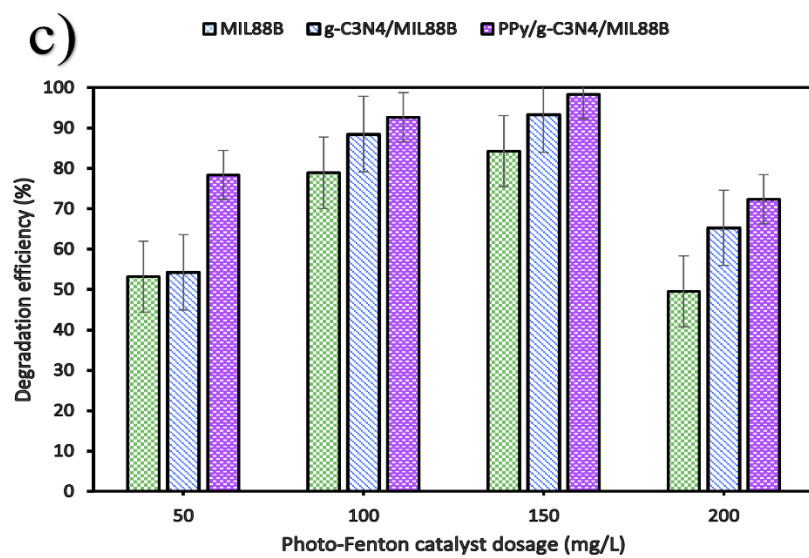
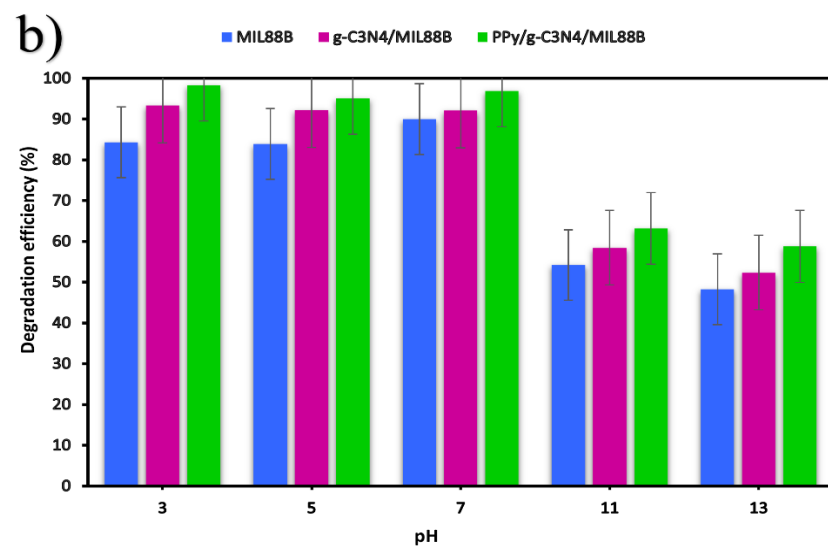
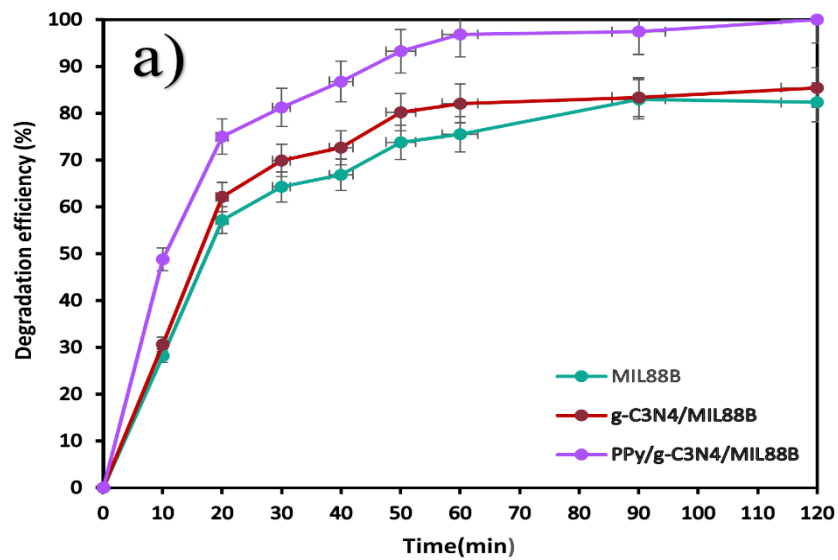
The addition of humic acid (HA) considerably diminished the efficiency of TCPP degradation. With the increase of HA dosage from 20 mg/L to 100 mg/L, the degradation efficiency declined from 98% to 73% (20 mg/LHA) and to 54% (100 mg/LHA) after 1h. This effect resulted from the shielding effect of HA addition to the solution, which lowered the intensity of LED light penetration into the solution, or from competition between HA and TCPP for $\cdot\text{OH}$ capture [365,368]. Isopropanol alcohol (IPA), which is a prominent surface-bound and free $\cdot\text{OH}$ radical scavenger impeded the photocatalytic reaction remarkably. As exhibited in

Fig. 5e, TCPP degradation efficiency decreased from 100% to 20% after 90 min of irradiation with the addition of 20 mg/L IPA, indicating that IPA had the strongest effect on TCPP degradation compared to the other examined radical scavengers. These observations establish the dominant role of $\cdot\text{OH}$ during the degradation of TCPP by the PPy-g-C₃N₄-MIL88B/H₂O₂/LED system, as showed before [364,365,369].

5.2.4.6. Stability and reusability

The stability and recyclability of a photocatalyst are important considerations for its industrial applications [370]. Hence, the photocatalytic degradation of TCPP by PPy-g-C₃N₄-MIL88B/H₂O₂/LED photo-Fenton system was assessed during five consecutive cycles (Fig. 5.3f). The degradation efficiency of TCPP diminished by around 5% at each cycle, decreasing from 97.23% to 92.21%, 85.12%, 79.4%, and 72.1% after 80, 160, 240, 320, and 400 min of irradiation, respectively. The small reduction in the degradation of TCPP through five consecutive cycles indicates the photocatalytic stability and remarkable reusability of PPy-g-C₃N₄-MIL88B for industrial applications.

The reusability of the PPy-g-C₃N₄-MIL-88B photocatalyst was evaluated over five consecutive cycles without any regeneration, showing stable TCPP degradation. While no regeneration was needed in these experiments, it could be considered for long-term use, for example via solvent washing, photoregeneration, or mild thermal treatment to remove adsorbed intermediates. Sequential or combined approaches effectively restore surface activity while preserving the structural and electronic properties of the hybrid catalyst.



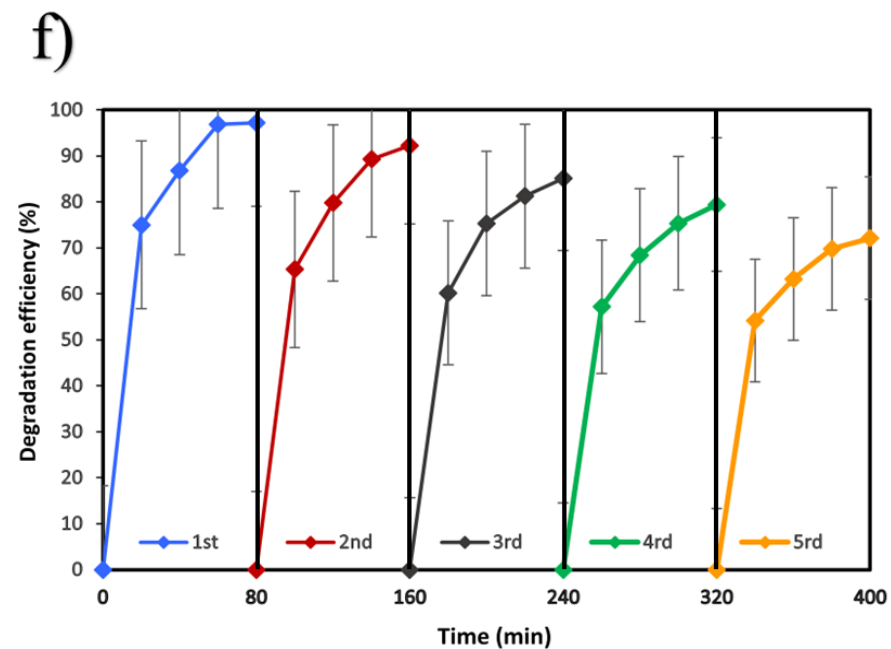
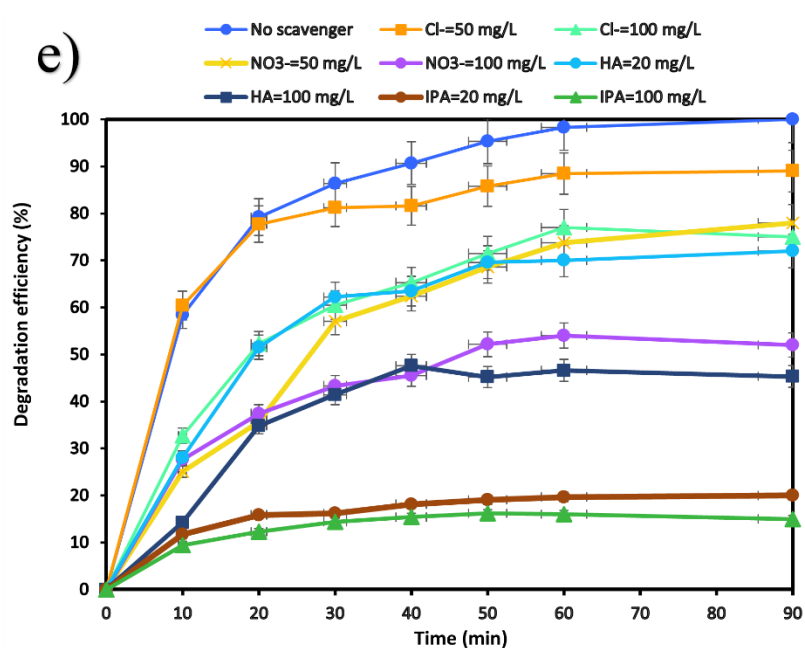


Figure 5.3. Degradation efficiency of TCPP under different environmental conditions; a) irradiation time b) pH, c) photocatalyst dosage d) initial TCPP concentration e) radical scavengers, with two doses of Cl^- ; two doses of NO_3^- ; two doses of HA; and two doses of IPA over PPy-g- C_3N_4 -MIL88B composite f) reusability of PPy-g- C_3N_4 -MIL88B over five consecutive cycles.

