



T.R.
EGE UNIVERSITY

Graduate School of Applied and Natural Science



PHOTOCATALYTIC OXIDATION OF AGRICULTURE HERBICIDE DIURON OVER MOF PHOTOCATALYSTS

MSc Thesis

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Department of Chemical Engineering

İzmir
2023

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PHOTOCATALYSTS**

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Department of Chemical Engineering
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ETİK KURALLARA UYGUNLUK BEYANI

EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliğinin ilgili hükümleri uyarınca Yüksek Lisans Tezi olarak sunduğum “Photocatalytic Oxidation of Agriculture Herbicide Diuron over MOF photocatalysts” başlıklı bu tezin kendi çalışmam olduğunu, sunduğum tüm sonuç, doküman, bilgi ve belgeleri bizzat ve bu tez çalışması kapsamında elde ettiğimi, bu tez çalışmasıyla elde edilmeyen bütün bilgi ve yorumlara atıf yaptığımı ve bunları kaynaklar listesinde usulüne uygun olarak verdiğimi, tez çalışması ve yazımı sırasında patent ve telif haklarını ihlal edici bir davranışımın olmadığını, bu tezin herhangi bir bölümünü bu üniversite veya diğer bir üniversitede başka bir tez çalışması içinde sunmadığımı, bu tezin planlanmasından yazımına kadar bütün safhalarda bilimsel etik kurallarına uygun olarak davrandığımı ve aksinin ortaya çıkması durumunda her türlü yasal sonucu kabul edeceğimi beyan ederim.

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ÖZET**TARIMDA HERBİSİT OLARAK KULLANILAN DİURON'UN MOF
KATALİZÖRLERİ ÜZERİNDE FOTOKATALİTİK
OKSİDASYONU**

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Bu tezde, bir dizi g-C₃N₄ destekli Ag/AgCl katkılı MIL-88A kompozitleri sentezlenmiş ve SEM, XRD, XPS, FT-IR, UV-vis DRS, N₂ adsorpsiyon çalışmaları ve PL ile karakterize edilmiştir. Ag/AgCl@MIL-88A/g-C₃N₄ kompozitleri, farklı indirgenme zamanlarında, Fe:Ag mol oranları değiştirilerek, çeşitli radikal yakalayıcılar varlığında ve farklı ışık kaynakları altında hazırlanmıştır. Hazırlanan kompozitlerin fotokatalitik performansları, herbisit Diuron'un (DRN) sulu çözeltisinde görünür ışık ışıması altında incelenmiştir. Oksidant yokluğunda, en iyi aktivite gösteren Ag/AgCl@MIL-88A/g-C₃N₄ fotokatalizörü ile 60 dakika içinde tam DRN fotodegradasyonu gerçekleştirilmiştir. Bununla birlikte, H₂O₂ ve persülfat varlığında, DRN'nin tam bozunmasına sırasıyla 15 dakika ve 30 dakika gibi daha kısa sürede ulaşılmıştır. Ag/AgCl@MIL-88A/g-C₃N₄ fotokatalizörü, inorganik anyonlar ve doğal organik madde (NOM) dahil olmak üzere farklı su matrisi türlerinde çok yüksek DRN giderimi sağlamıştır. Ayrıca, üç döngülü testler Ag/AgCl@MIL-88A/g-C₃N₄ kompozitinin yüksek kararlılığa sahip olduğunu göstermiştir. Radikal yakalama deneylerinin bulgularına göre, DRN'nin fotokatalitik oksidasyonunda O₂^{•-} ve h⁺ nın ana reaktif türler olduğunu sonucuna varılmıştır. Toksisite testlerinin sonuçları, arıtılmış DRN çözeltisinin, arıtılmamış DRN çözeltisinden %48.5 daha az toksik olduğunu ortaya çıkarmıştır. Aktif radikallerin rolü, MIL-88A/g-C₃N₄ ve Ag/AgCl@MIL-88A/g-C₃N₄ varlığında DRN'nin önerilen bozunma mekanizması aracılığıyla tartışılmıştır. DRN fotodegradasyon koşulları Minitab-21 istatistiksel deneysel tasarım programı kullanılarak optimize edilmiştir. Son olarak, DRN'nin sono-fotokatalitik oksidasyonu çalışılmıştır.

Anahtar sözcükler: Fotokatalizör, MIL-88A, MOF, Ag/AgCl@MIL-88A/g-C₃N₄ kompozit, herbisit, Diuron, sono-fotokatalitik oksidasyon.



ABSTRACT**PHOTOCATALYTIC OXIDATION OF AGRICULTURE
HERBICIDE DIURON OVER MOF PHOTOCATALYSTS**

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In this thesis, Ag/AgCl@MIL-88A/g-C₃N₄ composites were synthesized and characterized by SEM, XRD, XPS, FT-IR, UV-vis DRS, N₂ adsorption studies and PL. Ag/AgCl@MIL-88A/g-C₃N₄ were prepared by changing the photodeposition time, Ag loading amount and type of sacrificial agent and light source. The activities of as-prepared composites were examined on the photodegradation of herbicide diuron (DRN) in aqueous solution under visible LED light irradiation. Over the most active Ag/AgCl@MIL-88A/g-C₃N₄ composite, complete degradation of DRN was achieved within 60 min, in the absence of oxidants. However, in the presence of H₂O₂ and persulfate, complete degradation of DRN was reached in a shorter time of 15 min and 30 min, respectively. The Ag/AgCl@MIL-88A/g-C₃N₄ photocatalyst showed sufficient activity in different water matrix species including inorganic anions and natural organic matter (NOM). Moreover, during three-cycle tests, the composite retained excellent photocatalytic stability. Based on the radical trapping experiments, O₂^{•-} and h⁺ were determined as the main reactive species involved in the photocatalytic oxidation. The results of the toxicity tests revealed that the treated DRN solution was 48.5% less toxic than the untreated DRN solution. Role of active radicals was discussed via proposed degradation mechanism of DRN over MIL-88A/g-C₃N₄ and Ag/AgCl@MIL-88A/g-C₃N₄. Experimental design was performed via Minitab-21 software to optimize fotodegradation conditions. Finally, the sono-photocatalytic oxidation technique was utilized to study the degradation of DRN.

Keywords: Photocatalysis, MIL-88A, MOF, Ag/AgCl@MIL-88A/g-C₃N₄ composite, herbicide, Diuron, sono-photocatalytic oxidation.



PREFACE

In this thesis, the photocatalytic oxidation technique was used to examine the removal of the herbicide diuron from aqueous solutions in the presence of the Ag/AgCl@MIL-88A/g-C₃N₄ composites. For this purpose, various synthesis parameters were applied to Ag/AgCl@MIL-88A/g-C₃N₄ composites. After that, the prepared photocatalysts were characterized, and their catalytic activities were extensively studied.

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NOMENCLATURE

<u>Symbols</u>	<u>Explanation</u>
$\log K_{ow}$	n-octanol-water partition coefficient
pK_a	negative base-10 logarithm of the acid dissociation constant

Abbreviations

AFM	Atomic force microscope
ATP	Adenosine triphosphate
DABCO	1,4-diazabicyclo [2.2.2] octane
EDS	Energy Dispersive Spectroscopy
EIS	Electrochemical impedance spectroscopy
ESR	Electron spin resonance
FESEM	Field-Emission Scanning Electron Microscopy
IUPAC	International Union of Pure and Applied Chemistry
LC-MS	Liquid chromatography-mass spectrometer
MIL	Materials of Institute Lavoisier
NADPH	Nicotinamide adenine dinucleotide phosphate
WHO	World Health Organization
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric analysis



1. INTRODUCTION

Water pollution and scarcity have become a major global problem in recent decades as a result of the rapid industrialization and population expansion (Long et al., 2020). Industry and agricultural sectors are the most important sectors that cause water pollution. Wastewater from these sources typically contains suspended solids, heavy metals, metallic ions including pathogens, and organic pollutants such as degradation-resistant pharmaceuticals, pesticides, personal care products, surfactants, hormones, and endocrine disrupting chemicals (Bhoi et al., 2018).

Pesticides are widely used in agriculture to control pests and animals, as well as to increase product quality and stability. Pesticides, despite their broad applicability, are among the most harmful environmental pollutants (Bagheri et al., 2021). Most pesticides have a long half-life and are not biodegradable. Most frequently, pesticides interact with natural water sources via industrial waste, agricultural waste, soil permeation, and aquatic bodies. Among these sources, water-soluble species are the most hazardous since they have a high persistence rate and are difficult to eliminate entirely (Bano et al., 2021).

Diuron (DRN) is an herbicide belonging to the phenylurea family that is used to suppress weeds in a variety of crops (López-Ramón et al., 2019). DRN is mostly detected in surface waters and European Union Water Framework Directive listed it as a priority hazardous substance. Also, US Environmental Protection Agency classified DRN as a "known probable" human carcinogen (Mendiola-Alvarez et al., 2021).

Most of the conventional wastewater treatment plants are insufficient to remove DRN-containing wastewater, so it is necessary to develop new and efficient approaches to reduce the discharge of DRN-containing wastewater to the environment (López-Ramón et al., 2019; Vigneshwaran et al., 2021; Wu et al., 2019).

In this context, advanced oxidation processes (AOPs) can be utilized to treat wastewater that contains substances with low biodegradability, extremely stable chemicals, and organic contaminants (Anirudhan et al., 2018). Among AOPs, photocatalytic technology is regarded as a promising chemical method capable of degrading the majority of organic pollutants by generating numerous highly active

reactive oxygen species, hydroxyl radicals ($\text{OH}\cdot$) and photo-generated holes (h^+), via light irradiation and semiconductor materials (Huang et al., 2018).

In the present study, series of $\text{g-C}_3\text{N}_4$ supported by Ag/AgCl containing MIL-88A composites were synthesized by changing the photoreduction time, molar ratio of Fe to Ag in Ag/AgCl/MIL-88A , type of sacrificial agent and type of light that was used for photoreduction. The prepared samples were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), UV–vis diffuse reflectance spectroscopy (UV–vis DRS), nitrogen adsorption studies and photoluminescence spectroscopy (PL). The photocatalytic performances of as-prepared composites were examined by the photodegradation of diuron (DRN), which is used as an herbicide in agriculture. The effect of addition of oxidants in photocatalytic oxidation was examined. The photocatalytic oxidation was also conducted in different water matrix. In order to determine which active radicals play important role in the oxidation, radical trapping experiments were done. To assess the reusability and stability of the most active $\text{Ag/AgCl@MIL-88A/g-C}_3\text{N}_4$ catalyst, three-cycle experiments for photocatalytic degradation of DRN were performed. Toxicity tests were carried out to understand whether the intermediates formed during the photocatalytic oxidation of DRN were more toxic than DRN. To demonstrate superiority of $\text{Ag/AgCl@MIL-88A/g-C}_3\text{N}_4$ over $\text{MIL-88A/g-C}_3\text{N}_4$, radical formation mechanisms of mentioned to samples were determined. The experimental design method of Response surface methodology was used to determine the best conditions for DRN photodegradation with Minitab software. In addition to all these runs, degradation of DRN was also studied by hybrid oxidation method of sono-photocatalytic oxidation.

2. THEORETICAL BACKGROUND

2.1 General Information About Diuron

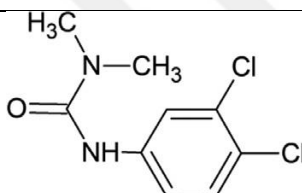
Pesticides are usually applied in modern agriculture to prevent plant diseases and to control a variety of pests that might affect agricultural productivity. According to their functional features, pesticides are typically categorized into the following groups: insecticides, herbicides, fungicides, acaricides, and plant growth regulators. An estimated several million tons of pesticides are utilized annually in industrial and agricultural output. Due of their chemical persistence and harmful effects, pesticides pose a significant hazard to human health and natural ecosystems even at low doses (Asgari et al., 2021). According to WHO standards, the maximum allowable pesticide concentration in drinking water is less than 0.1 µg/L (Vigneshwaran et al., 2021).

Herbicides are organic substances that are utilized in agricultural crops for the purpose of removing undesirable plants. Diuron (N-(3,4-dichlorophenyl)-N, N-dimethyl-urea) is an herbicide belonging to the phenylurea family (López-Ramón et al., 2019) that is commonly applied to a variety of crops, including sugarcane, coffee, cotton, banana, and pineapple (Lopes and Salgado, 2021). Diuron (DRN) is a chemical used to eradicate weeds pre- and post-harvest; it pollutes soil and water and is often detected in sediments, groundwater, and surface water (Oliveira et al., 2020). Because of its chemical stability, water solubility (42 mg/L, 20°C (Lopes and Salgado, 2021)), and non-biodegradability, DRN is capable of accumulating in water and causing issues for both plants and animals. In consideration of its environmental impact, Diuron is listed on the first priority substance list in Directive 2013/39/EU of the European Parliament (Yasmeen et al., 2019; Bumroongsakulsawat et al., 2020).

DRN is carcinogenic and genotoxic and has negative impacts on human health and aquatic ecosystems (Oliveira et al., 2020). Additionally, it might affect the digestive and respiratory systems (Lopes and Salgado, 2021). DRN can irritate the mucous membranes, skin, and eyes when it comes into contact with humans. Moreover, it can react with hemoglobin in the bloodstream to produce methemoglobin, resulting in loss of consciousness and abnormalities in the liver and spleen (Anirudhan et al., 2018). Animal studies demonstrated liver tissue damage, weight loss, and problems in offspring after exposure to DRN (Lopes and

Salgado, 2021). DRN is a potent photosynthesis II inhibitor in plants. DRN restricts the transfer of electrons from water to the electron acceptor and consequently negatively affects the formation of ATP and NADPH that are essential for a variety of metabolic activities in plants (Anirudhan et al., 2018). The half-life of DRN in soil is greater than 300 days, making it as a highly persistent chemical (López-Ramón et al., 2019). Some of the principal intermediate degradation products of DRN include N'-(3,4-dichlorophenyl)-N-methylurea (DCPMU), 3,4-dichlorophenylurea (DCPU), 3,4-dichloroaniline (DCA), and N'-(3-chlorophenyl)-N-methylurea (mCPMU). All of these intermediates are extremely hazardous to human health (Anirudhan et al., 2018). Due to its detrimental impacts, the removal of DRN from surface and ground waters is necessary. Table 2.1 displays the molecular structure and chemical properties of DRN.

Table 2.1 Diuron chemical properties (López-Ramón et al., 2019; Lopes and Salgado, 2021).