5.2.5. Machine learning approaches for the prediction of photocatalytic performance

Three machine learning models, including linear regression, K-Nearest Neighbours (KNN), and Random Forest, were applied to predict TCPP degradation. During the photocatalytic degradation of TCPP, operating parameters including irradiation time, pH, catalyst loading, and TCPP initial concentration affect photocatalytic degradation notably. 500 experiments were carried out with classification of the input data. The input parameters included irradiation time (min), photocatalyst dose (mg/L), TCPP initial concentration (ppb), and solution pH. The output variable was TCPP degradation efficiency (%). Prior to the development of ML models, the dataset was randomly divided into training and test datasets, with 80% of the data used as training and 20% used as testing. Regarding the assessment of the applied ML models, mean square error (MSE), and coefficient of determination (R^2) were considered. Fig. 5.4a exhibits the input variables, output, applied ML models, and assessment tools. The statistical assessment of the applied ML models, i.e. linear regression, KNN, and Random Forest is presented in Fig. 5.4b, c, d. The coefficient determination (R^2) and mean square error (MSE) were 0.616 and 222.599 for linear regression, 0.92 and 46.612 for KNN, and 0.974 and 15.196 for Random Forest, respectively. Among the applied models, Random Forest demonstrated the best performance with the highest R^2 (0.974) and lowest MSE (15.196), which makes it the most suitable model to estimate TCPP degradation. The feature correlation matrix of the studied conditions is provided in Fig. 5.4e, presenting how various experimental conditions relate to each other and specifically how they are related to the degradation efficiency. The matrix showed that pH has the strongest negative correlation with TCPP degradation efficiency ($r=-0.69$). This means that as pH increases, the degradation efficiency diminishes remarkably, suggesting that the highest degradation efficiencies are obtained in acidic conditions. The catalyst dose has a moderate positive correlation ($r=0.23$), indicating that the increase of catalyst dose may fairly improve TCPP degradation. Irradiation time also demonstrates a weak positive correlation ($r=0.14$) as longer reaction time would enhance degradation as expected.

The TCPP initial concentration has a negative correlation ($r=-0.27$), suggesting saturation effects and limited active sites. Correlations of all other parameters are weak ($|r| < 0.05$), possibly due to minimal multicollinearity. This implies independent effects, which is favourable for modelling purposes. Fig. 5.4f depicts the distribution of TCPP degradation efficiency with more frequent values between 60-90% range. The peak is around 80-85%, containing 60% of data points in this range. The spread of dataset between 0-100% indicates the presence of a diverse dataset with less than 10% at very low degradation efficiencies and the majority (more than 50%) at moderate to high degradation efficiencies. The obtained histogram suggests that the applied photocatalytic process is reliable under most examined conditions.

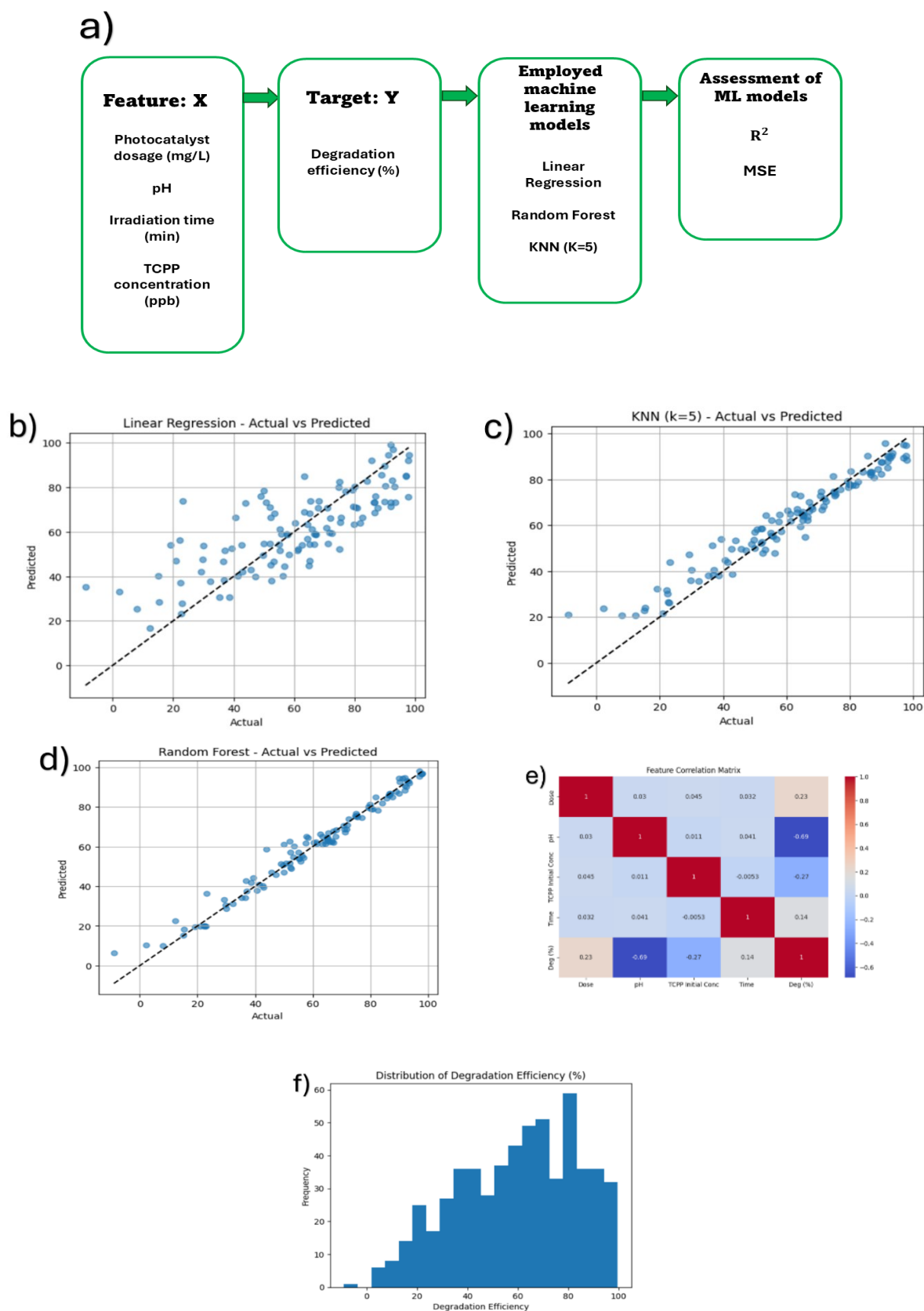


Figure 5.4. a) ML models flowcharts, b) linear regression, c) KNN, d) Random Forest, e) feature correlation matrix, f) distribution of degradation efficiency (%).

5.3. Summary

In this chapter, the effect of three reaction temperatures on the morphology of MIL88B photocatalysts was explored and reported. FE-SEM and TEM analyses established that diminishing the reaction temperature from 145 °C to 120 °C promoted MIL88B particle growth and provided a desirable foundation for further modifications to the structure of the photocatalyst by implanting g-C₃N₄ and PPy groups. After modifications, the PPy-g-C₃N₄-MIL88B photocatalyst showed a higher TCPD degradation efficiency by an average of 20% compared to sole MIL88 B. The influence of environmental parameters, including reaction time, catalyst loading, initial TCPD concentration, pH, and radical scavengers, on the efficiency of photocatalytic TCPD degradation was investigated. The performance of PPy-g-C₃N₄-MIL88B/H₂O₂/LED system was maximized (TCPD degradation of 98.3%) at pH 3, irradiation time of 60 min, catalyst loading of 150 mg/L, and initial TCPD concentration of 5 ppb. The impact of radical scavengers (NO₃⁻, Cl⁻, HA, and IPA) on TCPD degradation was demonstrated. The most significant radical scavenger for the photocatalytic reaction was isopropyl alcohol (IPA), which is a .OH radical scavenger, indicating that .OH radicals were the principal reactive species for degrading TCPD. The PPy-g-C₃N₄-MIL88B photocatalyst showed desirable reusability and stability over five consecutive cycles. The degradation efficiency of TCPD decreased by only 5-7% over each cycle from 97% to 92%, 85%, 79%, and 72%. The interactions between four key parameters, namely irradiation time, catalyst loading, pH, and initial TCPD concentration, were explored using RSM. A second-order polynomial model with an acceptable fit was suggested with R² value of 0.98 and a *P*-value of 0.0009. Finally, the electrical energy per order (E_{EO}) of the PPy-g-C₃N₄-MIL88B/H₂O₂/LED system was estimated to be 6.66 kWh/(m³ order). Modelling of the degradation process through machine learning offers Random Forest as a suitable model to predict TCPD degradation (R²=0.974). Based on

the results of this study, PPy-g-C₃N₄-MIL88B proves to be an effective photo-Fenton catalyst with high energy efficiency, desirable photodegradation ability for TCPP, and facile operation.

6. Chapter 6. Visible light-driven photocatalytic degradation of TCPP by PPy-g-C₃N₄-MIL88B photo-catalyst with Z-scheme heterojunction: Kinetics, degradation pathway, toxicity assessment, and optimization

The contamination of our environment with flame retardants poses a serious threat to public health, stemming from their extensive use in consumer products aimed at fire prevention [36–40]. Flame retardants have emerged as a growing concern due to their persistence, carcinogenicity, neurotoxicity, and bioaccumulation [41,42]. In the early 21st century, the production of polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), and brominated flame retardants (BFRs) was phased out, and they were replaced by organophosphate flame retardants (OPFRs) [42–45]. As the primary alternative to PBDEs, the production and use of OPFRs rapidly increased. OPFRs are added to consumer products, which accelerate their release and leach into the environment. In recent years, the production of chlorinated OPFRs has risen significantly, now comprising 52-75% of the OPFR family. The presence of tris (2-chloro-2-propyl) phosphate (TCPP), a highly persistent chlorinated OPFR, in aquatic environments is particularly notable which has been classified as the 4th substance of high concern by the European Union (EU) [11,46].

Recently, physical, chemical, biological, and combined approaches have been widely used for the removal of flame retardants from the environment. Among them, biological methods using biofilm reactors have been explored to enhance TCPP biodegradation. However, biological treatment is often hindered by the presence of organic contaminants that may inhibit microbial growth, negatively impacting the biodegradation efficiency [47–49].

Similarly, the potential generation of toxic or non-biodegradable byproducts by advanced oxidation processes (AOPs) will have negative impacts on the efficiency of integrated processes that combine AOPs with biodegradation [50,51].

Given these limitations, developing an AOP that optimizes costs while ensuring the complete mineralization of TCPP and its toxic byproducts into non-toxic or less harmful compounds will be a more effective solution. Previous studies have indicated that photo-Fenton catalysis is a suitable technique for the degradation of water-soluble flame retardants, including TCPP [41,52–54]. Accordingly, preparing an appropriate photo-Fenton catalyst to remove the concerning contaminants from water and minimize the toxicity of water media, while maintaining cost efficiency, stability, and reusability is crucial.

The Materials Institute Lavoisier (MILs), recognized as promising materials for environmental remediation due to their stability and unique pore structure, present a potential base for an effective photo-Fenton catalyst. Several MIL-based photo-Fenton catalysts have been assessed for the removal of emerging contaminants [55–60]. For instance, $\text{NH}_2\text{-MIL-101}$ photo-Fenton catalysts were fabricated to shorten the bandgap and improve the degradation rate through increased surface reactivity and enhanced hydrophilicity by NH_2 group [61]. In another study, $\text{g-C}_3\text{N}_4@\text{MIL-101}$ was constructed for a higher absorption in visible light and a lower bandgap. In this case, $\text{g-C}_3\text{N}_4$ was selected due to its suitable bandgap (2.65 eV), while the fabrication of $\text{g-C}_3\text{N}_4@\text{MIL-101}$ only reduced the bandgap by 3% (from 2.65 eV to 2.57 eV) [62]. Although the mentioned studies provide valuable insights and enhance treatment efficiency, further investigations are needed to elucidate electron transfer mechanisms. Moreover, most studies focus on a single contaminant without considering the presence of natural ions and mixtures of compounds in real environments. The long-term environmental impact of MIL-based systems also remains understudied. In particular, the potential leakage of Fe^{3+} ions and ligand decomposition products into water systems after photocatalysis requires further investigation

[63–65]. Meanwhile, many heterojunctions have been designed in previous research to enhance photocatalytic reactivity, reduce the recombination rate, and improve light energy absorption. Among these, Z-scheme heterojunctions promote photoelectron transfer while maintaining the original oxidation potential. Therefore, constructing a Z-scheme photo-Fenton catalyst that meets electrical requirements and exhibits strong photodegradation capability while addressing the gap in the literature is necessary.

In this study, a PPy-g-C₃N₄-MIL-88B/H₂O₂/LED system was designed, and its efficiency in TCPP degradation was systematically explored. The investigation focused on evaluating the system's ability to enhance the generation of •OH radicals, thereby facilitating TCPP degradation. The degradation performance of the developed photocatalyst was thoroughly analyzed by assessing its efficiency in the degradation of TCPP under various operating conditions and identifying the extent of TCPP mineralization and the generated by-products. Furthermore, the degradation mechanism, types and concentrations of by-products, potential degradation pathways, toxicity of contaminants, reaction kinetics, process modelling, and optimization were comprehensively examined and elucidated.

6.1. Materials and methods

The methodology involves photocatalyst preparation (presented in 5.1.1) and characterization (presented in 3.3). In the following subsections, photocatalytic experiments and analytical procedures are introduced.

6.1.1. Experimental set-up and photocatalytic experiments

The photocatalytic efficiency of the constructed photo-Fenton catalysts was evaluated by using TCPP aqueous solution. The reaction occurred in a cylindrical stainless-steel photo-reactor with a volume of 700 mL equipped with an LED lamp inside. A pump was used for water

recirculation to maintain a homogenous solution. A port at the bottom of the reactor was used to inject gas if needed. An LED lamp with a light intensity of 200 W/m^2 was used as the irradiation source. 10 mL of the sample was taken and analyzed after filtration. The photocatalytic degradation of TCPP was assessed by measuring the remaining TCPP concentration using liquid chromatography-mass spectroscopy (LC-MS).

At a light intensity of 200 W/m^2 , photocatalysts capable of efficient visible-light absorption and effective charge separation are expected to perform well. Materials with narrow or tunable band gaps, such as g- C_3N_4 , doped TiO_2 , or MOF-based hybrids like MIL-88B coupled with conductive polymers (e.g., PPy), can utilize a larger fraction of the incident light and generate sufficient photogenerated charge carriers for pollutant degradation. High surface area and abundant active sites further enhance adsorption and interfacial reactions, which is particularly important under moderate light flux where photon availability is limited. Additionally, catalysts must maintain structural stability and resist photodegradation under prolonged irradiation to ensure consistent performance. Therefore, modified visible-light-active semiconductors with optimized electronic and structural properties are most suitable for photocatalytic applications under these conditions.

6.1.2. Analytical procedure

Liquid chromatography-mass spectroscopy (LC-MS) analysis was performed on an Agilent 1290 LC system coupled with a Thermo LTQ Orbitrap Velos mass spectrometer equipped with a heated electrospray ion source at positive mode. A Spursil C18-EP column (50x2.1 mm and 3μ particle diameter, Dikma Technologies) was used, and target compounds were eluted using a 19-min gradient at a flow rate of $250 \mu\text{L/min}$ with mobile phase A (10 mM ammonium acetate and 1 mM ammonium fluoride water solution) and B (acetonitrile). The gradient started at 5% B, linear gradients were achieved to 95% B at 10 min, then followed by isocratic with 95% B

for 2 min and with 5% B for 7 min. 1 μ L of each sample was injected into the LC-MS analysis. MS spectra (m/z 150-500) were acquired in the Orbitrap at a resolution of 100,000. The spectra were internally calibrated using diisooctyl phthalate (m/z 391.2843 Da) as a lock mass. Peak area values were extracted using Thermo XCalibur software (v2.2 SP1.48).

Solid phase extraction (SPE) was employed to change the matrix to the organic phase and to decontaminate samples from the photocatalyst's residues in case any impurities had been left after filtration. The photocatalytic-treated water sample was first filtered using Cytiva Whatman Puradisc PES Syringe Filters (0.2 μ m PES). Then, SPE was applied to alter the aquatic matrix to organic while minimizing pollution. Strata C18-E cartridge (Phenomenex, 200 mg/3 mL) was selected for the SPE procedure. At first, the cartridge was equilibrated with 2 mL of 100% acetonitrile (ACN) and conditioned with 2 mL of a solution of 5% ACN and 95% water containing 0.1% formic acid. Next, the samples were acidified using a solution of 100 μ L formic acid in 100 mL Milli-Q water (0.1%) until the pH reached 3. After that, 6 mL of the sample with 30 mL of 0.5 ppm internal standard was loaded into the C18-E cartridge. The cartridge was washed once with 2 mL of the 5% ACN and 95% water solution containing 0.1% formic acid. In the end, the target compounds were eluted with 1.2 mL of a solution of 85% ACN and 15% water. The elutes were dried in a SpeedVac and then resolubilized in 0.15 mL of the 5% ACN and 95% water solution containing 0.1% formic acid.

For TCPH quantitation, the SPE process was quite different. The C-18 cartridge was first equilibrated with 2 mL of neat acetonitrile (ACN), 100%. It was conditioned subsequently with 2 mL of a solution of 5% ACN and 95% water containing 0.1% formic acid. The samples were acidified by adding 100 μ L of formic acid to 100 mL of Milli-Q water. Subsequently, 6 mL of the acidified sample was loaded on the cartridge along with 30 μ L of the 0.5 ppm internal standard solution (Leu-Enkephalin). The cartridge was washed following loading with 2 mL of the 5% ACN and 95% water solution containing 0.1%

formic acid. Elution was ultimately accomplished using 1.2 mL of a solution containing 85% ACN and 15% water. The elute was then collected for LC-MS analysis. The elutes were SpeedVac-dried and then resolubilized in 0.15 mL of the solution of 5% ACN and 95% water with 0.1% formic acid. The sample was finally centrifuged and injected into the LC-MS. For the evaluation of reproducibility of the SPE process, a 100 ppb TCPP standard was compared against 100 ppb SPE-treated TCPP, which produced 96% recovery. All of the experiments were performed in triplicate, and the mean is provided for statistical reliability.

The toxicity of TCPP and the generated by-products were evaluated using the Toxicity Estimation Tool (TEST). The consensus method was adopted and the toxicity was calculated through four different indicators, including fathead minnow LC50 (96h) (mg/L), bioaccumulation factor, developmental toxicity, and mutagenicity. Fathead minnow LC50 (96h) (mg/L) refers to the concentration of chemical in mg/L in water that causes 50% of the fathead minnows to die after 96h. Bioaccumulation factor considers the ratio of the chemical concentration in fish, while developmental toxicity considers whether or not the target chemical causes developmental toxicity effects to humans/animals. Mutagenicity refers to genotoxicity effects such as DNA damage in living beings.

Toxi-Chromotest™ kits purchased from Environmental Bio Detection Products Inc. were utilized to evaluate TCPP toxicity prior to and post-treatment. This biotoxicity test relies on colometric analysis (color development if the material is non-toxic) and is verified by the US Environmental Protection Agency (EPA). The biotoxicity procedure provided by the company included the addition of 100 µL reaction mixture to the first column of the plate, followed by the addition of 100 µL dilutant to columns with odd numbers (3, 5, 7, 9, and 11). After that, 200 µL standard toxicant was added to A3 cell, and serial dilution was applied to column 3 (A-H). Next, serial dilutions were performed using samples (TCPP, 400 ppm and 800 ppm; and

treated TCPP with initial concentrations of 400 and 800 ppm) for 5, 7, 9, and 11 columns. Then, 100 μL of the rehydrated bacteria was added to columns 3, 5, 7, 9, and 11. The plate was incubated at 37 $^{\circ}\text{C}$ for 90 min. After that, 100 μL chromogen was added to all the used cells, and the plate was incubated at 37 $^{\circ}\text{C}$ for 30 min until the blue color appeared. In the end, the plate was read using a UV-Vis spectrometer (UV-Vis- Cary5000) at 615 nm.

The photonic energy was calculated based on the TOC removal rate. Equation (6.1) shows the photonic efficiency ζ definition.

$$\zeta = \Delta\text{TOC} \times \Delta t^{-1} \times V \times E_m \times A \times I_0 \times 100 \quad (6.1)$$

Where ΔTOC is the moles of TOC removed per volume (mol/L); Δt is the removal time (s), V is the water sample volume (0.35L), E_m is the mean energy content of the LED light (300 kW. s/mol), A is the irradiated area of the reactor (0.015 m^2), and I_0 is the light intensity (200 W/m^2).

TCPP degradation using PPy-g- C_3N_4 -MIL88B/ H_2O_2 /LED system was evaluated by considering four variables using the RSM-CCD method with the assistance of Design Expert. In real environmental conditions, the interactions of effective parameters cannot be neglected. Four experimental factors, including irradiation time (X_1), photocatalyst quantity (X_2), pH (X_3), and airflow rate (X_4) were chosen and their effects on TCPP degradation were investigated. In order to better elucidate the interactions of parameters, response surface methodology (RSM) with central composite design (CCD) was used as a statistical/mathematical method to optimize the selected four parameters in photo-Fenton reactions. In this work, Design Expert version 12.0.3.0 software was used for experimental design and assessment of parameters interactions.

6.2. Results and discussion

6.2.1. Response surface methodology analysis

TCPP degradation by employing the PPy-g-C₃N₄-MIL88B/H₂O₂/LED system was investigated by considering four variables using RSM-CCD. Table 6.1 exhibits the range of independent parameters that were used in the central composite design. Design experiments consist of 30 experiments, including 24 non-center points and 6 center points (Table A1.). All experiments were conducted at an initial TCPP concentration of 5 ppb with no radical scavenger.

Table 6.1. Experimental values and levels of independent variables applied in RSM for TCPP degradation using PPy-g-C₃N₄-MIL88B/H₂O₂/LED system.

Factors	Unit	Symbol	Experimental range	levels				
				-2	-1	0	+1	+2
Irradiation time	min	A	10-60	10	20	40	50	60
Catalyst quantity	g/L	B	0.05-0.25	0.05	0.1	0.15	0.2	0.25
pH	-	C	3-11	3	5	7	9	11
Airflow rate	L/min	D	1-20	1	5	10	15	20

6.2.2. Modelling and optimization of TCPP photocatalytic degradation

6.2.2.1. Statistical analysis and model fitting

The photocatalytic degradation of TCPP using the PPy-g-C₃N₄-MIL88B/H₂O₂/LED system was modeled by the central composite design method as a function of irradiation time (min), pH, catalyst concentration (mg/L), and airflow rate (L/min). The reduced quartic model representing the response variables is suggested by ANOVA. Eq. (6.2) demonstrates the proposed model, dependent on the actual factors.

$$\begin{aligned} \text{Degradation efficiency (\%)} = & 70.16 + 12.75.06A + 0.25 B - 11.89 C + 4.97 D - 0.11AB + 0.53 \\ & AC + 0.09 AD - 0.25 BC + 0.38 BD - 0.21 CD - 0.91A^2 + 0.33B^2 + 0.45 C^2 + 0.45 D^2 + 0.40 \\ & ACD - 0.99 A^2B + 3.46 AB^2 - 4.15625 A^2B^2 \end{aligned} \quad (6.2)$$

The experimental data were analyzed by using ANOVA to confirm the validity of model. The *p-value* less than 0.0001 confirmed the significance of the proposed model. In the suggested model, A (time), C (pH), and D (airflow rate) terms are highly significant due to their *p-values* less than 0.0001. The lack of fit of 0.1091 is insignificant, indicating that the model accurately represents the experimental data. Based on the *F-values*, the significance of the input variables is in the order of: C>A>D>A²B²>AB²>A²>A²B>C²>D²>AC>B²>ACD>BD>CD>B>AB>AD.