Commercial name	Diuron
IUPAC Name	3-(3,4-dichlorophenyl)-1,1-dimethylurea
Molecular formula	C ₉ H ₁₀ Cl ₂ N ₂ O
Structure	
Molecular weight (g/mol)	233.1
pK_a	3.7
Log K_{ow}	2.6
Solubility in water (mg/L)	42

2.2 Advanced Oxidation Processes (AOPs)

For the removal of pesticides from aqueous media, numerous treatment approaches such as adsorption, coagulation and flocculation, membrane separation, biodegradation, and chemical treatments have been examined. However, the use of these methods is not efficient due to high chemical consumption, high treatment costs, require large space, incomplete removal, pH sensitive and time-consuming applications. Also, the most of herbicides are not eliminated entirely by the

employed techniques. Instead of traditional techniques in the treatment of organic pollutants from water sources, advanced oxidation processes are of interest to many researchers for reasons such as high efficiency, recovery, chemical stability, and low cost (Sajjadi et al., 2019; Vigneshwaran et al., 2021; López-Ramón et al., 2019; Rayaroth et al., 2022).

In wastewater treatment using AOPs, organic pollutants in water are transformed into potentially non-toxic products (H_2O and CO_2) with the effect of radicals such as hydroxyl ($\text{OH}\cdot$) and superoxide ($\text{O}_2\cdot^-$), which have greater selectivity and oxidation ability against organic pollutants (Kamandi et al., 2021; Vigneshwaran et al., 2021). Examples of AOPs include photocatalytic oxidation, sonocatalytic, ozonation, Fenton reactions, and sulfate radical-based AOPs (SR-AOPs) (Ma et al., 2021).

Currently prevalent advanced oxidation processes (AOPs) based on catalytic, electrochemical, and photochemical reactions are capable of degrading a wide variety of contaminants. AOPs are suitable as tertiary treatment in urban wastewater treatment facilities and have a high removal rate of organic contaminants in water, as well as an increase in biodegradability and a decrease in toxicity (López-Ramón et al., 2019).

In this study, photocatalytic oxidation, a kind of AOP, was examined for the treatment of DRN-containing wastewater. In addition, sonication and a hybrid sono-photocatalytic technique have been applied.

2.2.1 Photocatalytic oxidation

In the presence of light, the redox capacity of photocatalysts forms the basis of photocatalysis theory. Semiconductors are typically utilized as catalysts in photocatalytic processes to decompose organic pollutants into CO_2 and H_2O . Structures known as the valence band (VB) and the conduction band (CB) are both components of a semiconductor photocatalyst. The "forbidden band" refers to the region between the CB and the VB. Semiconductor catalysts produce electrons (e^-) and holes (h^+) with reduction and oxidation capabilities when photons with a specific energy are absorbed by them. Subsequently, the created e^-/h^+ will migrate to the surface of the catalyst, where a portion of them will directly contribute to the pollutant's degradation while the remainder will form reactive oxygen species

(ROS) to participate in the reaction. Nonetheless, throughout the transfer process, a portion of the photogenerated electrons recombine with holes, preventing them from participating in the reaction and lowering the quantum efficiency.

Figure 2.1 depicts the photocatalytic principle of the semiconductor catalyst (Long et al., 2020; Ma et al., 2021).

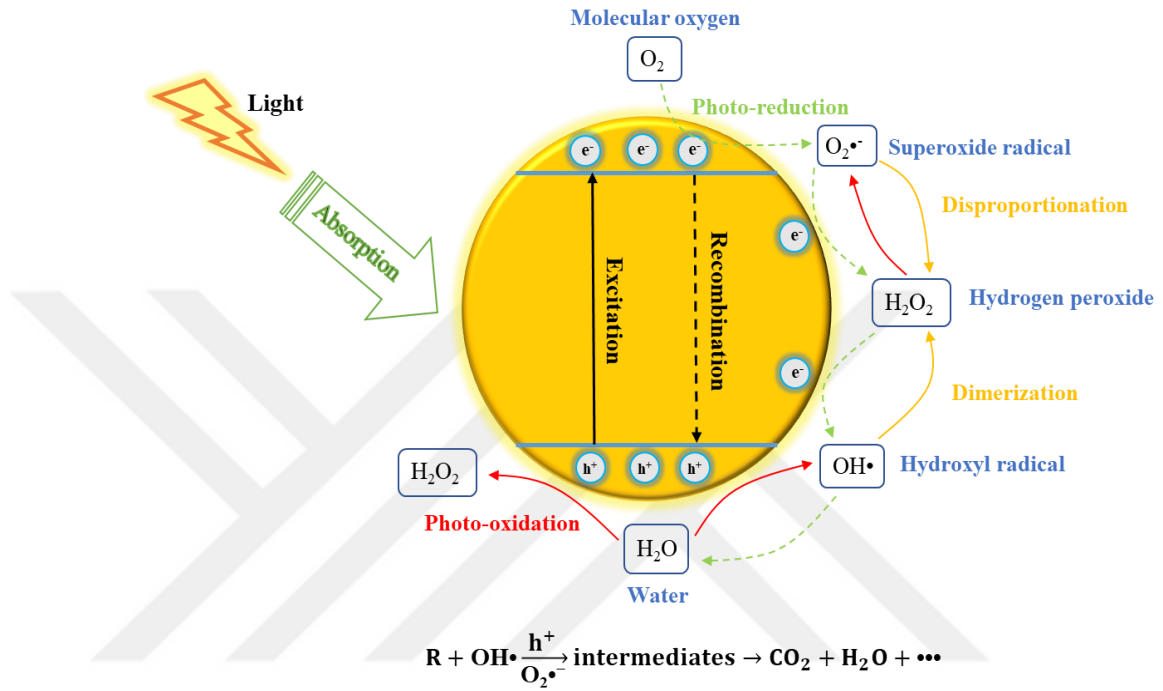
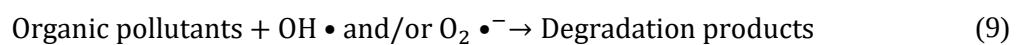
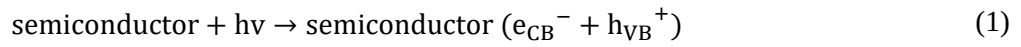
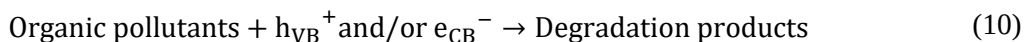


Figure 2.1 Schematic exhibiting the photocatalytic concept of semiconductor catalyst (Long et al., 2020; Ma et al., 2021).

The photocatalysis mechanism in accordance with the studies reported is outlined below, (Eqs. 1-10) (Gholizadeh Khasevani and Gholami, 2018).





The use of photocatalytic reactions to treat wastewaters that contains persistent pollutants has the following advantages:

- the ability to use direct photolytic processes without the addition of reagents,
- higher reaction rate compared to the identical approach without light,
- the avoiding of high pH levels (e.g., when using ozone without light, high pH values are required),
- a rise in the system's adaptability, enabling the treatment of a high number of contaminants under a variety of operating circumstances,
- low running costs due to the use of less energy to produce $\text{OH}^\bullet$ and $\text{O}_2^{\bullet-}$ radicals (López-Ramón et al., 2019).

However, there are two issues that cause to a decrease in the quantum efficiency of photocatalytic material: a higher rate of electron-hole pair recombination and a lower efficiency of light usage. To improve the quantum efficiency of photocatalytic materials in order to optimize their performance, the heterojunction method, noble metal deposition method, morphological control, and elemental doping can be utilized (Ma et al., 2021).

Defining the electron-hole transfer mechanism and establishing a relationship with the structure and catalytic activity of the photocatalyst are important factors for the effective design of photocatalytic processes. As shown in Figure 2.2, three types of heterojunction mechanisms can be identified according to their band gap energy levels.

Type 1: The conduction band (CB) energy of Semiconductor 1 (SC1) is more negative than the CB energy of Semiconductor 2 (SC2), the valence band (VB) energy of SC1 is more positive than the valence band energy of SC2, thus, electron-hole pairs is transferred from SC1 to SC2 (Figure 2.2A).

Type 2: If the CB energy of SC1 is more negative than the CB energy of SC2 and the VB energy of SC2 is more positive than the VB energy of SC1, electrons are

transferred from SC1 to SC2, and the valence band holes from SC2 to SC1. In other words, SC2 serves as an electron sink, whereas SC1 serves as a hole sink (Figure 2.2B).

Type 3: If the conduction band energy of SC2 is lower than the valence band energy of SC1, the valence band gaps are transferred from SC1 to SC2 (Figure 2.2C).

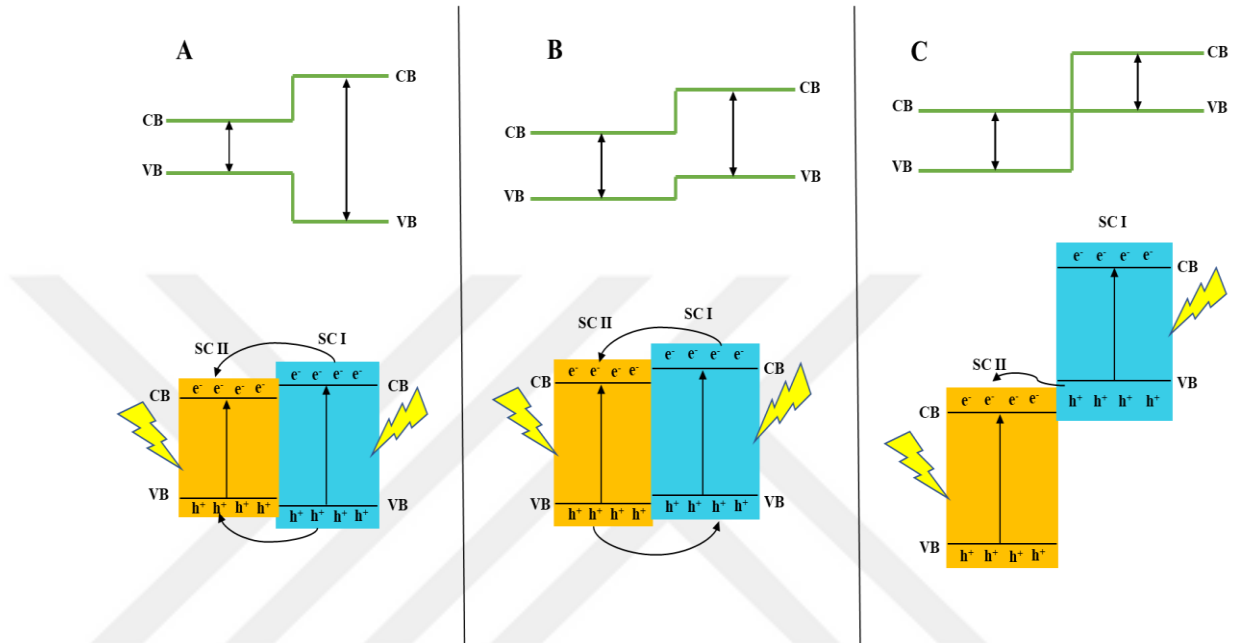


Figure 2.2 Charge-transfer mechanisms of semiconductors according to band position: (A) type I heterojunction; (B) type II heterojunction; (C) type III heterojunction (Martin et al., 2020).

Among the mentioned mechanisms, only the Type 2 heterostructure allows the rapid separation of electron and hole pairs (Martin et al., 2020).

Among the most studied photocatalysts, anatase form of TiO_2 is preferred mostly due to its advantages such as high surface area, strong oxidizing ability and high chemical stability. However, the use of TiO_2 as a photocatalyst has some constraints, such as its wide bandgap (3.2 eV), which makes its efficiency difficult under solar/visible irradiation, and rapid recombination of charge carriers, which significantly hinders its photocatalytic performance (Mendiola-Alvarez et al., 2021). UV light generates only a small fraction (5%) of solar energy compared to visible light (45%), so TiO_2 absorbs only 5% of the solar spectrum (Horovitz et al., 2016; Bo et al., 2017). Therefore, synthesizing the active photocatalysts in the visible light region ($\lambda > 400$ nm) is critical for the effective removal of organic pollutants from wastewater.

In this regard, among the various photocatalysts, metal organic frameworks (MOF) have been used successfully as a new type of visible light-sensitive catalysts in photocatalytic reactions (Huang et al., 2018).

2.2.1.1 Metal organic frameworks (MOFs)

Metal organic frameworks (MOFs), also known as coordination polymers, are crystalline and porous materials with a periodic network structure in which metal nodes/clusters and organic ligand units are connected by strong chemical bonds (Huang et al., 2016; Miao et al., 2019). In theory, MOFs might have a limitless number of different structures. Any metallic element in the periodic table can be used as an alternative metal node, and a variety of carboxylic and other organic compounds can be employed as linkers in MOF synthesis. With these various combinations, MOFs have exceptional features such as large surface area, well-defined porosity, and adaptive functionality. MOFs have many potential applications, including catalytic synthesis, gas storage/separation, biomedical applications, optics, electronic and magnetic materials, and heterogeneous photocatalysis (Gao et al., 2016; Liu et al., 2018; Yan et al., 2019; Fan et al., 2021).

MOFs have recently been utilized for the photocatalytic remediation of organic contaminants in water, as their chromophores can interact with light and stimulate photochemical processes (Xue et al., 2021). In terms of photocatalysis application, MOFs have features such as stronger light absorption ability, more active sites for photocatalytic reaction, better transfer rates and shorter transmission distance of photogenerated electrons to the photocatalyst surface compared to conventional photocatalysts (Yang et al., 2021). Additionally, some MOFs have the ability to create electron-hole pairs through the photoexcitation of metal ions and organic ligands, which is a characteristic of metal-oxide semiconductors (Cui et al., 2020). There are many MOFs synthesized and used in the field of photocatalysis such as MIL-53 (Liu et al., 2018), MIL-88A (Gholizadeh Khasevani and Gholami, 2019), MIL-88B (Nguyen et al., 2021), MIL-101 (Huo et al., 2019), UIO-66(NH₂) (Fan et al., 2021) and MIL-125 (Mahmoodi et al., 2019). However, drawbacks of MOFs, such as weak photoresponsivity, low utilization of visible light, and rapid recombination of photogenerated electron-hole pairs (Huo et al., 2019), and poor catalyst recycling (Liu et al., 2020) restrict their single use in photocatalysts. Researchers have tried to find solutions to these issues by combining MOFs with

other materials because to MOFs' ability to preserve structural integrity and physico-chemical characteristics (Xue et al., 2021).

In addition, most of the current research has been focused on the photocatalytic activities of MOFs in the removal of dyes from wastewater and the reduction of heavy metals, and there is relatively little work on the photocatalytic oxidation of herbicides in wastewater on MOF catalysts. Combining other functional materials with MOFs is necessary to further increase the visible light efficiency and to investigate its performance in herbicide removal mechanism (Huang et al., 2018; Wu et al., 2019, Viswanathan et al., 2021).