Coefficient of determination (R²) was used as a criterion for evaluating the degree of fit of the model. Herein, the predicted R², adjusted R², and R² values were 1.0, 0.9989, and 0.9995, respectively. The obtained values suggest that the proposed model can correctly predict TCPP degradation efficiency by PPy-g-C₃N₄-MIL88B. The adequate precision of 139.84 (signal to noise), higher than 4 shows that the model predicts TCPP degradation with a high level of accuracy.

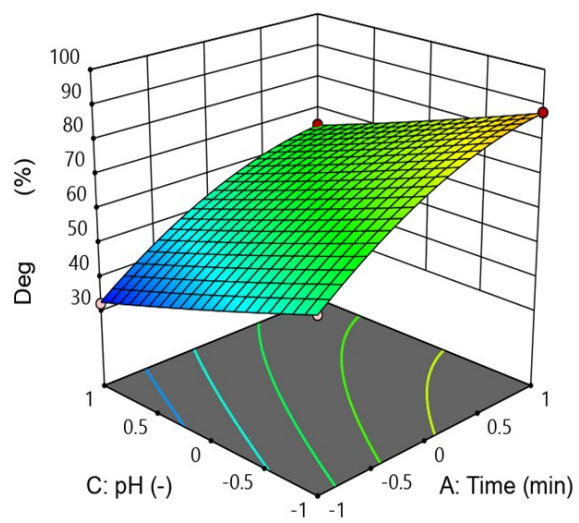
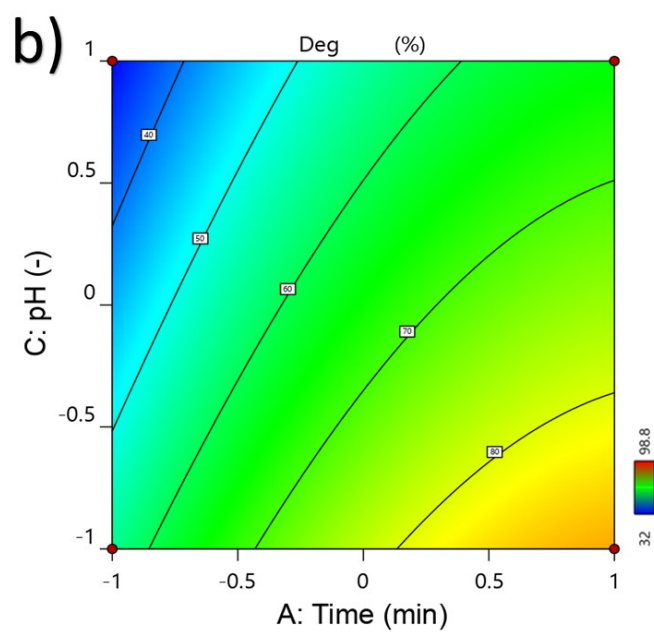
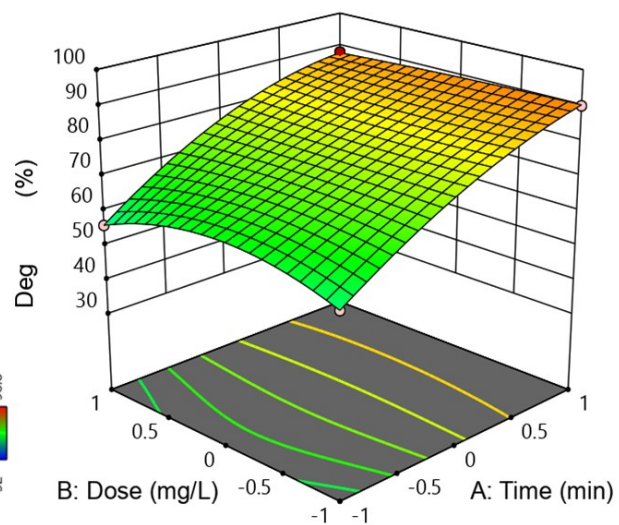
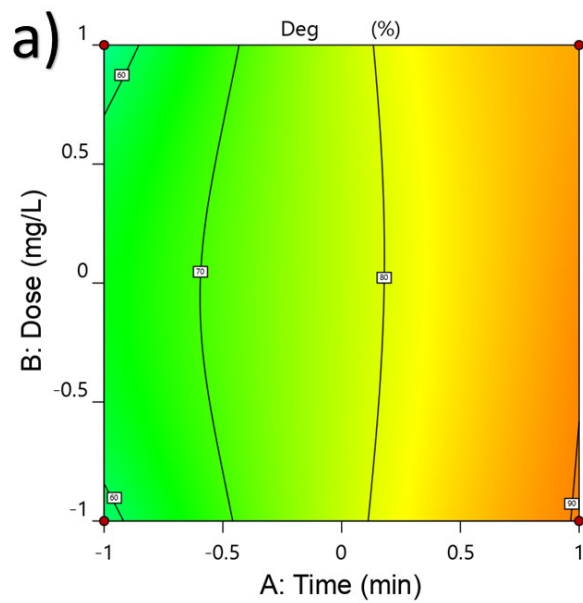
6.2.2.2. Effect of operating parameters using response surface analysis

The impact of operating parameters on the efficiency of photocatalytic degradation is important for both design and operation. For this reason, four leading parameters, including irradiation time (min), pH, catalyst concentration (mg/L), and airflow rate (L/min) were investigated and analyzed.

Fig. 6.1 illustrates the effect of parameters interactions on the TCPP degradation efficiency. According to the ANOVA results and the obtained *F-values*, the independent variables showed a remarkable effect on TCPP degradation. The change of degradation efficiency with the

variations of two selected parameters was assessed through three-dimensional response surface plots (Fig. 6.1). According to the obtained *F-values*, TCPP degradation efficiency is mostly affected by the interaction of pH and irradiation time. Experimental results showed that TCPP degradation efficiency reached its maximum level (98.7%) after 50 min at pH 5, photocatalyst dose of 150 mg/L, and airflow rate of 15 L/min. Fig. 6.1 a shows the predicted variations of TCPP degradation efficiency with changes in the catalyst concentration /irradiation time. TCPP degradation of 90% was achieved after 50 min, while the variation in catalyst dosage did not notably affect the degradation efficiency. With increasing the irradiation time from 20 to 50 min, the degradation efficiency of TCPP rose from approximately 60% to 90%. This may be due to the higher generation of .OH radicals with extended light exposure. The simultaneous effect of pH and irradiation time on the degradation of TCPP is exhibited in Fig. 6.1b. TCPP degradation tends to be maximized in an acidic environment along with the increase in irradiation time. By lowering the solution pH from 8 to 3, the degradation efficiency of TCPP rose from 40% to 90%. This improvement is due to the protonation of TCPP in an acidic environment, which enhances its electronic structure and exposes TCPP molecules to .OH radicals attack. Another reason for the observed improvement in the degradation efficiency of TCPP could be attributed to the higher stability and generation of .OH radicals under acidic conditions. Fig. 6.1 c explores the interaction of irradiation time and airflow rate. The results indicate that irradiation time has a greater impact on degradation efficiency compared to the airflow rate. Extending the irradiation time and airflow rate from 20 min and 5 L/min to 50 min and 15 L/min, respectively, enhanced the degradation efficiency from approximately 60% to 98%. The interaction of airflow rate and pH is also depicted in Fig. 6.1 d. The TCPP degradation efficiency changed linearly with the variations of these two parameters and reached its maximum (99%) at airflow rate of 15 L/min and pH 3.

In this work, an air flow rate in the range of 5–20 L·min⁻¹ was applied; although such aeration can generally enhance water evaporation by increasing convective mass transfer at the air–liquid interface, TCPP itself is not prone to volatilization due to its low vapor pressure and semi-polar nature. Increased airflow can reduce the boundary layer thickness and accelerate water loss, potentially leading to a decrease in solution volume, apparent increases in TCPP concentration, and indirect effects on adsorption equilibrium and photocatalytic kinetics. However, in this study, the reactor was closed, the experiments were of short duration, and the air was humidified, such that these evaporation effects were considered negligible, and the observed degradation behavior can be attributed predominantly to photocatalytic activity.



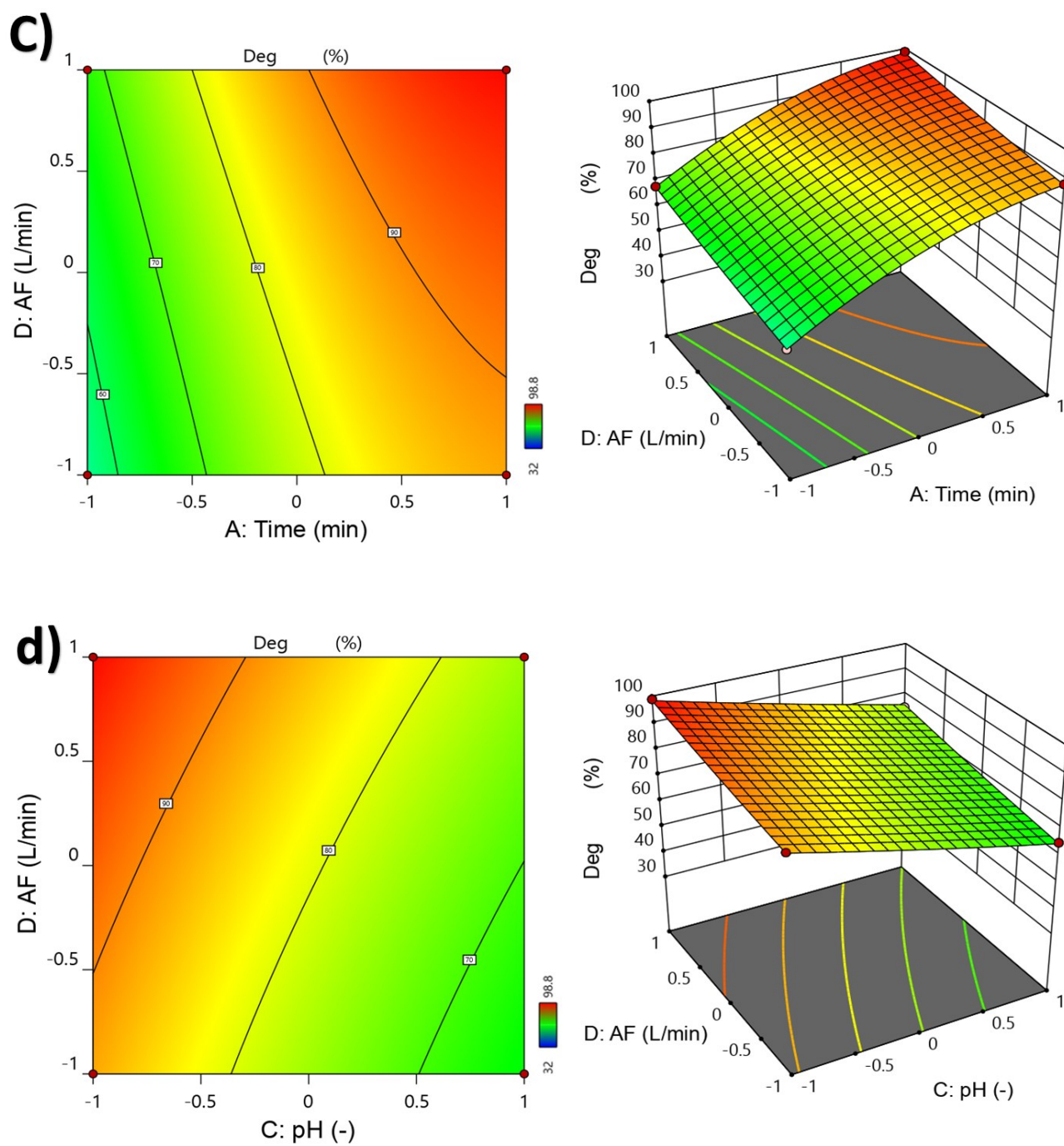


Figure 6.1. 2D contour and 3D response surface plots for TCPP degradation using PPy-g-C₃N₄-MIL88B as a function of a) catalyst dose and irradiation time, b) pH and irradiation time, c) air flow rate and time, and d) airflow rate and pH.

6.2.2.2. Optimization of TCPP degradation with verification test

Identification of the most effective operational conditions for TCPP degradation by the PPy-g-C₃N₄-MIL88B/H₂O₂/LED system through optimization of input variables was conducted. In the applied numerical optimization, energy efficiency, sustainability, and cost were taken into consideration while maintaining the highest efficiency. Therefore, the environmental conditions of 50 min irradiation time, photocatalyst dosage of 150 mg/L, pH 5, and airflow rate of 15 L/min are identified as the optimum operating conditions, which predicted the TCPP degradation of 99.96%. To confirm the validity of this prediction, a confirmation experiment was conducted under the predicted optimum conditions. The efficiency of experimental TCPP degradation under the predicted optimum conditions was 98.63%, which is close to the predicted value. The confirmation test verifies the validity of the proposed model in the prediction of optimum operating conditions.

6.2.3. Degradation mechanism

PPy-g-C₃N₄-MIL-88B demonstrated a high capacity as an efficient photo-Fenton catalyst. The degradation mechanism was investigated by adding three quenchers to the experimental system. The examined quenchers were isopropanol (IPA), oxalic acid, and ascorbic acid applied as hydroxyl radical ($\cdot\text{OH}$), hole (h^+), and superoxide radical ($\cdot\text{O}_2^-$) scavengers to observe the role of each species in TCPP degradation. As Fig. 6.2a reveals, by adding 1mM isopropanol, TCPP degradation declined from 98.7% to 42.4% at the irradiation time of 50 min, photocatalyst dose of 150 mg/L, pH 5, initial TCPP concentration of 5 ppb, and airflow rate of 15 L/min (optimum condition). This indicates that $\cdot\text{OH}$ radicals play a critical role in the photodegradation of TCPP. Conversely, the addition of 1mM oxalic acid and ascorbic acid produced less than 20% decrease, suggesting the minor role of these scavengers due to the

small number of holes and superoxide species formed during TCPD degradation under these conditions. Fig. 6.2 b shows the Z-scheme diagram of the prepared PPy-g-C₃N₄-MIL88B.

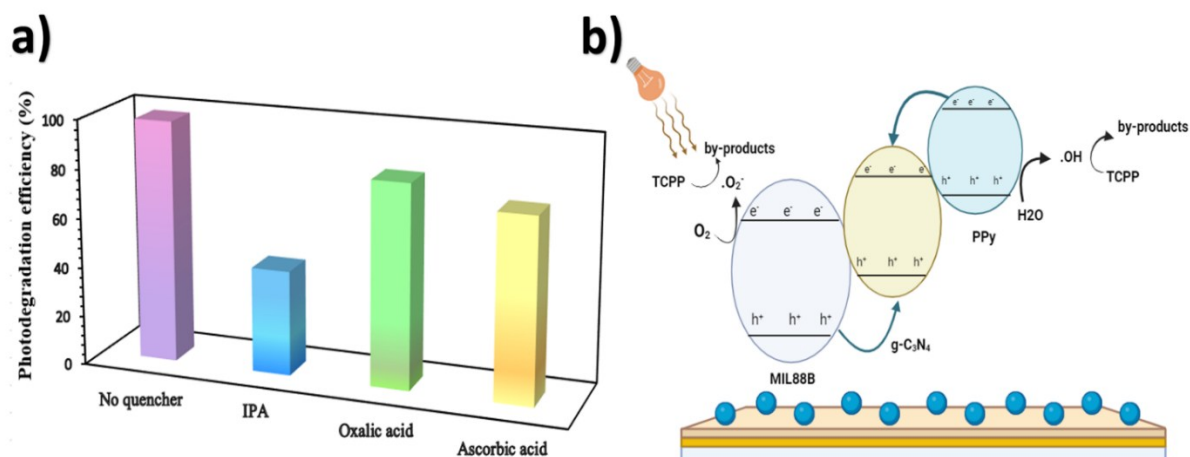


Figure 6.2. a) Effect of different quenchers on TCPD degradation efficiency, and b) Z-scheme diagram of PPy-g-C₃N₄-MIL88B charge transformation.

6.2.4. Degradation pathway, by-products quantification, and intermediates toxicity assessment

The identification and relative quantification of TCPD degradation intermediates generated from PPy-g-C₃N₄-MIL88B photo-Fenton reaction under LED lighting were conducted by employing LC-MS. The limited availability of isotope-labeled standards and the inherent complexity in data interpretation inhibited the use of these standards for the identification of BPs. Therefore, in this study, relative quantification was conducted by comparing the relative area of BPs at each reaction time. 5 ppb TCPD was degraded by the PPy-g-C₃N₄-MIL88B photocatalyst at the concentration of 150 mg/L and pH 7 through the PPy-g-C₃N₄-MIL88B/H₂O₂/LED system. Samples were taken after 5, 10, 15, 20, 25, and 30 min. One control sample was prepared under identical conditions, only without the addition of photocatalyst and with 30 min irradiation time. The purpose of the control sample is to highlight

the effect of the prepared photocatalyst in the degradation of TCPP and its transformation by-products.

Five by-products at different m/z values of 343.0030, 307.0263, 323.0213, 251.0001, and 174.9921 were detected with a high level of certainty (mass error <5ppm). The detailed information on the TCPP mixture of isotherms and the detected intermediates are summarized in Table 6.2 and Fig. 6.4b, presenting the retention time and life span of each intermediate. Fig. 6.3 depicts LC-MS chromatographic profiles of the samples taken after 30 min photocatalytic treatment using PPy-g-C₃N₄-MIL88B/H₂O₂/LED system. TCPP molecule with m/z of 327.0081 is an aliphatic chlorinated organophosphate compound in which the chlorinated isopropyl part is mostly affected and altered during the degradation processes. BP343 by-product with m/z value of 343.0030 was formed through .OH attack at -CH₃ group of isopropyl chain. Cl atom cleavage of TCPP molecule, followed by the oxidation of -CH₃ group, resulted in BP307 formation. BP323 was generated from either BP307 or BP343 through Cl separation and the synchronous hydroxylation and oxidation of TCPP. The cleavage of one chloro-isopropyl group through the attack of .OH radicals to the phosphorous center leads to BP251 formation.

Table 6.2. Molecular formula, retention time (RT), theoretical and observed m/z values, and relative mass error $\Delta(\text{ppm})$ for TCPP and the detected by-products.

BPs name	Molecular formula	RT (min)	Theoretical m/z value [M+H]⁺	Observed m/z value [M+H]⁺	Mass error (Δppm)
TCPP	C ₉ H ₁₈ Cl ₃ O ₄ P	6.67	327.0081	327.0088	2.1
BP343	C ₉ H ₁₈ Cl ₃ O ₅ P	5.57	343.0030	343.0036	1.7
BP307	C ₉ H ₁₇ Cl ₂ O ₅ P	4.71-5.30	307.0263	307.0268	1.6
BP175	C ₃ H ₈ ClO ₄ P	6.67	174.9921	174.9924	1.7
BP323	C ₉ H ₁₇ Cl ₂ O ₆ P	3.33-4.03	323.0213	323.0213	0
BP251	C ₆ H ₁₃ Cl ₂ O ₄ P	6.67	251.0001	251.0005	1.6

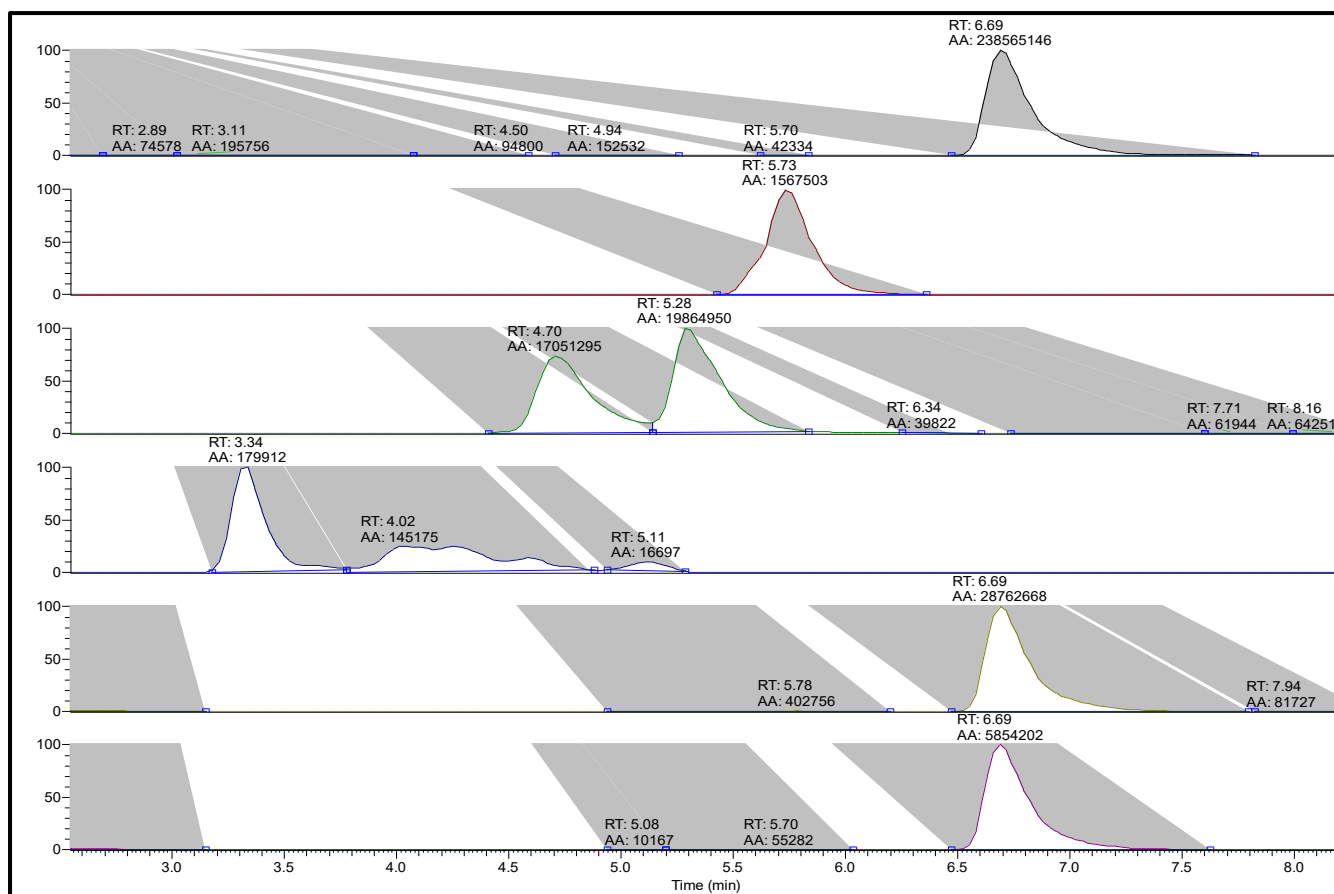


Figure 6.3. LC-MS chromatographic profiles of TCPP contaminated sample after 30 min photocatalytic treatment applying PPy-g-C₃N₄-MIL88B/H₂O₂/LED system for full scan and scan filtered *m/z* ions.