Among many MOFs, Fe-based MOFs may be a class of photocatalyst with practical applications. Environmental safety, economic effectiveness, and photoreactivity are among the benefits of Fe-MOFs. Moreover, MIL series MOFs are the most common Fe-based MOFs (Yan et al., 2019).

2.2.1.2 MIL-88A photocatalyst

As a typical Fe-based MOFs built by coordination bonding between iron (III) chloride hexahydrate and fumaric acid, MIL-88A(Fe) has proven to be an excellent visible-light photocatalyst with considerable potential. In addition to its ease of synthesis (requires low temperature), stable structure, low cost, and eco-friendliness, environmental friendliness (can be prepared with water as a solvent) MIL-88A(Fe) has a substantial and reversible swelling impact. This impact of MIL-88A(Fe) swelling not only increases the exposure of active sites, but also facilitates adsorption and enriches the reaction substrate surrounding the active site for photocatalytic reaction. Therefore, with its large swelling effect, MIL-88A is crucial for mass transfer in photocatalytic performance (Yang et al., 2021; Gholizadeh Khasevani and Gholami, 2019).

The preparation of most MOF catalysts with toxic/carcinogenic solvents rather than by green synthesis is a major disadvantage of this class of materials. The most of Fe-based MOFs are typically fabricated with dimethylformamide (DMF), a carcinogenic organic solvent. In this context, the focus has been on the use of MIL-88A(Fe) photocatalysts prepared with water, not organic solvents, in MOF photocatalysts, and studies to increase their activity (El Asmar et al., 2021).

MIL-88A(Fe) has a regular form and a broad light absorption spectrum (200-600 nm). This is an advantageous characteristic for combining with other semiconductor photocatalysts (Yuan et al., 2020).

2.2.1.3 Ag/AgCl

Improving the separation efficiency of charge carriers and increasing their sensitivity to visible light are essential for increasing the photocatalytic activity of semiconductor photocatalysts in the presence of visible light. It can be managed with the addition of noble metals into the structure of semiconductor. Ag nanoparticles (Ag NPs), one of these noble metals, can capture electrons, thus, improve the separation efficiency of photogenerated charge carriers (Fan et al., 2021; Liu et al., 2018). In comparison to other plasmonic elements, such as platinum (Pt) and gold (Au), silver (Ag)-based plasmonic photocatalysts are more practical since they are relatively affordable (Sun et al., 2020).

Recent research has focused on plasmonic Ag@AgX (X = Cl, Br, and I) compounds with high visible absorption for use in the photocatalytic degradation of organic contaminants (Gao et al., 2016). The visible light photocatalytic activity of Ag@AgX is further increased by the localized surface plasmon resonance (LSPR) effect of Ag nanoparticles. Surface plasmons are defined to be the collective oscillation of a nanomaterial's free charge that stays on the surface. Due to the electric field of incoming light, the free electrons of an irradiated metal nanoparticle (NP) become polarized. Positive charges in a metal NP are thought to remain stationary, whereas negative charges (i.e., free electrons) move in response to external influences (Figure 2.3). Therefore, when NP is placed in an electric field, the negative charges are displaced from the positive charges. While a net charge difference occurs at the NP boundaries, this results in a linear force to restore the system. As a result, a dipolar oscillation of the electrons is produced; this oscillation is known as the surface-plasmon oscillation. The oscillating electric fields generated by the SPR effect are significantly more powerful than those generated by the source photons. Hence, when the frequency of the incoming light is equal to the frequency of the plasmon, an absorption resonance has the potential to take place, which results in the production of high electric fields on the surface of the nanoparticles (Belessiotis and Kontos, 2022; Liang et al., 2012; Cheng et al., 2014).

In a summary, when a strong interfacial contact was established between Ag nanoparticles and semiconductors, energetic electrons would directly inject into the semiconductor surface, thereby increasing the photocatalytic activity of semiconductors (Huang et al., 2022).

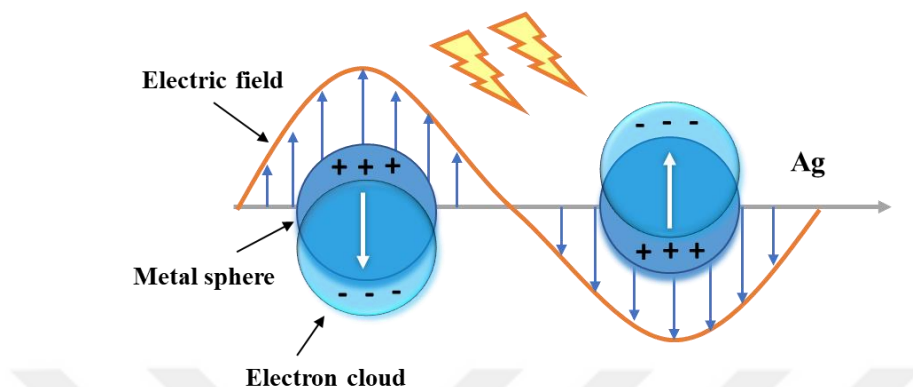


Figure 2.3 LSPR phenomena on a metal nanoparticle (Ag NPs) (Belessiotis and Kontos, 2022; Cheng et al., 2014).

Under visible light irradiation, Ag/AgCl, a composite-type plasmonic photocatalyst, is very effective in producing highly active charge carriers (Fan et al., 2021; Liu et al., 2018). However, the photocatalytic impact of Ag/AgCl under visible light irradiation is weak because of its low adsorption property and comparatively poor reduction capacity. There are several studies reported in the literature where Ag/AgCl was used as a cocatalyst to modify g-C₃N₄ (Zhang et al., 2014), TiO₂ (Yu et al., 2009; Guo et al., 2012), Bi₂MoO₆ (Zhang et al., 2015), BiVO₄ (Qiao et al., 2015), WO₃ (Fang et al., 2019), SrTiO₃ (Yang et al., 2017) and other semiconductor photocatalysts. The energy-matched band structure of Ag nanoparticles not only provides a new source of light absorption via the LSPR effect, but also increases the lifetime of the photogenerated electron-hole pair. Therefore, Ag/AgCl is utilized as a co-catalyst to enhance the electron-hole pair separation and migration to the visible light-responsive MOFs and, consequently, to eliminate organic contaminants from water (Huang et al., 2018; Wu et al., 2019, Viswanathan et al., 2021).

2.2.1.4 g-C₃N₄ photocatalyst

Recent studies have shown that graphitic carbon nitride (g-C₃N₄) can be effectively used in photocatalytic reactions. Among semiconductor photocatalysts, metal-free graphitic carbon nitride (g-C₃N₄) demonstrates photocatalytic

performance in the degradation of organic pollutants and the reduction of carbon dioxide. g-C₃N₄ may absorb a wider spectrum of visible light because of its narrow optical bandgap (2.7 eV). Additionally, g-C₃N₄ has various benefits such as strong chemical stability, abundance on earth, low cost, non-toxicity, high conductivity, flexibility, and mobility of charge carriers. However, the photocatalytic efficiency of bare g-C₃N₄ is limited by its low surface area, fast recombination of photoinduced charges and poor dispersion (Gholizadeh Khasevani and Gholami, 2018; Shao et al., 2019; Cui et al., 2020). Many strategies have been proposed to solve these problems, including modification, the doping of extraneous elements, the design of porous structures, and coupling with other semiconductors. These strategies aim to improve photocatalytic performance by inhibiting charge transfer recombination and narrowing the band gap (Gholizadeh Khasevani and Gholami, 2019). It has been observed that the construction of heterojunctions using exclusively narrow band gap semiconductors can significantly improve both the visible light absorption and the separation of e⁻/h⁺ pairs, resulting in the production of more charge carriers and extending their lifetime dispersion (Gholizadeh Khasevani and Gholami, 2018). The optimal strategy to increase the photocatalytic activity of g-C₃N₄ is to combine this material with other hybrid materials such as MOFs. Thus, by providing extra active areas, heterostructures that strengthen the charge separation are formed (Kamandi et al., 2021).

2.2.1.5 Ag/AgCl@MIL-88A/g-C₃N₄ photocatalyst

In the present study, a series of Ag/AgCl@MIL-88A(Fe)/g-C₃N₄ composite catalysts were synthesized. MIL type MOFs are highly stable structures in water with high porosity within MOF catalysts. MIL-88A(Fe) crystals exhibit an unprecedented "breathing effect" to change the pore size and shape relative to guest molecules without degradation of the framework structure. In addition to all these, they can be easily synthesized (does not require very high temperatures) and prepared with water without organic solvents which makes them environmentally friendly (Viswanathan et al., 2021; Gholizadeh Khasevani and Gholami., 2019; Shao et al., 2019). They also act as Fenton catalysts in the presence of H₂O₂ due to the iron in their structure, thus increase the degradation efficiency. Ag/AgCl nanoparticles can be easily dispersed on the surface of MIL-88A (Fe) crystals and increase their photocatalytic activity through the SPR effect. Ag/AgCl@MIL-88A

can be synthesized by the in-situ growth method using Cl fixed to the surface of MIL-88A to form Ag/AgCl nanoparticles (Wu et al., 2019).

When MOF and g-C₃N₄ are combined, the interaction between the numerous aromatic rings of the organic ligands in MOF and the triazine rings of g-C₃N₄ can lead to a significant surface electrostatic interaction. This will make it simpler to successfully build the heterojunction and realize the efficient electron transfer (Fan et al., 2021).

The charge transfer mechanism of the MIL-88A/g-C₃N₄ composite photocatalyst is schematized in Figure 2.4. Due to their low band gap energies, both MIL-88A (2.05 eV) (Gholizadeh Khasevani and Gholami, 2018) and g-C₃N₄ (2.7 eV) (Shao et al., 2019) form conduction band electrons-valence band holes under visible light. Since the conduction band electrons levels (e_{CB}^-) of g-C₃N₄ are more negative than those of MIL-88A, e_{CB}^- are transferred from g-C₃N₄ to MIL-88A. The valence band holes are moved from the MIL-88A valence band to the g-C₃N₄ valence band because the energy levels of the valence band holes (h_{VB}^+) of MIL-88A are more positive (Type 2 heterojunction). So, the separation of the $h_{VB}^+ - e_{CB}^-$ is accomplished. If the h_{VB}^+ energies of g-C₃N₄ are more positive than the oxidation potentials of OH⁻/OH• (1.99 eV) and H₂O/OH• (2.37 eV), h_{VB}^+ will react with OH⁻ and H₂O to form OH• radicals or directly oxidize Diuron. In addition, if the e_{CB}^- energy levels of MIL-88A are more negative than the O₂/O₂•⁻ reduction potential (-0.046 eV), the conduction band electrons of MIL-88A react with the surface adsorbed O₂, converting molecular oxygen to O₂•⁻ radicals (Huang et al., 2017; Zhang et al., 2017; Li et al., 2015; Shao et al., 2019) (Figure 2.4).

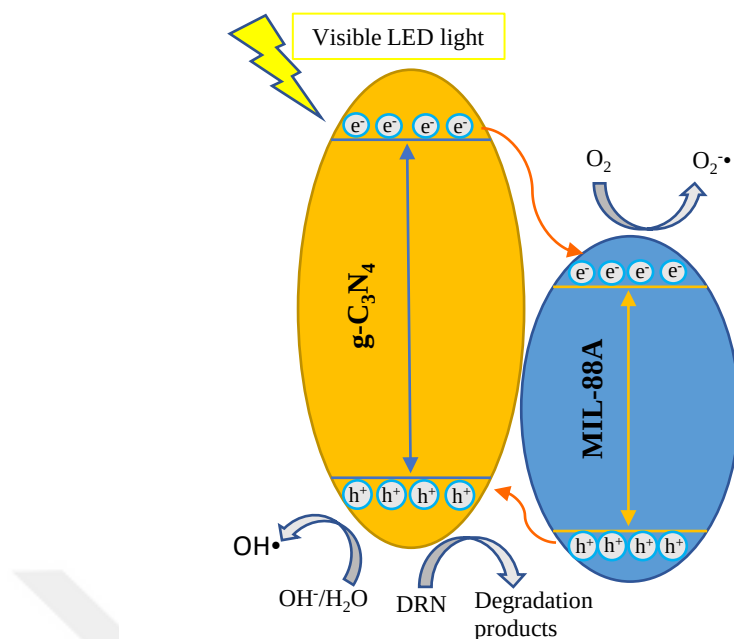


Figure 2.4 Schematic diagram of charge transfer mechanism of MIL-88A/g-C₃N₄.

The radical generation mechanism in the Ag/AgCl@MIL-88A/g-C₃N₄ triple composite photocatalyst is fundamentally different (Figure 2.5). Because of its surface plasmonic feature, metallic silver (Ag⁰) quickly produces electron-hole pairs when exposed to visible light, but silver chloride (AgCl) does not exhibit this behavior due to possess large band energy of 3.4 eV (Yentür and Dükkancı, 2020a). Therefore, both Ag and g-C₃N₄ conduction band electrons are transferred to the AgCl conduction band. MIL-88A conduction band electrons also combine with valence band holes on the Ag⁰ surface. Thus, conduction band electrons of AgCl react with O₂ to form O₂^{•-} radicals, while the valence band holes in MIL-88A react with OH⁻ and H₂O to create OH[•] radicals, in addition the valence band holes in g-C₃N₄ contribute to the oxidation of Diuron.

Although the charge transfer mechanism of MIL-88A/g-C₃N₄ photocatalyst has been tried to be explained in the literature (Shao et al., 2019; Gholizadeh Khasevani and Gholami, 2019), there is no study on the use of Ag/AgCl@MIL-88A/g-C₃N₄ ternary composite photocatalyst in photocatalytic reactions, and thus its mechanism was tried to be explained in the content of this study.