Multiple isomers were observed in the LC-MS chromatographic profiles, and the relative areas of those with the sharpest peaks were considered in this study. For BP307 and BP323, the retention times of 5.28 and 3.32 min were chosen (Fig.6.3). Fig.6.4 a depicts TCPP degradation after 30 min photocatalytic treatment under the following conditions: TCPP concentration = 5 ppb, pH 7, and PPy-g-C₃N₄-MIL88B photocatalyst dose =150 mg/L. The TCPP decay trend shows a sharp decrease in TCPP level after 5 min treatment, followed by a gentle abatement. After 20 min treatment, the TCPP level was reduced to half, from nearly 550 million to 250 million.

For the by-products, as Fig. 6.4 b illustrates, BP251 achieved its peak area after 5 min irradiation time, followed by a gradual decrease until 20 min irradiation. From 20 to 30 min, its abundance did not change notably. This shows that BP251 was generated at the first stage of photocatalysis, while after 15 min, most BP251 was converted into secondary generated by-products. BP307 also attained its highest level between 5-15 min as another major by-product. Sharp decrease after 15 min shows its further decomposition into other BPs. BP343 is observed as a secondary by-product as it reached its maximum area at 15min. Finally, BP323 and BP175 formation at a slower growth and decay rate proved their generation in the final stages of the degradation pathway.

These results demonstrate the phosphate core persistence against degradation in the primary stages of photocatalytic process. In contrast, the detected dechlorinated BPs showed a rapid release of Cl⁻ ions during photocatalysis.

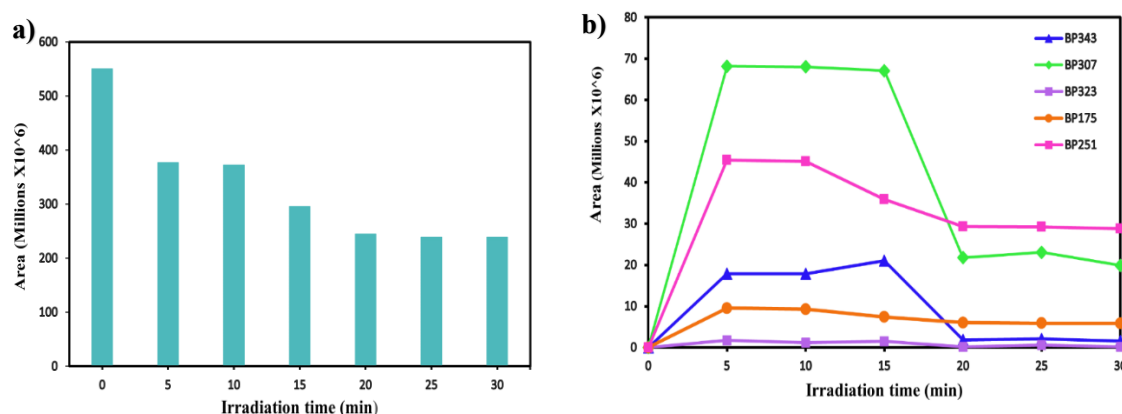
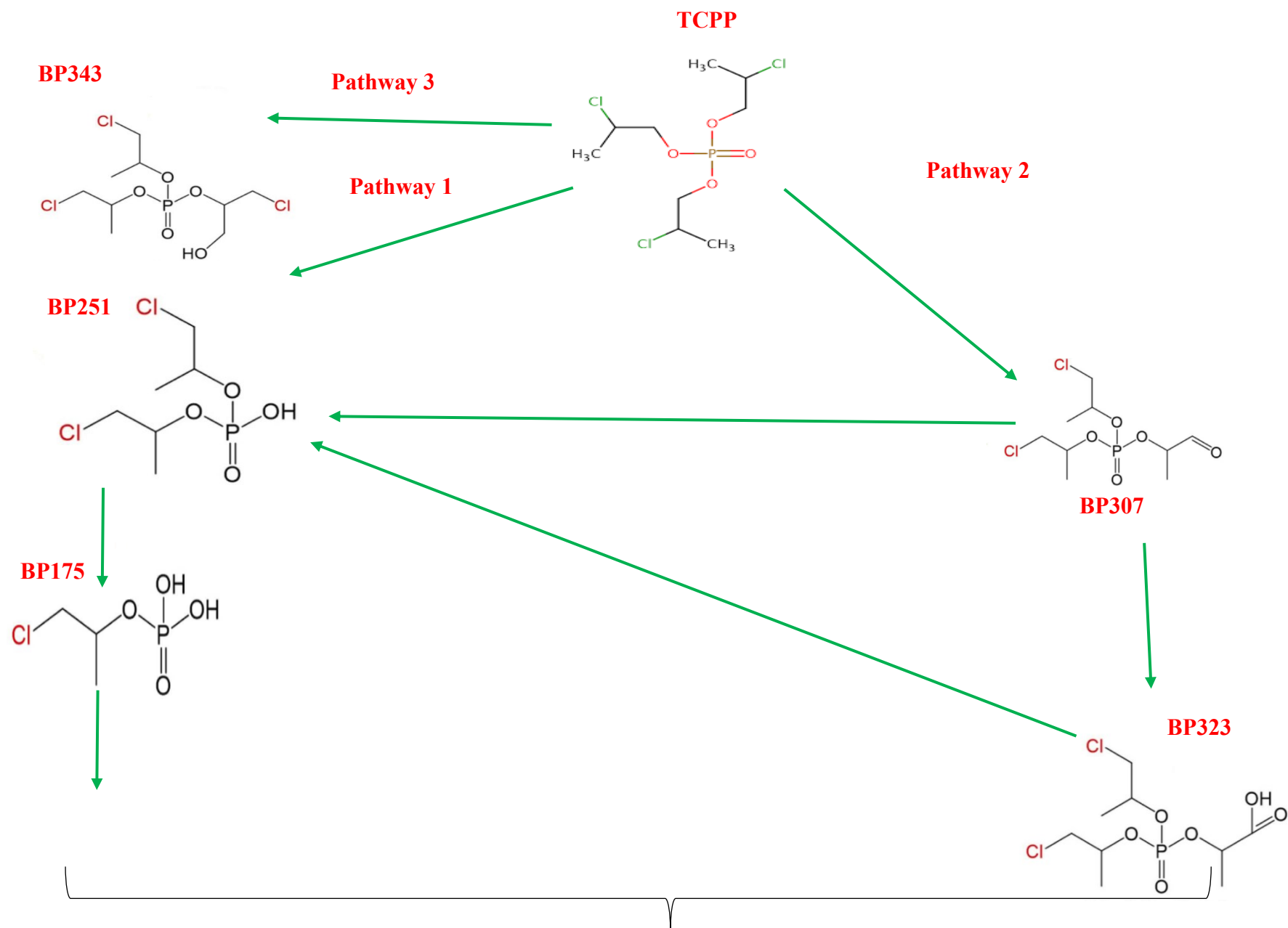


Figure 6.4. a) TCPP deterioration and b) production dynamics of identified BPs over 30 min irradiation time ([TCPP]= 5 ppb, pH 7, and 150 mg/L of PPy-g-C₃N₄-MIL88B photocatalyst).

6.2.5. Proposed degradation pathways

Based on the evaluation of generated by products, three possible degradation pathways are proposed (Fig. 6.5), which are aligned with the suggested degradation mechanism in section 6.2.3. The degradation pathways of TCPP encompassed dechlorination and carboxylation. In the degradation pathway 1 (dechlorination process), the phosphoric center of TCPP was attacked by .OH radicals leading to the cleavage of -chlorinated isopropyl group attached to oxygen atom, resulting in BP251 formation. BP175 was also generated through the cleavage of another oxygen-chlorinated isopropyl arm when BP251 was further oxidized by .OH. Through the same procedure (oxygen-chlorinated isopropyl arm by .OH radical), H₃O₄P is formed from BP175.

Degradation pathway 2 showed that the cleavage of one Cl atom from the chlorinated isopropyl arm led to the generation of BP307, and then the transformation of BP307 with the attack of .OH radical resulted in BP323 production. The hydroxylation of BP323 formed BP251, and through dechlorination process, BP251 further degraded into BP175 and CO₂, H₂O, Cl⁻, and PO₄³⁻. Another possibility is the formation of BP251 directly from BP307 hydroxylation, followed by degradation through pathway1. Another possibility is the oxidation of one methyl group in TCPP by .OH radicals and the generation of BP343 hydroxylated product (pathway3). Therefore, TCPP degradation pathway by PPy-g-C₃N₄-MIL88B/H₂O₂/LED system included dechlorination and hydroxylation through .OH attack, which is in agreement with the degradation mechanism reported in section 6.2.3. According to the proposed degradation pathway and detected BPs, oxalic acid, formic acetic, glycolic, and phosphates are the final .



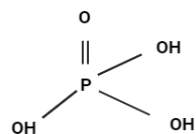


Figure 6.5.Proposed degradation pathways based on detected by-products.

6.2.6. TCPP and the degradation by-products toxicity assessment

Table 6.3 displays the results of the toxicity assessment of TCPP and the detected by-products. The toxicity values related to fathead minnow, bioaccumulation factor, developmental toxicity, and mutagenicity demonstrate that the cleavage of oxygen chlorinated arm and Cl cleavage reduced the toxicity of TCPP and the generated BPs, except for BP343, which is slightly more toxic than TCPP regarding developmental toxicity and mutagenicity. Nevertheless, BP343 was further converted to less toxic BPs, i.e., BP175 and BP323, which showed a lower degree of toxicity. Obviously, as observed from Table 6.3, hydroxylation and cleavage of Cl atom reduced the toxicity to a higher level compared to dichlorination and BP175 generation.

Table 6.3. Toxicity values of TCPP and its by-products during photocatalysis using the consensus method.

Compounds	Fathead minnow	Bioaccumulation factor	Developmental Toxicity	Mutagenicity
	LC ₅₀ (96 hr) (mg/L)			
TCPP	7.24	13.78	0.59	0.97
BP343	8.31	10.78	0.62	1.24
BP307	10.24	2.78	0.57	0.68
BP175	19.12	2.28	0.31	0.49
BP323	58.23	0.67	0.24	0.21
BP251	23.75	1.46	0.45	0.32

Biotoxicity of TCPP prior to and post-treatment was analyzed, compared, and reported as the half-maximal effective concentration (EC₅₀). EC₅₀ was calculated using the regression results

obtained from the absorbance data at each TCPP concentration (Fig. 6.6a). The EC50 values obtained for the treated and untreated solutions with an initial concentration of 800 ppm TCPP were 80.88 and 10.42, respectively. These findings indicate that at 80.88 molar concentration of treated TCPP solution, half of its maximal response was exerted. The lower EC50 molar concentration of the untreated sample, 10.42, compared to the value for the treated sample, 80.88, indicates the high potency and biological effect of TCPP.

The lower biotoxicity of treated TCPP using the PPy-g-C₃N₄-MIL88B photo-Fenton catalyst compared to untreated samples revealed the mineralization of TCPP and production of less biotoxin by-products.

6.2.7. Total organic carbon and photonic efficiency ζ

Total organic carbon (TOC) variations during the photo-Fenton reaction were detected using a TOC analyzer (TOC-L shimadzu) with the initial TOC of 80 mg/L for 100 ppb of TCPP. Fig.6.6 b illustrates the TOC reduction during the photocatalytic degradation of TCPP by the PPy-g-C₃N₄-MIL88B/H₂O₂/LED system. As the figure suggests, the applied system is unable to completely mineralize TCPP, and the generation of by-products is inevitable. During the first 20 min, TCPP degradation was less than 40%, which suggests the generation of transformation by-products. After 20 min, an increase in the TOC removal from 37% to 79% and further to 93% was observed. This trend shows the mineralization of by-products after 20 min and a significant reduction in their concentration. After 30 min, TCPP degradation and TOC removal were fairly in the same range of 96.86% and 93.21%, respectively.

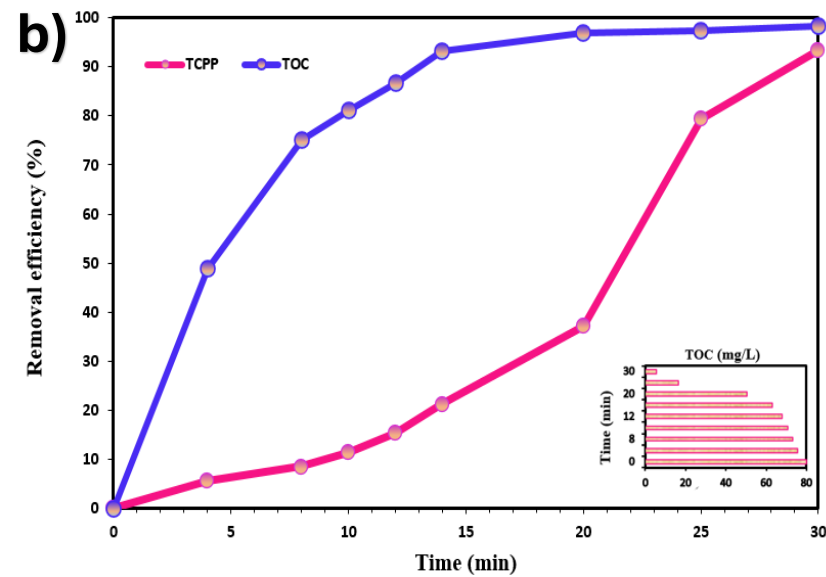
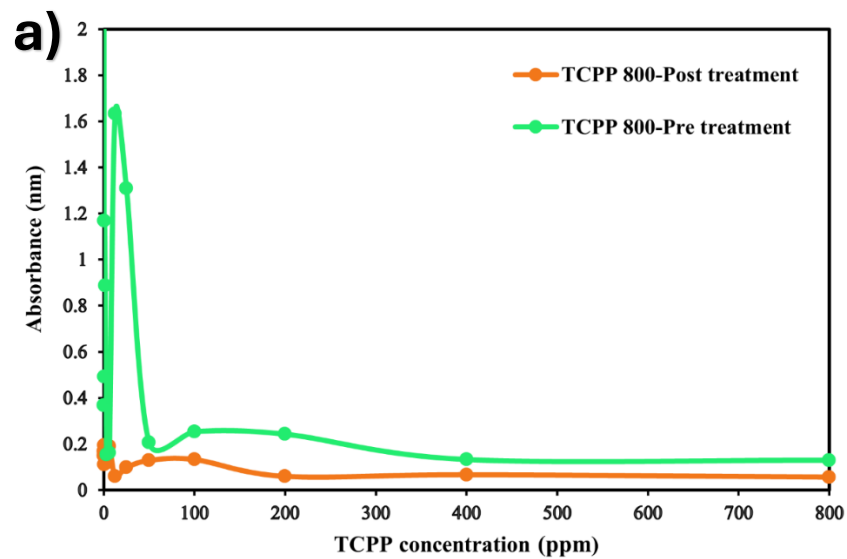


Figure 6.6.a) pre- and post-treatment TCPP absorbance ; b) TOC and TCPP degradation by PPy-g-C₃N₄-MIL88B /H₂O₂/ LED over time.

Table 6.4 illustrates photonic energy variations over time. During the first 10 min, photonic energy diminished from 1.13% to 0.59% due to insignificant TOC removal in this period. From 10 min to 25 min, the photonic energy surged from 0.59% to 8.70% due to the increase in the removal of TOC per volume. The observed increase in photonic efficiency (%) is favorable, meaning that a greater fraction of photons was converted to chemical energy, demonstrating elevated reaction rates along with cost-effectiveness and sustainability of the process. The low TOC content after 25 min of treatment is probably the result of the mineralization of generated by-products.

Table 6. 4. Photonic efficiency (%) and TOC removal (%) from 10 to 60 min.

Parameter	Time (min)					
	4	8	10	14	20	25
ζ (%)	1.13	0.61	0.59	1.22	3.27	8.70
TOC removal (%)	5.50	8.61	11.42	21.26	37.17	79.48

5

6.2.8. Kinetic studies

The evaluation of kinetics of TCPP degradation under visible light using MIL88B, g-C₃N₄-MIL88B, and PPy-g-C₃N₄-MIL88B photo-Fenton catalysts are presented in Fig. 6.7. TCPP degradation by the three photocatalysts under visible light followed first order kinetics, and the kinetic parameters including the apparent rate constants, half-life ($t_{1/2}$), and correlation coefficients (R^2) are presented in Table 6.5. Based on the apparent rate constants and half-life, the degradation kinetics comply with the following trend:

PPy-g-C₃N₄-MIL88B > g-C₃N₄-MIL88B > MIL88B

The apparent half-life and rate constants of degradation processes were calculated using the following equations:

$$\ln \frac{C}{C_0} = -Kt \quad (6.2)$$

$$t_{1/2} = \frac{0.693}{K} \quad (6.3)$$

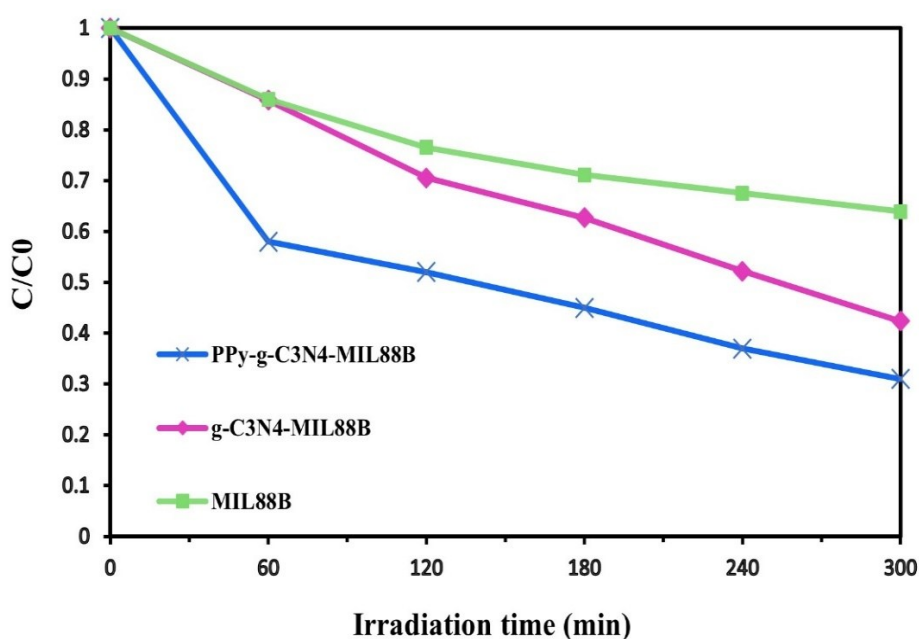


Figure 6.7. Degradation kinetics of TCP by fabricated photocatalysts under LED light ([TCP] = 50 ppb, [catalyst] = 50 mg/L).

Table 6.5. Kinetic parameters, including apparent rate constants, half-life ($t_{1/2}$), and correlation coefficients (R^2) for TCP degradation under visible light ([TCP] = 50 ppb, [catalyst] = 50 mg/L).

Photocatalyst	$K \times 10^{-3} \text{ (min}^{-1}\text{)}$	$t_{1/2} \text{ (min)}$	R^2
MIL-88B	1.4	495	0.9502
g-C ₃ N ₄ -MIL88B	2.8	247.5	0.9955

PPy-g-C₃N₄-MIL88B	3.5	198	0.9248
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According to the kinetics results, each step of modification improved photocatalytic efficiency compared to the unmodified MIL-88B. This could be the result of narrower E_g and higher visible light absorption.

6.2.9. Reliability of PPy-g-C₃N₄-MIL88B for the treatment of Canadian surface water samples

To verify the applicability and accuracy of the prepared PPy-g-C₃N₄-MIL88B photo-Fenton catalyst for practical applications, four real samples taken from Canadian lakes and rivers, including the St. Laurent River, Prairies River, Mont Royal Lake, and Saint Pierre River, were assessed (Table 6.6). For the real water samples, TCPP degradation was in the range of 65% to 79.6% at the optimum operational conditions. The highest degradation for synthetic TCPP solution (TCPP in MilliQ water) under the same conditions was 98.3%. The slight drop observed in TCPP degradation in real surface water samples is probably due to the presence of ions, complex compounds such as Hg^{2+} , Pb^{2+} , Cd^{2+} [371,372], and 4-aminophenol compounds [373]. The results prove that the fabricated photocatalyst has desirable practical applications for addressing the issue of flame retardants in Canadian surface waters. Table 6.6 presents the degradation rates and calculated standard deviations (SD) for the four examined surface water samples in Canada.

Table 6.6. Applicability of PPy-g-C₃N₄-MIL88B photocatalyst for the removal of TCPP from four Canadian surface water samples.