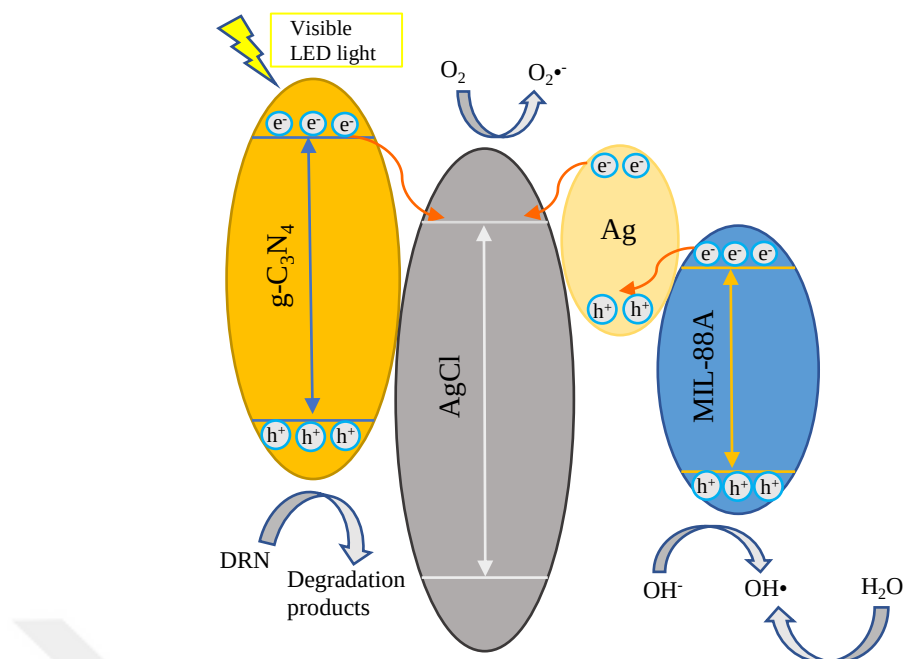


Figure 2.5 Schematic diagram of charge transfer mechanism of Ag/AgCl@MIL-88A/g-C₃N₄ under visible light irradiation.

2.2.2 Sonication

Sonolysis (sonication) is a type of AOPs in which sonochemical reactions are affected, facilitated, or accelerated by ultrasound (Theerthagiri et al., 2021). Sonolysis has recently attracted a great deal of interest for the mineralization of various organic contaminants as a result of its numerous benefits, which include operating simplicity, safety, and environmental friendliness (Qiu et al., 2018). Due to the absence of extra chemicals, sonolysis is considered a green method for water purification (Rayaroth et al., 2022).

Ultrasound is defined as any sound wave having a frequency exceeding 16 kHz that is inaudible to human ears. The frequency ranges of ultrasound waves include low (20–100 kHz), medium (300–1000 kHz), and high (2–10 MHz) (generally used in diagnostic medicine). The sonochemical phenomena is predominantly observed in the medium frequency range and, to a lesser extent, in the low frequency range (Andrade et al., 2021).

An aqueous solution is subjected to ultrasonic sound waves during sonolysis or sonochemical processes, resulting in the creation of bubbles (i.e., acoustic cavitation). Several chemical and physical reactions, such as the production of micro-sized bubbles, are dependent on the cavitation that is generated. In a fraction

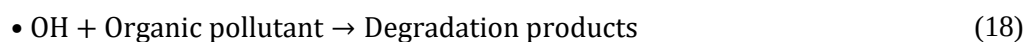
of a microsecond, the bubbles merge, collapse, and violently implode, producing shock waves at a high temperature of $\sim 5,000$ °C and pressure of $\sim 2,000$ atm. (Theerthagiri et al., 2021) Typically, the "Hotspot theory" is used to describe this phenomenon. In the hotspot theory, cavitation microbubbles are viewed as microreactors that generate heat and conduct chemical reactions. Inside the microbubbles, the severe conditions caused by the collapse of the bubbles result in the destruction of bonds and the dissociation of the solvent (generally water) or other vapors/gases, resulting to the formation of free radicals or excited states (Abdi et al., 2022).

There are three regions where the sonochemical process can occur:

1. The interior of the bubble cavity, also known as the gaseous region. Due to the high temperatures inside the cavity, pyrolytic reactions decompose volatile compounds and hydrophobic molecules in this region. As vaporized water molecules inside the bubble degrade, hydroxyl radicals are also produced in this region.
2. The second region is the bubble and liquid interface. This region is dominated by hydroxyl radical reactions that produce H_2O_2 and oxidize organic substrates.
3. The third region is bulk liquid. In this region, secondary sonochemical reactions, primarily involving oxidizing species and organic substrates, are produced by free radicals that escape from the bubble-liquid interface (Theerthagiri et al., 2021; Andrade et al., 2021; Joseph et al., 2009)

The following equations illustrate some of the main reactions that could result from cavitation (Eqs. 11-18). (Pang et al., 2011; Abdi et al., 2022; Andrade et al., 2021).





Frequency of ultrasound is the most important parameter that influence the size and quantity of the microbubbles. Microbubbles form in greater quantities and smaller sizes as the applied frequency rises. The massive amount and homogeneous distribution of microbubbles will encourage the generation and release of more radicals in the bulk solution. Additionally, boosting the ultrasonic equipment's power will increase the quantity of cavitation and radical production due to enhance the negative pressure exerted by ultrasound. Because of this negative pressure, the cavitation bubble expands more, become bigger and the cavity reaches the resonance size immediately; this results in the pyrolysis of water and reaction with $\text{OH}\bullet$. All these result in an enhancement in cavitation efficiency and thus sonochemical degradation (Abdi et al., 2022; Dükkancı, 2019).

To produce a fast ultrasonic degradation rate by ultrasound alone often requires a substantial amount of electrical energy because of the huge loss of input energy in thermal dissipation (> 50%). This circumstance impedes the widespread implementation of sonolysis for practical water treatment. The creation of a heterogeneous sonocatalyst is one of the most promising methods for expanding the application of sonolysis, because solid sonocatalyst could provide additional active sites for nucleation of bubbles that increases the quantity of cavitation bubbles formed (Qiu et al., 2018). Sonochemical processes generate free radicals that can rapidly convert harmful organic pollutants into less toxic or harmless substances, such as H_2O and CO_2 (Theerthagiri et al., 2021). However, sonolysis is an effective method for degrading hydrophobic contaminants, it is ineffective for hydrophilic substances (Yentür and Dükkancı, 2021). Diuron, the model contaminant employed for this study, is a moderately hydrophobic chemical with a $\text{Log } K_{\text{ow}}$ value of 2.6. It is thus expected that sonication will have a good impact on the degradation of diuron in wastewater.

In addition, the semiconductivity of catalyst particles and the sonoluminescence that happens during the collapse of microbubbles promote the creation of active radicals through charge separation and electron/hole generation. Sonocatalytic and sonophotocatalytic processes are two of the most prevalent in the

field of ultrasound application in AOPs with respect to this feature (Abdi et al., 2022). Sono-photocatalytic oxidation is a hybrid process that involves the combination of ultrasound, catalysis, and either visible or ultraviolet light. The benefits of ultrasonic irradiation extend beyond the generation of $\text{OH}\cdot$ radicals that oxidize organic contaminants and also include the reduction of mass transfer restrictions in heterogeneous catalytic systems via the induction of turbulence in solution. The catalyst surface is cleaned by ultrasonic irradiation, which aids in maintaining catalytic activity. Moreover, the mechanical effect of acoustic cavitation inhibits the aggregation of catalyst particles in aqueous solution (Yalçın and Dükkancı, 2022).



3. LITERATURE SURVEY

3.1 Literature Survey on Photocatalytic Oxidation of Various Organic Pollutants over MIL-88A based Photocatalysts

According to literature survey results, summary of some studies on the photocatalytic oxidation of various organic pollutants over MIL-88A based photocatalysts are given below. The photocatalytic reaction conditions and results are summarized in Table 3.1.

In the study by Viswanathan et al. (2021), two composites of Ag/AgCl@MIL-88A(Fe), referred to as MAG-1 and MAG-2, with molar ratios of Fe to Ag of 5:1 and 2:1, respectively, were effectively synthesized using simple in situ hydrothermal techniques and UV reduction. The produced composite materials were characterized by PXRD, FT-IR, UVDRS, FESEM/EDX, PL, TEM and BET analysis. In the presence of sunlight, the Ag/AgCl@MIL-88A(Fe) (MAG-2) composite photocatalyst demonstrated significant photocatalytic activity for the degradation of p-nitrophenol (PNP), rhodamine B (RhB), and methylene blue (MB). When MAG-2 was used as a catalyst under sunlight irradiation, 91% of PNP was found to degrade in 80 min, 99% of RhB in 70 min, and 94% of MB in 70 min. Isopropyl alcohol (IPA), benzoquinone (BQ), AgNO₃, and ethylenediaminetetraacetic acid (EDTA) were utilized as trapping agents for OH•, O₂•⁻, e⁻, and h⁺, respectively, to determine the major active species responsible for the photodegradation of PNP over Ag/AgCl@MIL88A(Fe). According to the findings, O₂•⁻ species were identified as the main radical responsible for the photocatalytic oxidation of PNP. Through the cycling test, the reusability of the Ag/AgCl@MIL-88A(Fe) photocatalyst was evaluated. During three consecutive photocatalytic processes, the Ag/AgCl@MIL-88A(Fe) photocatalyst exhibited no apparent decrease in PNP degradation.

Wu et al. (2019) effectively synthesized various shapes Ag/AgCl@MIL-88A (ACML) catalysts using different polar solvents utilizing the in-situ growth approach method. The catalysts were characterized by XRD, SEM, EDS, UV-Vis DRS, XPS, FT-IR, N₂ adsorption–desorption isotherms, PL, and TEM analysis. Rhodamine B (RhB) was used as a model organic pollutant to investigate the photocatalytic activity of ACML composites under simulated sunlight and visible light irradiation. The results of the photocatalytic studies showed that s-ACML was

significantly more effective than m-ACML and l-ACML in degrading RhB, the removal was 99.1% (s-ACML), 95.1% (m-ACML), and 85.8% (l-ACML) after 20 min of simulated solar irradiation. However, the degradation rate was 98.3% (s-ACML), 91.5% (m-ACML), and 35.1% (l-ACML) under visible light irradiation within 120 min, respectively. During the four-cycle test under simulating light or visible light, the s-ACML composite demonstrated high photocatalytic stability. In the trapping experiments, isopropyl alcohol, EDTA, and benzoquinone were utilized for scavenging $\text{OH}^\bullet$, h^+ , and $\text{O}_2^{\bullet-}$, respectively. According to results, EDTA and benzoquinone affected the photocatalytic efficiency of s-ACML negatively, indicating that h^+ and $\text{O}_2^{\bullet-}$ were the main active species in the visible light photocatalytic degradation of RhB.

In the study done by Huang et al. (2018), Ag/AgCl was combined with MIL-88A(Fe) to create Ag/AgCl@MIL-88A(Fe) (ACMA) nanocomposites using a simple one-pot solvothermal technique. AgCl@MIL-88A(Fe) nanocomposites were termed ACMA-1 (Fe:Ag = 5:1), ACMA-2 (Fe:Ag = 2:1), and ACMA-3 (Fe:Ag = 1:1). The photocatalysts were characterized by XRD, FT-IR, SEM-EDS, XPS, PL, UV-vis DRS and TEM. ACMA-2 exhibited highly effective photocatalytic activity in photocatalytic oxidation of ibuprofen (IBP), and the resulting photo-degradation rate was 10.8 and 40.4 times higher than that of MIL-88A(Fe) and Ag/AgCl, respectively. IBP was almost completely degraded over ACMA-2 within an irradiation period of 3.5 h, whereas the degradation efficiency of IBP was 76% for ACMA-1 and 93% for ACMA-3 in the same reaction duration. The reduction of total organic carbon (TOC) of 91% was achieved in the presence of ACMA-2 catalyst. As a result of trapping experiments, $\text{O}_2^{\bullet-}$, e^- and h^+ were found as the main reactive species in the photodegradation process.

Gholizadeh Khasevani and Gholami (2019) fabricated MIL-88A/g-C₃N₄ composite using an easy hydrothermal technique. Under visible light, the photocatalytic performance of MIL-88A/g-C₃N₄ was evaluated on the decomposition of Methylene Blue (MB). The photocatalysts were characterized by XRD, FT-IR, SEM, TEM, EDX, EIS, UV-Vis DRS and BET. The photoactivity of the MIL-88A/g-C₃N₄/H₂O₂ system was superior to that of the pure samples; about 85% of MB was degraded in 120 min under visible light irradiation. Under the same conditions, MIL-88A, g-C₃N₄, and MIL-88A/g-C₃N₄ remove 24.8%, 20%, and

75% of MB, respectively. For the purpose of determining the photostability of MIL-88A/g-C₃N₄ composite, recycling experiments were conducted, and the photodegradation of MIL-88A/g-C₃N₄ composite remained unchanged after three cycles of MB photodegradation. In order to investigate active species effect on degradation of MB, t-BuOH (TBA), 1,4-benzoquinone (BQ) and KI were used as scavengers for OH•, O₂⁻ and h⁺ respectively. The results demonstrated that the radical species OH• and O₂⁻ played the major influence in the photodegradation of MB dye.

Shao et al. (2019) manufactured MIL-88A/g-C₃N₄ composites with varying MIL-88A content (with mass ratios of the MIL-88A for 3%, 7%, 10%, 15% and 20%) using a simple hydrothermal technique. XRD, SEM, TEM, XPS, and DRS were utilized to characterize as-prepared materials. The photocatalytic activity of the MIL-88A/g-C₃N₄ photocatalyst was examined for Rhodamine B (RhB), tetracycline, and phenol degradation under visible light irradiation. M88/g-C₃N₄-10 (with MIL-88A mass ratio of 10%) was the most active photocatalyst, degrading RhB completely in 30 min when exposed to visible light. Also, after 120 min of reaction time, M88/g-C₃N₄-10 was capable of degrading nearly 22% of tetracycline and 45% of phenol. Radical scavenger runs were conducted to investigate the role of active species in the photocatalytic reaction and possible degradation pathway of the degradation process. The quenchers used to trap the OH•, h⁺, and O₂⁻ were isopropanol (IPA), disodium ethylenediamine tetraacetic acid (EDTA-2Na), and 1,4-benzoquinone (BZQ), respectively. The results showed that OH• was the main active species on photocatalytic degradation of RhB in the presence of M88/g-C₃N₄-10.

In the study done by Huang et al. (2022), the three types of g-C₃N₄ (bulk, tubulous and rod) and MIL-88A structures were combined using the ball milling technique by modifying the MIL-88A and g-C₃N₄ content (x%MIL-88A@CN where x = 3%, 6%, and 9%). The prepared catalysts were characterized by XRD, XPS, SEM, TEM, ESR, BET and UV-vis DRS. When TCN (tubulous g-C₃N₄) alone was employed for phenol removal, no significant change was seen, however 73.8% degradation was observed within 30 min when pure MIL-88A was used as catalyst. In the presence of 6%MIL-88A@TCN (tubulous) catalyst, photodegradation was 99.9% at 30 min. In addition, trapping agents (t-butanol for

$\text{OH}\cdot$, benzoquinone for $\text{O}\cdot_2^-$, and EDTA-2Na for h^+) were added to the reaction system, and it was concluded that h^+ , $\text{O}\cdot_2^-$ and $\text{OH}\cdot$ were the main active radicals in the applied reaction process. The results of recycling experiments revealed that after five recycles, the 6%MIL-88A@TCN showed no noticeable reduction, indicating high stability for the photocatalyst.