	Injected	Sample geographic	Detected	TCPP	Standard		
Sample	Volume	location	TCPP	degradation	Deviation	Other detected	
	(μL)		(ppb)	(%)	(SD)	compounds (<i>m/z</i>)	
St. Laurent River	0.4	45.44513135985562, -73.53890551852238	62.45	67.3	3.29	354.9, 132.9, 220.9, 72.9, 44, 73	
Prairies River	0.4	45.577476854118, -73.66583498397301	30.50	74	10.8	43.8, 76.7, 96.7, 132.9, 192.8, 208.8	
Beaver Lake	0.4	45.499017135984744, -73.59668290137829	28.43	79.6	4.26	133, 77	
Saint Pierre River	0.4	45.75830519719861, -73.65843233300295	61.47	65	2.7	220.8, 266.8, 280.8, 72.8, 192.8, 280.8,	

6.3. Summary

The synthesis of a Z-scheme heterojunction photo-Fenton catalyst, PPy-g-C₃N₄-MIL88B, and its application in decomposition of the polluting fire retardant TCPP was investigated in this chapter. The enhanced performance of PPy-g-C₃N₄-MIL88B compared to g-C₃N₄-MIL88B and MIL-88B is attributed to the p- π conjugation of C=C bond in PPy and O₂, which resulted in improved reactivity of photocatalyst and reactive oxygen species (ROS) generation. The Z-scheme PPy-g-C₃N₄-MIL88B provides a shortcut for charge transformation and diminished charge recombination. UV-DRS results revealed 28% reduction in the bandgap of PPy-g-C₃N₄-

MIL88B compared to that of MIL88B (2.3 eV to 3.2 eV). Meanwhile, the diminished PL intensity of PPy-g-C₃N₄-MIL88B reduced recombination. Biototoxicity study of TCPD before and after treatment demonstrated a notable increase in EC50 level from an initial value of 10.42 at pre-treatment to 80.88 post-treatment. Kinetics analysis showed improvements in the TCPD degradation rate, with half-life reduction by half from 495 min (MIL88B) to 198 min (PPy-g-C₃N₄-MIL88B). Numerical and experimental optimizations of the process led to the identification of optimum operating conditions of 50 min irradiation time, 150 mg/L catalyst dosage, pH 5, and 15 L/min airflow rate, resulting in around 99% TCPD degradation. The practical application of PPy-g-C₃N₄-MIL88B was explored by the treatment of four real water samples taken from Canadian waterways. The obtained degradation range of 65% to 79.6% emphasized that the prepared Z-scheme photocatalyst offers a promising solution for the degradation and mineralization of TCPD and its by-products, and removal of this hazardous compound from surface waters.

Chapter 7: Conclusions and Recommendations

7.1. Conclusions and contributions

Tris(1-chloro-2-propyl) phosphate (TCPP) is a widely used organophosphate flame retardant increasingly detected in surface waters due to its persistence, moderate solubility, and resistance to conventional wastewater treatment. Its accumulation in aquatic systems has raised ecological and public-health concerns, as flame retardants can impair growth, reproduction, and development in aquatic organisms and act as endocrine disruptors. In humans, chronic exposure through drinking water or bioaccumulation pathways has been associated with neurotoxicity, developmental disorders, and hepatic effects. These risks underscore the urgent need for efficient, sustainable treatment technologies capable of removing TCPP and structurally similar emerging contaminants.

In this thesis, a series of photocatalysts, MIL-88B, g-C₃N₄-MIL-88B, and the newly engineered PPy-g-C₃N₄-MIL-88B, were designed, synthesized, and optimized for TCPP degradation. Manipulating the reaction temperature during MIL-88B synthesis demonstrated clear morphological control, with lower temperatures (120 °C) promoting crystal growth and enabling subsequent structural modifications. Coupling MIL-88B with g-C₃N₄ and PPy generated a robust Z-scheme heterojunction characterized by improved charge separation, enriched Fe³⁺ active sites, and a reduced band gap, as confirmed by XPS and UV–Vis DRS analyses. These enhancements translated into a ~20% increase in TCPP removal efficiency using PPy-g-C₃N₄-MIL-88B compared with pristine MIL-88B.

The PPy-g-C₃N₄-MIL-88B/H₂O₂/LED system achieved optimal degradation (98–99%) under acidic conditions (pH ≈ 3–5), 50–60 min irradiation, and 150 mg L⁻¹ catalyst. Hydroxyl radicals were identified as the dominant reactive species, supported by the strong inhibitory effect of isopropyl alcohol. The catalyst demonstrated excellent stability and reusability, with only a

modest decline in performance (5–7% per cycle) over five consecutive cycles. LC-MS analyses verified the generation and subsequent oxidation of five major TCPP intermediates, ultimately leading to low-toxicity carboxylic acids. The developmental toxicity index decreased substantially (from 0.59 to 0.24–0.31), confirming that both TCPP and its by-products were effectively detoxified.

Response Surface Methodology (RSM) and machine learning provided further insight into process behavior. pH and irradiation time emerged as the most influential parameters affecting degradation efficiency. The Random Forest model exhibited strong predictive capability ($R^2 = 0.974$), reinforcing the system's reliability across operational conditions. The calculated electrical energy per order ($EEO = 6.66 \text{ kWh m}^{-3} \text{ order}^{-1}$) demonstrated that the proposed Z-scheme photo-Fenton process is energy-efficient relative to conventional advanced oxidation processes.

The catalyst's practical applicability was demonstrated through treatment of real Canadian surface waters, where TCPP removal ranged from 65% to 79.6%, confirming the robustness of PPy-g-C₃N₄-MIL-88B under natural water matrices.

A complementary study in this thesis examined the degradation of BDE-47, another persistent halogenated flame retardant, under anaerobic TiO₂-assisted photocatalysis and UVB photolysis. Photocatalysis achieved greater debromination (68.4%) and substantially higher mineralization (85% TOC removal) than photolysis (60%), while requiring significantly less electrical energy (69.87 vs. 103.82 MW·h m⁻³). Machine learning modelling particularly the Gradient Boosted Decision Trees algorithm—demonstrated excellent predictive accuracy ($R^2 = 0.9849$), highlighting its value in forecasting contaminant fate in photocatalytic systems. Together, these findings further reinforce photocatalysis as a superior approach for mitigating the environmental persistence and toxicity of brominated flame retardants.

Overall, this thesis demonstrates that PPy-g-C₃N₄-MIL-88B is a highly efficient, stable, and energy-effective Z-scheme photo-Fenton catalyst capable of degrading TCP and reducing the toxicity of its transformation products. Its enhanced optical properties, strong hydroxyl radical generation, and favourable reusability underscore its potential for real-world application in advanced water treatment. In parallel, the successful application of ML models positions data-driven tools as valuable assets for optimizing and predicting photocatalytic processes involving emerging organic pollutants.

7.2. Recommendation for future work

Based on the findings of this study and the identified limitations, the following suggestions for future work are presented:

1) Future research should move beyond conventional batch photocatalytic experiments toward the development of continuous-flow reactor systems, which more accurately represent industrial effluent treatment processes. In batch systems, pollutant degradation is typically analyzed under idealized conditions and simplified kinetic models; however, real wastewater treatment involves dynamic flow, non-uniform irradiation, and mass transfer limitations that strongly influence photocatalytic efficiency. Microchannel reactors, with their high surface-to-volume ratios and short diffusion paths, provide enhanced light penetration and mass transfer. Slurry-based continuous-flow reactors allow higher throughput, but require elaborate strategies for catalyst recovery. Incorporating hydrogel-supported or immobilized MIL-88B-based composites into these systems offers a promising solution, as hydrogels can prevent catalyst loss, enable recyclability, and maintain stability under continuous operation. Moreover, future studies should integrate kinetic and hydrodynamic modelling, such as residence time distribution and computational fluid dynamics, to better understand the interplay of reaction kinetics, mass transfer, and photonic efficiency. Transitioning from model pollutants to real

industrial effluents within such flow systems would provide critical insights into the scalability, practicality, and environmental relevance of the synthesized photocatalysts.

2) Another important direction for future work is the development of advanced kinetic models that couple the intrinsic photocatalytic reaction mechanisms with mass transfer and light distribution effects. Conventional kinetic analyses, which often rely on pseudo-first-order assumptions, do not adequately capture the complex interplay between pollutant diffusion, photon absorption, and surface reactions in heterogeneous photocatalytic systems. To address these limitations, computational approaches such as computational fluid dynamics (CFD) can be employed to simulate fluid flow, residence time distribution, and photon transport within photocatalytic reactors. By integrating experimental kinetic data with such multiphysics modelling, it would be possible to establish predictive frameworks that account for both chemical reaction rates and physical transport limitations. This approach would not only enhance the fundamental understanding of photocatalytic processes but also inform the rational design of reactor geometries and operating conditions for improved performance in continuous-flow systems.

3) Future studies should also focus on investigating the influence of catalyst geometry, whether dispersed powders, immobilized films, or structured hydrogel beads, on photocatalytic efficiency in continuous-flow systems. In slurry reactors, powdered catalysts typically provide the highest surface area and maximum exposure of active sites; however, they present significant challenges in terms of catalyst recovery, aggregation, and light scattering, which reduce long-term applicability. Immobilized films offer the advantage of easy separation and continuous use. However, their limited active surface area and mass-transfer resistance often result in lower degradation rates than those of suspended catalysts. Hydrogel beads and hydrogel-coated supports represent a promising compromise, as they provide high porosity for pollutant diffusion, mechanical stability under flow conditions, and minimal catalyst leaching.

The geometry of these materials strongly affects hydrodynamics, residence time distribution, and light penetration within reactors, which, in turn, govern the balance between surface reactions and transport processes. A systematic comparison of these geometries under identical flow conditions would allow for the identification of optimal catalyst configurations, guiding the design of scalable and efficient photocatalytic reactors for real wastewater treatment applications.

4) An emerging direction for future work involves the integration of machine learning (ML) techniques to predict photocatalytic degradation efficiency based on intrinsic catalyst properties. Parameters such as band gap energy, BET surface area, porosity, morphology, and the presence of dopants or defect sites are critical in determining photocatalytic activity. Their relationships with performance are often nonlinear and difficult to capture with traditional modelling. By compiling experimental datasets from literature and in-house studies, supervised ML models could be trained to establish quantitative structure–activity relationships that link material properties with pollutant degradation efficiencies. Such predictive frameworks would not only accelerate the screening of candidate materials but also enable the rational design of novel composites by highlighting optimal property ranges for specific applications. In particular, coupling ML predictions with experimental validation would create a closed feedback loop that reduces the trial-and-error nature of photocatalyst development, thereby improving efficiency in material discovery and guiding the design of next-generation MIL-88B–based composites and hydrogel-supported systems.

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Appendix

Table A1. Designed experiments using RSM-CCD, and experimental/predicted TCP degradation efficiencies using the PPy-g-C₃N₄-MIL88B photocatalyst.

Run	Time (min)	Photocatalyst Dose (mg/L)	pH	Air flow rate (L/min)	TCP Degradation efficiency (%)	
					Experimental	Predicted
1	20	200	5	15	68.23	71.18
2	40	150	7	10	70.56	70.16
3	20	200	9	5	32.81	40.36
4	20	100	5	5	58.35	64.64
5	50	100	9	15	78.02	76.18
6	50	100	5	5	90.37	90.14
7	40	250	7	10	72.06	69.66
8	60	150	7	10	92.13	95.66
9	40	150	7	10	70.66	70.16
10	40	150	7	10	70.24	70.16
11	40	150	7	10	70.78	70.16
12	40	150	3	10	96.33	93.94
13	20	150	5	15	68.07	74.46
14	40	150	7	20	82.75	79.98
15	10	150	7	10	41.00	44.66
16	50	150	9	15	75.27	75.68
17	20	150	5	5	56.00	64.14
18	50	150	5	15	98.70	99.96

19	40	150	7	10	70.55	70.16
20	50	200	5	5	88.23	89.64
21	20	100	1	5	35.91	40.86
22	40	150	2	10	48.46	46.38
23	50	200	9	5	65.00	65.86
24	20	100	9	15	42.04	50.68
25	20	200	9	15	42.37	50.18
26	40	50	7	10	71.30	70.66
27	40	150	7	10	71.46	70.16
28	50	200	5	15	98.80	99.46
29	40	150	7	1	62.03	60.34
30	50	100	9	5	67.00	66.36