Tan et al. (2022) synthesized different MIL-88A/g- C_3N_4 photocatalysts (as 3-M88A/CN, 5-M88A/CN, 7-M88A/CN, and 9-M88A/CN with MIL-88A contents of 30 wt%, 50 wt%, 70 wt%, and 90 wt%, respectively) and studied the activity of the photocatalyst in Acid Red 1 (AR1) dye degradation. The prepared catalysts were characterized by FESEM, XPS, XRD and UV-vis DRS. The 3-M88A/CN composite demonstrated a degradation efficiency of 100% within 30 min for AR1 dye degradation under simulated sunlight irradiation. This was accomplished without addition of an oxidizing agent. When subjected to repeated usage of catalyst, the composite preserved its degradation efficiency at 97%. Isopropanol (IPA), ammonium oxalate (AO), and nitrogen (N_2) were used as the trapping agents of hydroxide radicals ($\text{OH}\cdot$), photogenerated holes (h^+), and superoxide radicals ($\text{O}\cdot_2^-$), respectively, to confirm the major active species in the photocatalytic reaction system. Based on the findings, it was determined that the major active species involved in the photocatalytic activity was the h^+ .

MIL-88A was produced in a range of sizes (MIL-88A-1 and MIL-88A-2) at room temperature by Fu et al. (2020). The prepared catalysts were characterized using SEM, XRD, FTIR, and UV-vis DRS. After 80 min of visible light irradiation, both MIL-88A-1 and MIL-88A-2 catalysts displayed nearly complete degradation towards RhB and BPA in the presence of H_2O_2 . Also, active species tests were conducted using EDTA and IPA as trapping agents to capture h^+ and $\text{OH}\cdot$ radical, respectively, and it was demonstrated that $\text{OH}\cdot$ radicals contributed significantly to the photocatalytic destruction of RhB and BPA. Additionally, the prepared photocatalysts had acceptable reusability, and the degradation efficiency did not decrease after five cycles.

$\text{BiOI@MIL-88A(Fe)@g-C}_3\text{N}_4$ nanocomposite was produced hydrothermally with core@shell structure in the study done by Gholizadeh Khasevani and Gholami (2018). XRD, FT-IR, SEM, TEM, EDX, EIS, UV-vis DRS, and BET analyses were

utilized to characterize photocatalysts. The photocatalytic activities of synthesized samples were tested for the degradation of Acid Blue 92 (AB92), Rhodamine B (RhB), and phenol under visible light. BiOI@MIL-88A(Fe)@g-C₃N₄ showed significant photocatalytic degradation activity when exposed to visible light. After 180 min of irradiation, it was able to degrade almost 88% of AB92, 75% of RhB, and 70% of phenol, respectively. In the experiments, trapping agents were used to capture active species such as 1,4-benzoquinone for O₂^{•-}, KI for h⁺ and OH[•], and tertbutyl alcohol for OH[•]. In the presence of BiOI@MIL-88A(Fe)@g-C₃N₄ photocatalyst, the results revealed that the O₂^{•-} radical was the major active species in the degradation reaction.

Viswanathan et al. (2020) fabricated three different morphologies of MIL-88 A(Fe), such as rod (r), diamond (d), and spindle (s), and examined their photocatalytic activity to degrade RhB in the presence of H₂O₂ under sunlight. FT-IR, PXRD, UVDRS, SEM, TEM, PL, XPS, and BET were used to characterize these three catalysts. Using d-MIL-88A(Fe) and s-MIL-88A(Fe) as catalysts, the percentage degradation of RhB was 72% and 51%, respectively. A degradation of 98% was achieved within 50 min over r-MIL-88A(Fe) in the presence of H₂O₂. In addition, after five cycles, the r-MIL-88 A(Fe) catalyst showed just a small drop of about 5%, confirming its good stability. Also, trapping studies were performed using p-benzoquinone (O₂^{•-} scavenger), AgNO₃ (electron scavenger, e⁻), isopropyl alcohol (OH[•] scavenger), and EDTA-2Na (h⁺ scavenger) to identify the main active species involved in the decomposition of RhB under natural sunlight. According to the findings, the major active species in the photodegradation of RhB were O₂^{•-}, e⁻, and OH[•] radicals.

In another study done by Govarthanan et al. (2021) photocatalytic degradation of methylene blue (MB) and rhodamine-B (RhB) were investigated over molybdenum disulfide (MoS₂)-linked metal-organic frameworks (MOFs) under visible light irradiation. SEM, EDX, HR-TEM, PXRD, FTIR, BET, TGA, UV-Vis DRS, PL, ESR and LC-MS were used for the characterization of prepared catalysts. The MoS₂@MIL-88(Fe) catalyst showed significant photocatalytic performance compared to the MIL-88(Fe) framework and MoS₂. The degradation efficiency of MB and RhB over the as-synthesized MoS₂@MIL-88(Fe) framework were 98.5% and 97.4%, respectively, within 60 min. Isopropyl alcohol (IPA), 5,5-

dimethyl-1-pyrroline-N-oxide (DMPO), benzoquinone (BQ), and ethylenediaminetetraacetic acid (EDTA) were used as trapping agents to capture the SO_4^{2-} , $\text{OH}\cdot$, $\text{O}_2^{\cdot-}$, and h^+ species, respectively. As a result of the trapping experiments, $\text{OH}\cdot$ and $\text{O}_2^{\cdot-}$ were the main active species in the photodegradation process. After five successive cycles, the $\text{MoS}_2@\text{MIL-88(Fe)}$ framework showed insignificant loss of catalytic activity, demonstrating the photocatalyst's exceptional stability and reusability.

In the work of Li et al. (2021), a series of $\text{MIL-88A(Fe)/Bi}_2\text{WO}_6$ (M88/BWO) heterojunction photocatalysts were synthesized by a low-temperature hydrothermal process. According to the mole ratios of the BWO (3%, 7%, 10%, and 15%), the obtained photocatalysts were named as M88/BWO-3, M88/BWO-7, M88/BWO-10, and M88/BWO-15. The photocatalysts were characterized by XRD, SEM, TEM, HRTEM, XPS, BET, FT-IR, TGA, UV-vis DRS and PL. To assess the visible-light photocatalytic activity of the produced samples, Rhodamine B (RhB) and Tetracycline (TC) were chosen as the model pollutants. The M88/BWO-7 composite displayed better photocatalytic activity than M88 and BWO, with 96% (RhB) and 71% (TC) degradation within 50 min and 80 min, respectively. In addition, the reusability and stability of photocatalysts were investigated, and the results indicating that the composite exhibited high photostability after four cycles of photocatalytic tests. The ethylenediamine tetra acetic acid disodium salt (EDTA-2Na), p- benzoquinone (BQ), and isopropanol (IPA) were used as trapping agents for holes (h^+), superoxide radicals ($\text{O}_2^{\cdot-}$), and hydroxyl radicals ($\text{OH}\cdot$). $\text{O}_2^{\cdot-}$ and h^+ were the main active species involved in the photodegradation of RhB, as determined by the results of trapping tests.

In the study of Liu et al. (2018), the $\text{MIL-88A(Fe)/Graphene oxide}$ composites were synthesized by adjusting the mass ratios of MIL-88A(Fe) vs Graphene oxide by a simple one-pot solvothermal technique. The obtained composites with 1 wt%, 5 wt%, 9 wt%, 11 wt% graphene oxide (GO) was denoted as M88/GO-1, M88/GO-5, M88/GO-9, and M88/GO-11, respectively. The prepared photocatalysts were characterized by XRD, FT-IR, SEM, TEM, XPS, BET, UV-vis DRS and PL. Rhodamine B (RhB) was degraded over the prepared M88A/GO composites with H_2O_2 under visible light irradiation. Almost complete degradation was achieved in the M88/GO-9/ H_2O_2 /Vis system within 80 min. Cycle

tests were conducted to investigate the reusability of the M88/GO-9 photocatalyst. After five recycles, a very low decrease in the photocatalytic activity of M88/GO-9 was observed. This indicated that the catalyst had sufficient stability during the photodegradation process. To investigate the active species involved in the RhB removal by the M88/GO-9/H₂O₂ system, radical scavengers of p-benzoquinone (for O₂^{•−}), AgNO₃ (for electron, e[−]), isopropyl alcohol (for OH[•]), and EDTA-2Na (for h⁺) were used to capture active species. As a result, it could be said that, O₂^{•−}, e[−] and OH[•] were the main active species involved in the photodegradation of RhB.

Vigneshwaran et al. (2021) synthesized a bio-assisted 2D/2D TiO₂/MIL-88(Fe) (TCS@MOF) heterojunction and the sample was characterized by XRD, FT-IR, SEM, EDX, TGA-DTA, UV–Vis DRS, BET and XPS. The TCS@MOF composite was fabricated using a solvothermal technique for monocrotophos (MCP) degradation in the presence of visible light. Under optimal conditions, where the initial pH was 6 and the initial MCP concentration was 20 mg/L, it was observed that MCP degraded by around 98.79% in 30 min of irradiation. According to the electron spin response (ESR) spectra results, hydroxyl (OH[•]) and superoxide (O₂^{•−}) radicals were the active radicals involved in the photocatalytic degradation of MCP. The TCS@MOF photocatalyst exhibited acceptable reusability, and the degradation efficiency did not diminish after five cycles.

In the study of Tang et al. (2022), Ag/AgBr@MIL-88A(Fe) (ABM) photocatalyst was fabricated by in-situ growth method and characterized by XRD, FT-IR, SEM, TEM, XPS, BET, UV–vis DRS and PL. The Ag/Fe mole ratios were selected as 2.5% (ABM-1), 10% (ABM-2) and 20% (ABM-3). The ABM-2 composite exhibited superior photocatalytic activity for tetracycline hydrochloride (TC-HCl) degradation than that of Ag/AgBr and MIL-88A(Fe) under simulated sunlight. The degradation efficiency of the ABM-2 photocatalyst was observed to be 95.1% in 90 min of reaction time. During the four-cycle test under simulating light, ABM-2 displayed good photocatalytic activity, with the TC-HCl degradation efficiency persisting at around 83%. In order to carried out trapping experiments, O₂^{•−}, h⁺ and OH[•] were captured by BQ, TEOA and IPA, respectively. The experiments revealed that O₂^{•−} and h⁺ were the main active species in the TC-HCl photodegradation process.

Gu et al. (2022) developed a new ternary MIL-88A(Fe)/BiOBr/SrFe₁₂O₁₉ (MBSr) nanocomposite using a hydrothermal technique and evaluated its activity on Rhodamine B (RhB) and Methylene blue (MB) degradation under visible light irradiation. The mole ratio of SrFe₁₂O₁₉ in ternary composites was adjusted to be 0.5%, 1%, and 3%, resulting in MBSr-0.5%, MBSr-1%, and MBSr-3%, respectively. The photocatalysts were characterized by XRD, FT-IR, BET, SEM, TEM, XPS, PL, and UV–vis DRS. In presence of MBSr-1% composite, 96.2% and 90.1% degradation of RhB and MB were achieved within 60 min and 90 min, respectively. During trapping experiments, OH•, h⁺, and O•⁻ were captured by isopropanol (IPA), ethylenediamine tetra acetic acid disodium salt (EDTA-2Na), and p-benzoquinone (BQ), respectively. As a result of these experiments over MBSr-1%, the major reactive species were h⁺, O•⁻ and OH• for RhB photodegradation. In addition, six recycling runs demonstrated that MBSr-1% had remarkable stability and reusability.

Table 3.1 The photocatalytic oxidation reaction conditions and results of various organic pollutants over MIL-88A based photocatalysts.

Pollutant types, concentration, and volume	Photocatalyst type and amount	Solvent type	Oxidant type and amount	Light type and power	Degradation efficiency (%)	Illumination time (min)	Active species	Reference
p-nitrophenol (PNP), Rhodamine B (RhB), Methylene blue (MB) (10 ppm, 50 mL)	Ag/AgCl@MIL-88A(Fe) (2 g/L for PNP experiments and 0.5 g/L for RhB and MB experiments)	Water	-	natural sunlight, 60 000–65 000 lux	91 (PNP) 99 (RhB) 94 (MB)	80 70 70	$O_2^{\bullet -}$	Viswanathan et al., 2021
Rhodamine B (RhB) (20 ppm, 100 mL)	Ag/AgCl@MIL-88A (s-ACML) (0.5 g/L)	Dimethylformamide (DMF)	-	simulated solar light and visible light, 500 W halide lamp	99.1 98.3	20 (solar) 120 (vis)	h^+ and $O_2^{\bullet -}$	Wu et al., 2019
Ibuprofen (10 ppm, 50 mL)	Ag/AgCl@MIL-88A(Fe) (ACMA-2) (0.4 g/L)	DMF	-	visible light, 500 W Xenon lamp	~100	210	$O_2^{\bullet -}$, e^- and h^+	Huang et al., 2018
Methylene Blue (MB) (100 mL)	MIL-88A/g- C_3N_4 (0.1 g/L)	Deionized water	H_2O_2	visible light, 300 W Xenon lamp	85	120	$OH^{\bullet}$ and $O_2^{\bullet -}$	Gholizadeh Khasevani & Gholami, 2019
Rhodamine B (RhB), tetracycline and phenol (10 ppm, 100 mL)	MIL-88A/g- C_3N_4 (M88/g- C_3N_4 -10) (1 g/L)	Ultrapure water	-	visible light, 1000 W iodine tungsten lamp	100 (RhB) 22 (tetracycline) 45 (phenol)	30 120 120	$OH^{\bullet}$	Shao et al., 2019

Table 3.1 The photocatalytic oxidation reaction conditions and results of various organic pollutants over MIL-88A based photocatalysts (continued).

Pollutant types, concentration, and volume	Photocatalyst type and amount	Solvent type	Oxidant type and amount	Light type and power	Degradation efficiency (%)	Illumination time (min)	Active species	Reference
Phenol (100 ppm, 150 mL)	MIL-88A/g-C ₃ N ₄ 6% MIL-88A@TCN (tubulous) (0.1 g/L)	Water	H ₂ O ₂ , (100 µL)	visible light, 500 W xenon lamp	99.9	30	h ⁺ , O ₂ ^{•-} and OH [•]	Huang et al., 2022
Acid Red 1 (AR1) dye (10 ppm, 50 mL)	MIL-88A/g-C ₃ N ₄ (3-M88A/CN) (1 g/L)	Deionized water	-	visible light, 500 W xenon lamp with a light intensity of 273 W/m ²	100	30	h ⁺	Tan et al., 2022
Rhodamine B and Bisphenol A (10 ppm, 50 mL)	MIL-88A (0.2 g/L)	Ultrapure water	H ₂ O ₂ (100 µL)	visible light, 350 mW LED lamp	100	80	OH [•]	Fu et al., 2020
Acid Blue 92 (AB92), Rhodamine B (RhB), and phenol (10 ppm, 100 mL)	BiOI@MIL-88A(Fe)@g-C ₃ N ₄ (0.1 g/L)	Ultrapure water	-	visible light, 300 W xenon lamp	88 (AB92) 75 (RhB) 70 (phenol)	180	O ₂ ^{•-}	Gholizadeh Khasevani & Gholami, 2018
Rhodamine B (RhB) (10 ppm, 100 mL)	MIL-88A(Fe) (r-MIL-88A(Fe)) (0.2 g/L)	Water	H ₂ O ₂ (20 mM)	natural sunlight	98	50	O ₂ ^{•-} , OH [•] and e ⁻	Viswanathan et al., 2020
Methylene Blue (MB) and Rhodamine B (RhB) (50 ppm, 50 mL)	MoS ₂ @MIL-88A(Fe) (2 g/L)	Ethanol/ water medium	-	visible light, 250 W xenon lamp (400-800 nm with a light intensity of 0.15 mW/cm ²)	98.5 (MB) 97.4 (RhB)	60	OH [•] and O ₂ ^{•-}	Govarthanan et al., 2021

Table 3.1 The photocatalytic oxidation reaction conditions and results of various organic pollutants over MIL-88A based photocatalysts (continued).

Pollutant types, concentration, and volume	Photocatalyst type and amount	Solvent type	Oxidant type and amount	Light type and power	Degradation efficiency (%)	Illumination time (min)	Active species	Reference
Rhodamine B (RhB) Tetracycline (TC) (10 ppm, 50 mL)	MIL-88A(Fe)/Bi ₂ WO ₆ (M88/BWO-7) (0.4 g/L)	Deionized water	-	visible light, 300 W Xenon lamp	96 (RhB) 71 (TC)	50 80	O ₂ ^{•-} and h ⁺	Li et al., 2021
Rhodamine B (RhB) (10 ppm, 50 mL)	MIL-88A(Fe)/graphene oxide (M88/GO-9/H ₂ O ₂ /Vis) (0.4 g/L)	ultrapure water	H ₂ O ₂ (20 mM)	visible light, 500W Xe lamp	~100	80	O ₂ ^{•-} , e ⁻ and OH [•]	Liu et al., 2018
Monocrotophos (MCP) (20 ppm)	TiO ₂ /MIL-88(Fe) (TCS@MOF) (0.05 g/L)	DMF	-	visible light, 350 W Xenon lamp	~98.79	30	OH [•]	Vigneshwaran et al., 2021
Tetracycline hydrochloride (TC-HCl) (10 ppm, 100 mL)	Ag/AgBr@MIL-88A(Fe) (ABM-2) (0.2 g/L)	Ultrapure water	-	simulated sunlight, 300 W Xe lamp	95.1	90	O ₂ ^{•-} and h ⁺	Tang et al., 2022
Rhodamine B (RhB) and Methylene blue (MB) (10 ppm, 50 mL)	MIL-88A(Fe)/BiOBr/SrFe ₁₂ O ₁₉ (MBSr-1%) (1 g/L)	Deionized water	-	visible light, 300 W Xenon lamp	96.2 (RhB) 90.1 (MB)	60 90	h ⁺ , O ₂ ^{•-} , and OH [•]	Gu et al., 2022

3.2 Literature Survey on Photocatalytic Oxidation of Diuron over Various Photocatalysts

There are several investigations on the photocatalytic oxidation of pesticide diuron over various photocatalysts in literature. The photocatalytic reaction conditions and results are summarized in Table 3.2.

In the study by Lopes and Salgado (2021), Diuron (DRN) photodegradation was carried out over TiO_2 and ZnO catalysts. Experimental design was performed to evaluate the impact of pH, catalyst, and substrate concentration on DRN degradation. DRN was completely degraded over TiO_2 in 180 min at pH=10, and ZnO gave the photocatalytic activity greater than 98%. In trapping agent experiments, the $\text{OH}^\bullet$, $\text{O}_2^{\bullet-}$, and h^+ were captured by methanol, ascorbic acid, and EDTA, respectively. In the presence of TiO_2 catalyst, $\text{OH}^\bullet$ and $\text{O}_2^{\bullet-}$ were observed to be the primary active species, while $\text{OH}^\bullet$ was the primary active species in the presence of ZnO catalyst.

In the investigation conducted by López-Ramón et al. (2019), a nickel organic xerogel (X-Ni) was employed as a photocatalyst to degrade DRN. To decompose DRN from water, both direct photolysis and photocatalytic degradation were studied, and the efficiency of solar radiation was analyzed. The degradation of DRN increased from 35.6% to 79% when the initial concentration of DRN was decreased in direct photolysis process. It was stated that the introduction of X-Ni to the process (photocatalytic) greatly enhanced degradation under solar radiation. Consequently, when 4167 mg/L X-Ni photocatalyst was added to the solution, both the degradation and mineralization percentages reached to 88.5%, and the removal rate of DRN was 3 times higher than the removal rate obtained by direct photolysis. The stability of nickel xerogel was tested with four consecutive photocatalytic experiments, and the results suggested that the photocatalyst exhibited good stability, as just a minor decline in catalytic activity was detected.

Anirudhan et al. (2018) fabricated carboxylic graphene/polyaniline (ZnR@CGR/PANI) composite and assessed the photocatalytic activity of the ZnR@CGR/PANI composite by DRN degradation. FTIR, XRD, SEM, TEM, Surface Area Analyzer, Raman spectroscopy, AFM, DRS, PL, and Cyclic voltammetry were used to characterize the photocatalyst. The degradation

efficiency of the ZnR@CGR/PANI photocatalyst was observed as 100% in 40 minutes. Five photocatalytic test cycles were done to examine the stability of the ZnR@CGR/PANI composite.

In the study by Mendiola-Alvarez et al. (2021), the photocatalytic performance of P-doped $\text{Fe}_2\text{O}_3/\text{TiO}_2$ ($\alpha\text{Fe-Ti/P}$) mixed oxide was evaluated under UV and visible light irradiation in the photodegradation of DRN. The TiO_2 containing P (Ti/P) and $\alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2$ (Fe-Ti) were also produced under similar circumstances. The catalysts were characterized by XRD, UV–VIS with DRS, PL, N_2 adsorption, XPS, HRTEM, and FTIR analysis. The Ti/P catalyst demonstrated higher photocatalytic activity for DRN degradation compared to the other produced catalysts. Using the Ti/P catalyst, complete degradation was achieved in 240 min under UV and visible light. Moreover, the Ti/P catalyst provided 60% mineralization under UV light and 48% mineralization under visible light.

Yasmeen et al. (2019) developed g- C_3N_4 nanosheets linked with varied mass ratios of bismuth tungstate (Bi_2WO_6) nanosheets (i.e., 5, 10, 15 and 20%) to decompose DRN under visible-light irradiation. The synthesized photocatalysts were characterized by XRD, XPS, UV-vis DRS, TEM, HRTEM, and PL. The $15\text{Bi}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ (15% Bi_2WO_6) heterostructure demonstrated greater photocatalytic activity (75%) than pure g- C_3N_4 (33%) and Bi_2WO_6 (35%) after 60 min of reaction. Five recycling tests were conducted to determine the stability of the 15BWO/CN photocatalyst, and it was determined that the structure of the catalyst was highly stable. The radical trapping studies was performed using of p-benzoquinone (p-BQ), EDTA-2Na, and isopropyl alcohol (IPA), in order to capture $\text{O}\cdot^-$, h^+ , and $\text{OH}\cdot$, respectively. The outcomes demonstrated that during the photocatalytic degradation of DRN in the presence of 15BWO/CN composite, $\text{OH}\cdot$ radicals were the main active species.

In the study done by Saber et al. (2021), ternary $\text{Au@TiO}_2/\text{rGO}$ nanocomposites were prepared using a solvothermal one-pot approach. The nanocomposites were characterized by XRD, Raman spectroscopy, HRTEM, XPS, BET and UV-vis DRS. Photodegradation of MB and DRN was used to examine the photocatalytic activity. The ternary nanocomposite demonstrated excellent

photocatalytic degradation of the organic contaminants DRN (100% degradation in 120 min) and MB (100% degradation in 180 min).

Kesarla et al. (2019) synthesized g-C₃N₄/CeO₂ composite in the presence of l-arginine and the synthesized catalysts were characterized by XRD, UV–Vis, BET, XPS, SEM and HR-TEM. Photocatalytic activities of g-C₃N₄, exfoliated g-C₃N₄, and the g-C₃N₄/CeO₂ composite were tested on DRN degradation. According to photocatalytic activity studies, bulk g-C₃N₄, exfoliated g-C₃N₄, and g-C₃N₄/CeO₂ catalysts decomposed 15%, 34%, and 46% of DRN after 120 min of reaction time, respectively. Based on the radical scavenger run results, O₂^{•−} radicals were determined as the main active species in the oxidation of DRN in the presence g-C₃N₄/CeO₂ photocatalyst. The g-C₃N₄/CeO₂ composite was evaluated over four consecutive cycles for stability and the composite remained stable over all cycles.

In the research carried out by Oliveira et al. (2020), the Pechini method was used to produce TiO₂ and TiO₂:CoFe₂O₄ catalysts, while the combustion approach was utilized to produce CoFe₂O₄. Additionally, CoFe₂O₄ was utilized in the following mass ratios: 90TiO₂:10CoFe₂O₄ (90Ti), 70TiO₂:30CoFe₂O₄ (70Ti), and 50TiO₂:50CoFe₂O₄ (50Ti). XRD, BET, SEM, granulometric analysis, FT-IR, zeta potential and magnetic measurements were used to characterize the nanocatalysts. All of the tested nanocatalysts (CoFe, 50Ti, 70Ti, and 90Ti) exhibited significant photocatalytic degradation efficiency and were able to completely remove DRN under UV irradiation in 300 min of reaction time. Moreover, it was determined that the mineralization efficiency of photocatalytic systems improved as the CoFe₂O₄ concentration decreased.

In the study of Bhoi et al. (2018), a series of CuS/Bi₂W₂O₉ photocatalysts were synthesized and the photocatalytic activities of these catalysts were investigated on the degradation of DRN under visible light. The CuS/Bi₂W₂O₉ heterojunction photocatalysts containing 5, 10, 15, and 20 wt% CuS were prepared. The analyses of XRD, XPS, FESEM, TEM, FT-IR, UV-vis-DRS, and PL were utilized in order to characterize the photocatalysts. The CuS20BWO photocatalyst showed the highest photocatalytic degradation and among the several oxidants applied (O₂ flow 30 ml/min, O₃ flow 30 ml/min, H₂O₂ 200 µl), the highest degradation of 95% was obtained after 180 min in the presence of H₂O₂. To

examine the influence of pH, the pH of the DRN solution was adjusted to between 2 and 10. The rate of DRN decomposition was reported to be greater at acidic pH and to decrease with rising pH. The $\text{OH}^\bullet$, $\text{O}_2^\bullet$, e^- , and h^+ were trapped by t-butyl alcohol, benzoquinone, AgNO_3 , and ammonium oxalate, respectively, in the trapping studies. In the presence of CuS20BWO catalyst, the major active species were identified as $\text{OH}^\bullet$ and h^+ . Furthermore, the photocatalyst CuS20BWO displayed stable activity for five consecutive cycles.

Saidani et al. (2019) synthesized Ag/ZnO photocatalysts utilizing a modified polyol method with triethylene-glycol (TEG) as a solvent, reducing agent, and stabilizing agent. The photocatalysts were characterized using XRD, TEM, N_2 adsorption, inductively coupled plasma optical emission spectroscopy (ICP-OES), BET, and UV–Vis DRS. Under solar light, the photocatalytic activity of Ag/ZnO catalysts has been examined on the degradation of DRN. The obtained results showed that the incorporation of Ag nanoparticles with the proper amount on ZnO surface demonstrated greater photocatalytic performance than pure ZnO. In the presence of 0.7%Ag/ZnO photocatalyst, the DRN was completely degraded after 90 min of solar irradiance. The stability of the 0.7% Ag/ZnO photocatalyst under sunlight was also investigated. After five consecutive cycles of degradation tests, it was observed that the photocatalytic activity of the catalyst did not decline considerably.

Anirudhan et al. (2020) fabricated a titanium dioxide (mTiO_2) conducting molecularly imprinted polymer (mTiO_2 -MIP) for the degradation of DRN. The photocatalyst was characterized using FT-IR, XRD, SEM, AFM, TEM, VSM, XPS, UV–Vis DRS, photoluminescence spectroscopy, cyclic voltammetry, and electrochemical impedance spectroscopic techniques. A degradation of 98.0% of the DRN was achieved over mTiO_2 -MIP composite within 40 min of visible light exposure. Additionally, the photodegradation of DRN was investigated for a pH range between 2.0 and 9.0. The results indicated that the maximum degradation occurred at pH 3.5. The stability of mTiO_2 -MIP was evaluated, and the results indicated the stability of the catalyst.

Table 3.2 The reaction conditions and results of photocatalytic oxidation of Diuron on various photocatalysts.

Diuron concentration (ppm) and volume (mL)	Photocatalyst type and amount	pH	Light type and power(W)	Diuron Degradation (%)	Illumination time (min)	Active species	Reference
20 ppm	TiO ₂ and ZnO (1 g/L)	10	35 W Xe lamp (wavelength ranging from 350 to 800 nm)	100	180	OH• and O ₂ ⁻	Lopes and Salgado, 2021
25 ppm	Nickel organic xerogel (X-Ni) (4.167 g/L)	2	solar radiation, 450W/m ² Xe lamp (300 to 800 nm)	88.5	240	-	López-Ramón et al., 2019
5 ppm, 50 mL	ZnR@CGR/PANI (zinc oxide nanorod incorporated carboxylic graphene/polyaniline) (2 g/L)	3	visible light 100 mW/cm ² , Solar simulator	100	40	-	Anirudhan et al., 2018
10 ppm, 450 mL	mixed oxide α -Fe ₂ O ₃ /TiO ₂ doped with P (α Fe-Ti/P) (1g/L)	7	20 W/m ² UV-lamp (365nm) 400 W/m ² visible light lamp (400–700 nm)	100	240	-	Mendiola-Alvarez et al., 2021
20 ppm, 50 mL	Bi ₂ WO ₆ /g-C ₃ N ₄ (15Bi ₂ WO ₆ /g-C ₃ N ₄) (4 g/L)	-	visible light, 150 W Xe light ($\lambda > 400$ nm)	75	60	OH•	Yasmeen et al., 2019
7 ppm, 30 mL	Au@TiO ₂ /rGO (0.23 g/L)	7	Visible lamp (400 W Metal Halide equipped with a 400 nm filter) UV lamp (300 W Hg equipped with a 365 nm filter)	100	120	-	Saber et al., 2021

Table 3.2 The reaction conditions and results of photocatalytic oxidation of Diuron on various photocatalysts (continued).

Diuron concentration (ppm) and volume (mL)	Photocatalyst type and amount	pH	Light type and power(W)	Diuron Degradation (%)	Illumination time (min)	Active species	Reference
25 ppm, 200 mL	g-C ₃ N ₄ /CeO ₂ (0.15 g/L)	-	Solar simulator, 1500 W xenon lamp	46	120	O ₂ ^{•-}	Kesarla et al., 2019
40 ppm, 150 mL	TiO ₂ :CoFe ₂ O ₄ (0.5 g/L)	3	125 W high-pressure Hg vapor UV lamp (λ = 360 nm)	100	300	-	Oliveira et al., 2020
10 ppm, 100 mL	CuS/Bi ₂ W ₂ O ₉ (0.075 g/L)	2	visible light (150 W Xe lamp) (λ > 400 nm)	95	180	OH [•] and h ⁺	Bhoi et al., 2018
10 ppm, 100 mL	Ag/ZnO (0.1 g/L)	-	Solar light (1700 W Air- cooled Xenon lamp) (300–800 nm)	100	90	OH [•]	Saidani et al., 2019
10 ppm, 50 mL	mTiO ₂ -MIP (2 g/L)	3.5	visible light 100 mW/cm ² , Solar simulator	98	40	OH [•] and O ₂ ^{•-}	Anirudhan et al., 2020

In the present study, photocatalytic oxidation of diuron-containing wastewater over a novel triple Ag/AgCl@MIL-88A/g-C₃N₄ composite was investigated. According to the findings of the literature search, it was observed that the activity of MIL-88A-based photocatalysts was mostly investigated on the photocatalytic oxidation of organic pollutants such as rhodamine B, methylene blue, tetracycline, and phenol. As seen in Table 3.1, most of the research centered on dye degradation. It has been observed that studies using MOF-based materials in the photocatalytic treatment of pesticide-containing wastewater are limited. To the best of our knowledge, there is no study on the photocatalytic oxidation of DRN using Ag/AgCl@MIL-88A/g-C₃N₄ MOF-based heterostructure under visible LED light irradiation. Ag/AgCl@MIL-88A/g-C₃N₄ triple composites were prepared by changing the photodeposition time, Ag loading amount and type of sacrificial agent for the first time in the present study.

As seen in the Table 3.1 and 3.2, in recent years studies of photocatalytic oxidation have generally involved Xenon lamps but these are expensive and short-lived light sources that are not easy to install. In this study, long-lasting, flexible and low-cost LED (light-emitting diode) lamps was used as a light source which is an important factor which increases the significance of the study.

4. EXPERIMENTAL STUDY

4.1 Materials

Diuron (DRN) (>98%) and melamine (99%) were purchased from Sigma Aldrich. Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), silver nitrate (AgNO_3), hydrogen peroxide (H_2O_2), potassium peroxodisulfate (PS), p-Benzoquinone, isopropyl alcohol, sodium nitrate (NaNO_3), sodium sulfate (Na_2SO_4), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), hydrochloric acid (HCl), glycerol and acetonitrile were obtained from Merck. Ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4$) was purchased from Carlo Erba. Fumaric acid was procured from Alfasol. Ethanol was received from ISOLAB chemicals. Sodium chloride (NaCl) was obtained from Riedel. All the chemicals utilized in this study were commercially available and were employed without additional purification. Deionized water from a Millipore Direct Q3 purification system was used in each experiment.

4.2 Catalyst Preparation

4.2.1 Synthesis of g- C_3N_4

The g- C_3N_4 was fabricated via calcination method using melamine as a precursor. 5 g of melamine was put inside a ceramic crucible with a lid. Then, placed in a furnace and heated at 550 °C for 4 h. After cooling to room temperature, the g- C_3N_4 powder was grinded. Afterwards, the ceramic crucible without a lid was placed in a furnace and heated at 530°C for 3 h. The yellow powder obtained is g- C_3N_4 (Zhao et al., 2020).

Schematic representation of catalyst preparation steps for g- C_3N_4 , MIL-88A, MIL-88A/g- C_3N_4 , Ag/AgCl@MIL-88A, Ag/AgCl@MIL-88A/g- C_3N_4 (ACM-gC-2) catalysts are given in Figure 4.1-5.

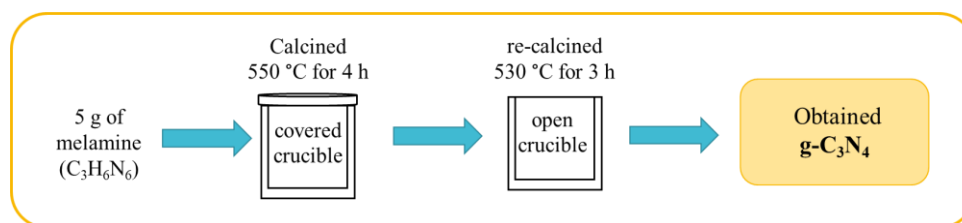


Figure 4.1 Schematic representation of g- C_3N_4 photocatalyst preparation steps.

4.2.2 Synthesis of MIL-88A

The MIL-88A was produced using a facile hydrothermal process. Firstly, fumaric acid (3.2 mmol) and 75 mL of ultrapure water was stirred for 30 min at room temperature, and then for 10 min at 35°C. After that, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3.2 mmol) was added to the fumaric acid solution, and it was stirred for 1 h. Next, the solution was transferred to the Teflon-lined stainless-steel autoclave and heated to 65 °C for 12 h. After cooled down to the room temperature, the products were collected, washed with water and ethanol repeatedly and dried at 65 °C for 6 h (Gholizadeh Khasevani and Gholami, 2019; Shao et al., 2019).

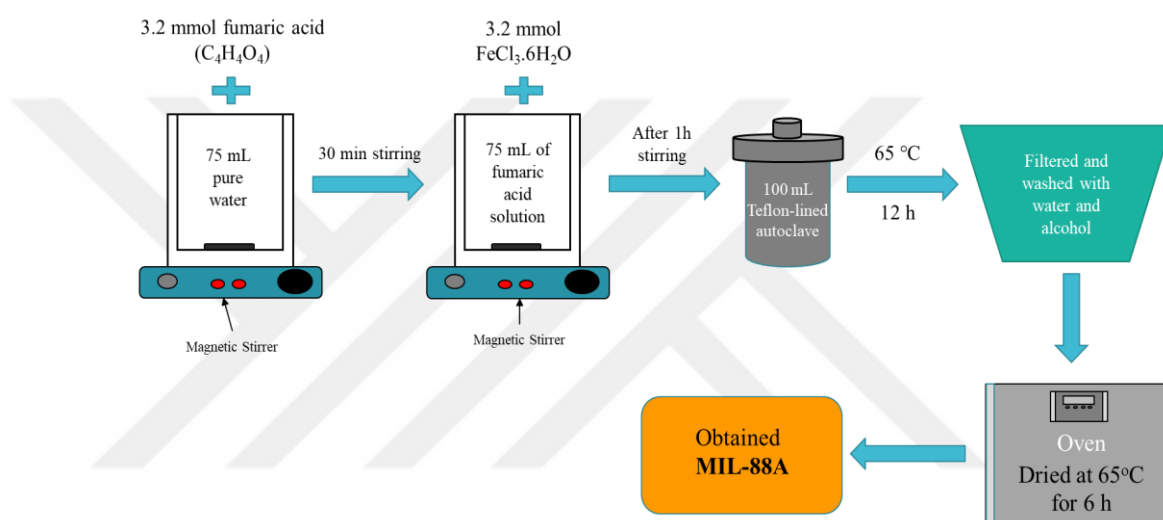
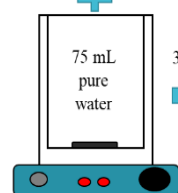


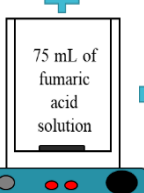
Figure 4.2 Schematic representation of MIL-88A photocatalyst preparation steps.

4.2.3 Preparation of MIL-88A/g- C_3N_4

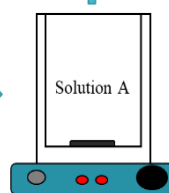
The MIL-88A/g- C_3N_4 composite was fabricated via hydrothermal growth of MIL-88A on the surface of g- C_3N_4 . Firstly, fumaric acid (3.2 mmol) was dissolved in 75 mL of ultrapure water for 30 min at room temperature, and then for 10 min at 35°C. Then, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3.2 mmol) was added to the fumaric acid solution, and stirred for 1 h. 0.4 grams of g- C_3N_4 and 5 mL ultrapure water were mixed in ultrasonic bath for 30 min and then slowly added to the solution. Next, this mixture was stirred for 1 h. The produced solution was poured into the Teflon-lined stainless-steel autoclave and kept there at 65 °C for 12 h. Subsequently, the products cooled to room temperature, and washed with ultrapure water and then with ethanol. Finally, the products were dried at 65 °C for 6 h (Gholizadeh Khasevani and Gholami, 2019).

Solution A3.2 mmol fumaric acid
($C_4H_4O_4$)

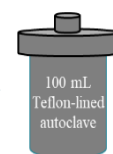
30 min stirring

3.2 mmol
 $FeCl_3 \cdot 6H_2O$ 

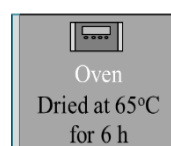
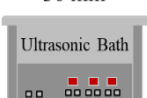
1h stirring

Solution B

1h stirring

65 °C
12 h**Solution B**0.4 g $g-C_3N_4$ 

30 min

Obtained
MIL-88A/g- C_3N_4 **Figure 4.3** Schematic representation of MIL-88A/g- C_3N_4 photocatalyst preparation steps.**4.2.4 Preparation of Ag/AgCl@MIL-88A/g- C_3N_4**

The Ag/AgCl@MIL-88A/g- C_3N_4 composites were prepared via a hydrothermal method by controlling the mole ratios of fumaric acid with Fe and Ag content. Magnetic stirrer and ultrasonic bath were used for mixing. The preparation procedure of the Ag/AgCl@MIL-88A/g- C_3N_4 catalyst that has the same metal moles (Fe: Ag ratio of 0.5:0.5) with fumaric acid (Fumaric acid: Fe: Ag ratio of 1:0.5:0.5), prepared with ammonium oxalate as sacrificial agent, and under 1 h of photo-reduction was proceeded as follows: Fumaric acid (3.2 mmol) and 75 mL of ultrapure water were stirred for 30 min at room temperature and for 10 min at 35°C. After that, $FeCl_3 \cdot 6H_2O$ (1.6 mmol) was added to the fumaric acid solution, and it was stirred. Then, $AgNO_3$ (1.6 mmol) was added, and the solution was mixed for 1 h. 0.4 grams of $g-C_3N_4$ and 5 mL ultrapure water were mixed in ultrasonic bath for 30 min and then slowly added to the above solution. This mixture was stirred for 1 h at room temperature, and then transferred to a Teflon-lined stainless-steel autoclave and heated at 65 °C and kept there for 12 h. Subsequently, the products cooled to room temperature, and washed with ultrapure water and then with ethanol. For the reduction of Ag^+ to Ag NPs, produced new powder product was added to

aqueous ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4$) (0.08 g/50 ml) and kept under LED light with stirring for 1 h. Afterwards, the products were washed with ethanol and after that, dried at 65°C for 6 h (Gholizadeh Khasevani and Gholami, 2019; Shao et al., 2019; Huang et al., 2018; Viswanathan et al., 2021; Wu et al., 2019).

$\text{Ag}/\text{AgCl}@/\text{MIL-88A}$ was prepared with the same procedure but without addition of $\text{g-C}_3\text{N}_4$ (Figure 4.4).

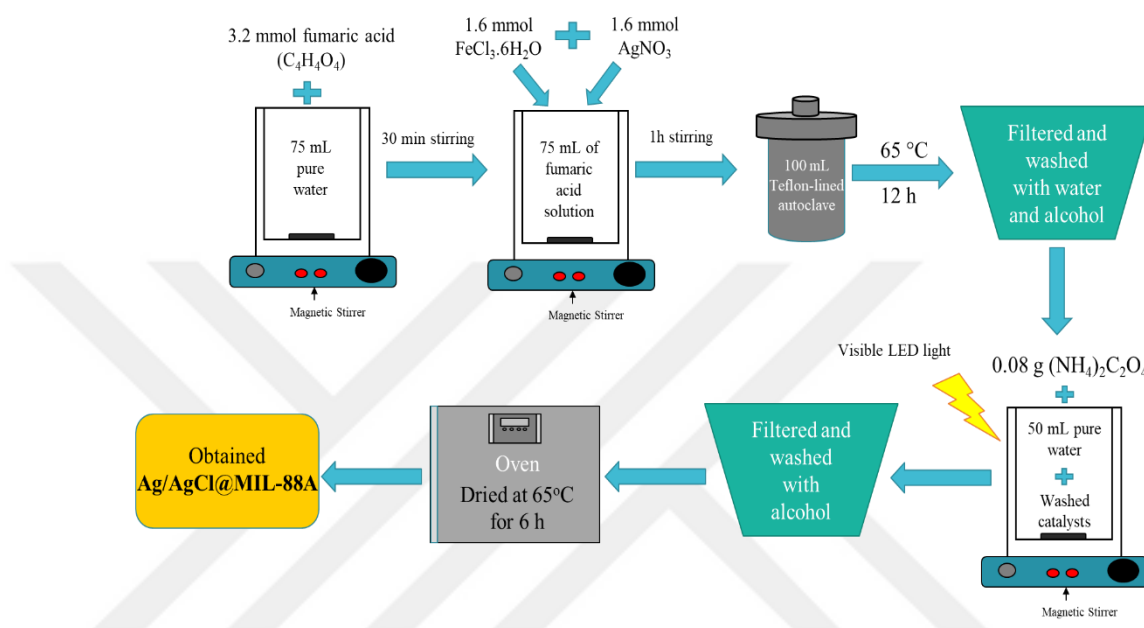


Figure 4.4 Schematic representation of $\text{Ag}/\text{AgCl}@/\text{MIL-88A}$ photocatalyst preparation steps.

In this study, $\text{Ag}/\text{AgCl}@/\text{MIL-88A}/\text{g-C}_3\text{N}_4$ photocatalysts were prepared with different photodeposition times of 30 min (ACM-gC-1), 1 h (ACM-gC-2) and 2 h (ACM-gC-3) (prepared with 3.2 mmol fumaric acid+1.6 mmol Fe+1.6 mmol Ag (Fe:Ag ratio of 0.5:0.5) with ammonium oxalate (AO) as sacrificial agent). Also, the different $\text{Ag}/\text{AgCl}@/\text{MIL-88A}/\text{g-C}_3\text{N}_4$ composites were synthesized using AO as a sacrificial agent under 1 h of photodeposition by changing the Fe:Ag ratio but keeping the total metal:ligand ratio at 1:1. The obtained products were labelled as ACM-gC-2 (Fe:Ag = 0.5:0.5), ACM-gC-4 (Fe:Ag = 0.25:0.75) and ACM-gC-5 (Fe:Ag = 0.75:0.25). In addition, $\text{Ag}/\text{AgCl}@/\text{MIL-88A}/\text{g-C}_3\text{N}_4$ photocatalysts were prepared using different sacrificial agents such as ammonium oxalate (ACM-gC-4), ethanol (ACM-gC-6) and glycerol (ACM-gC-8) with a Fe:Ag ratio of 0.25:0.75 under a 1 h photodeposition time. Moreover, the ACM-gC-7 catalyst was synthesized under the same conditions but without addition of a sacrificial agent (only water). For photoreduction, the $\text{Ag}/\text{AgCl}@/\text{MIL-88A}/\text{g-C}_3\text{N}_4$ photocatalysts

were synthesized under several light sources, including visible LED (ACM-gC-7) and high-pressure Na Lamps (ACM-gC-9). The synthesizing parameters abbreviations of all catalysts are summarized in Table 4.1.

Table 4.1 Synthesizing parameters of all samples.

Photocatalysts	Photo-deposition time	Fumaric Acid- Fe:Ag molar ratio	Hole scavenger	Light Type
MIL-88A	—	1–1	—	—
g-C ₃ N ₄	—	—	—	—
MIL-88A/g-C ₃ N ₄	—	1–1	—	—
Ag/AgCl@MIL-88A	1 h	1 – 0.5:0.5	Ammonium oxalate (AO)	LED Lamps
Ag/AgCl@MIL-88A/g-C ₃ N ₄	30 min	1 – 0.5:0.5	AO	LED Lamps
ACM-gC-1				
ACM-gC-2	1 h	1 – 0.5:0.5	AO	LED Lamps
ACM-gC-3	2 h	1 – 0.5:0.5	AO	LED Lamps
ACM-gC-4	1 h	1 – 0.25:0.75	AO	LED Lamps
ACM-gC-5	1 h	1 – 0.75: 0.25	AO	LED Lamps
ACM-gC-6	1 h	1 – 0.25:0.75	Ethanol	LED Lamps
ACM-gC-7	1 h	1 – 0.25:0.75	Only water	LED Lamps
ACM-gC-8	1 h	1 – 0.25:0.75	Glycerol	LED Lamps
ACM-gC-9	1 h	1 – 0.25:0.75	Only water	Na Lamps

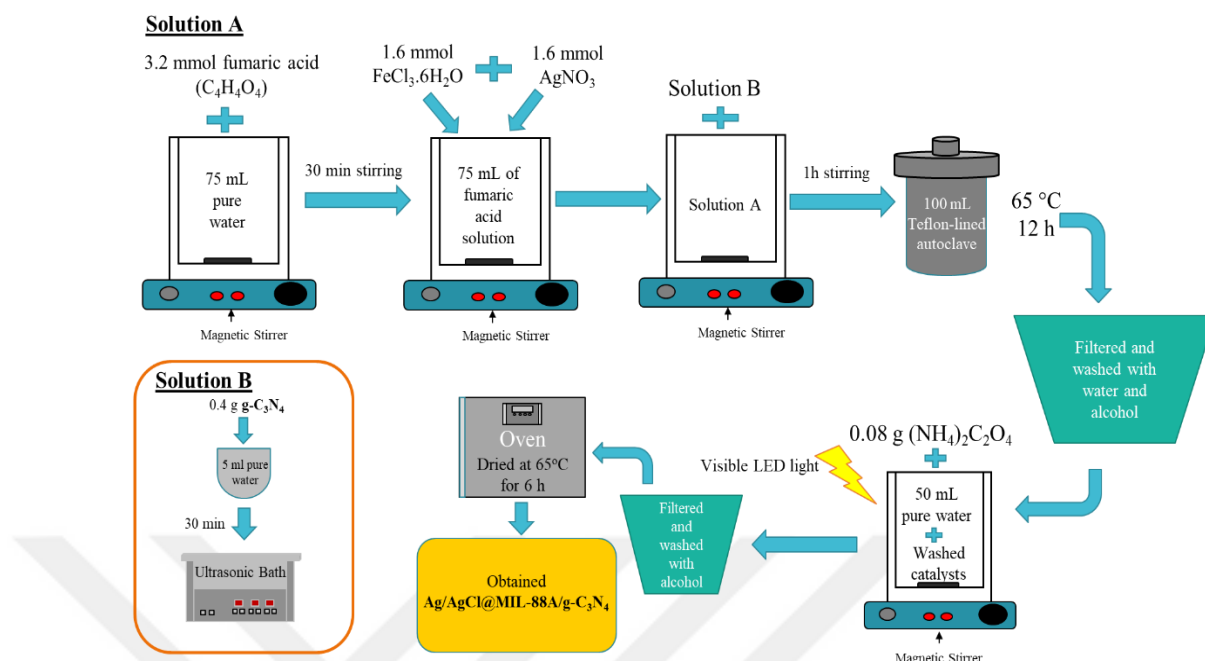


Figure 4.5 Schematic representation of Ag/AgCl@MIL-88A/g-C₃N₄ (ACM-gC-2) photocatalyst preparation steps.

4.3 Characterization of Prepared Catalysts

The surface morphology of the synthesized catalysts was characterized by a Scanning Electron Microscope (SEM, Thermo Scientific Apreo S LoVac, Ege University, Central Research Test and Analysis Laboratory Application and Research Center). The crystalline phase structures of all prepared catalysts were characterized using X-Ray Diffraction (XRD, Panalytical Empyrean, Izmir Katip Çelebi University, Central Research Labs) analysis. The surface properties of the catalysts were confirmed by X-ray Photoelectron Spectrometer (XPS, Thermo Scientific K-Alpha, Ege University, Central Research Test and Analysis Laboratory Application and Research Center). The optical activity and band gap of prepared samples were determined with UV–Vis Diffuse Reflectance Spectra (DRS, UV–Vis DRS/Shimadzu 2600 spectrophotometer with ISR apparatus). The Fourier transform infrared (FT-IR) spectroscopy of the samples was conducted by an infrared spectrometer type Shimadzu IRPrestige-21 FTIR-8400S at Izmir Institute of Technology, Chemical Engineering Department. The photoluminescence spectra (PL) of the catalysts were obtained using a Spectrofluorometer (Edinburgh Instruments, FS5, Izmir Katip Çelebi University, Central Research Labs). The

specific surface area and pore size distribution of photocatalysts were calculated using the Brunauer–Emmett–Teller (BET) method from N₂ adsorption-desorption isotherms (BET Micrometrics 3 Flex, Izmir Katip Çelebi University, Central Research Labs).

4.4 Experimental Procedure for Photo-degradation of Diuron

The schematic representation of LED light photoreactor for the degradation of diuron is shown in Figure 4.6. This illustrated system is housed in a sealed box with a lid. This is because an external light source of sunlight has no effect on the experiment. Batch reactor, 93.4 W LED light lamps (531.5 nm) and magnetic stirrer for mixing process were used in this experiment.

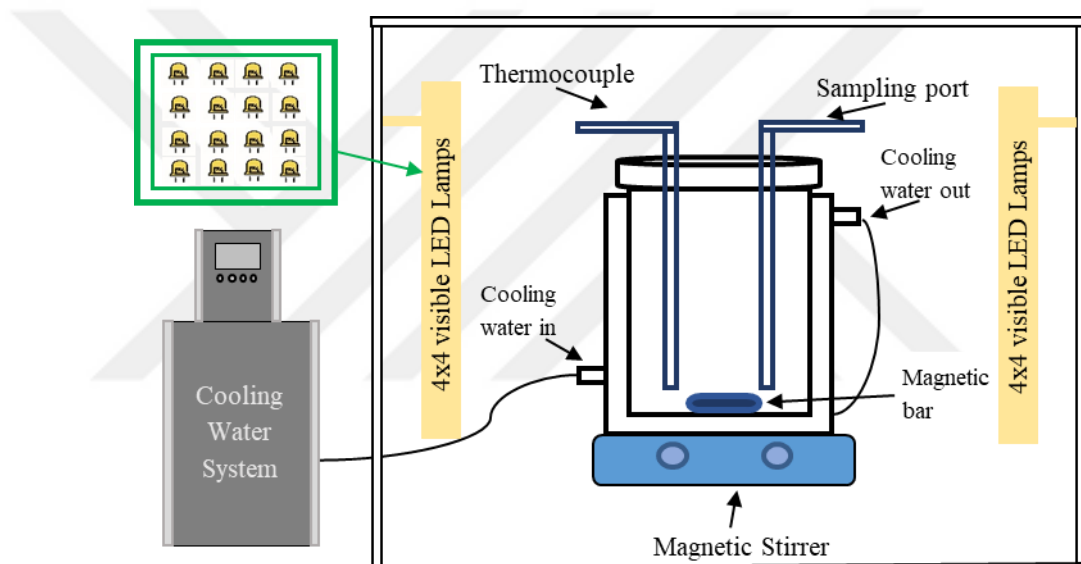


Figure 4.6 Schematic representation of LED light photoreactor.

In a typical experiment, 150 mL of 10 ppm aqueous diuron solution was poured into the batch reactor and stirred continuously. The reaction temperature was kept constant at 25 °C with the aid of circulating cooling water to avoid significant heating of the reaction medium. The first sample was taken from the diuron solution, and then, 1 g/L of catalyst was added into the reactor. The adsorption-desorption process was started in the dark while the lid of the experimental setup was closed, and the magnetic stirrer was on. This adsorption process took 30 min. The amount of the diuron adsorbed by the catalyst was determined by measuring the diuron concentration after 30 min in the absence of

visible light illumination. Then LED light lamps were turned on. After the LED light was turned on, samples were taken from the solution at regular intervals. The pH value was measured at the end of 120th min. Finally, the samples taken during the experiment were filtered with PTFE (0.45 µm) filter (ISOLAB) and then the unreact DRN concentration was measured with High Performance Liquid Chromatography (HPLC) at the following conditions: Eclipse Plus C18, 4.6x150 mm, 5 µm column. Detection of DRN was achieved with an UV detector at 248 nm, with a 20 µL sampling loop. The mobile phase, ultrapure water/acetonitrile (40/60, v/v) was run in an isocratic mode at a flow rate of 0.5 mL min⁻¹. The column oven was maintained at 30 °C.

DRN photodegradation was determined using the following equation (Eq.19) after concentration was obtained by HPLC:

$$\text{Degradation (\%)} = \frac{C_0 - C}{C_0} * 100 \quad (39)$$

where C_0 was the initial DRN concentration and C was the DRN concentration at the time of sampling.

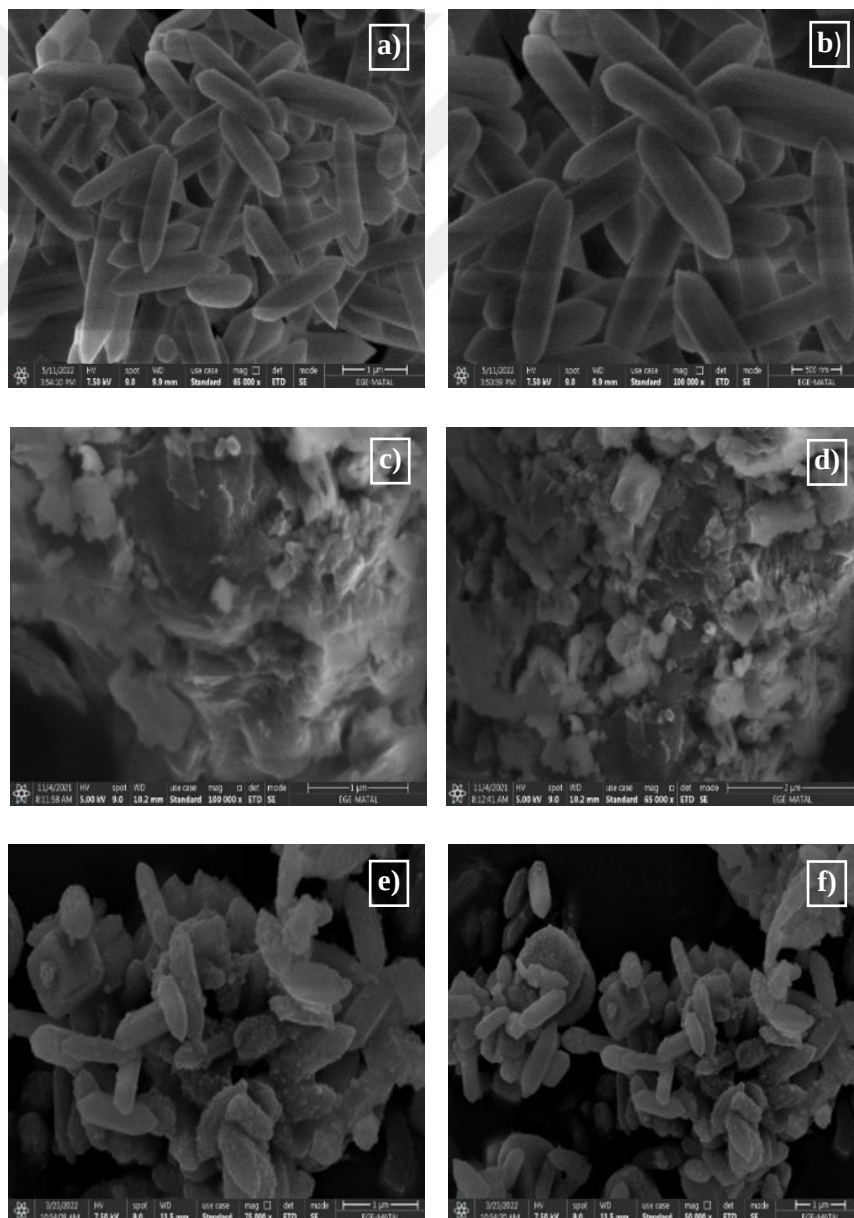
5. RESULTS and DISCUSSION

5.1 Catalyst Characterization

5.1.1 SEM images of prepared catalysts

All of the synthesized samples were characterized by SEM images to investigate the surface morphologies.

SEM observations verified that MIL-88A photocatalyst was very well crystallized with regular and independent hexagonal microrods having a smooth surface at almost 1.6 μm in length, see Figure 5.1a and b.



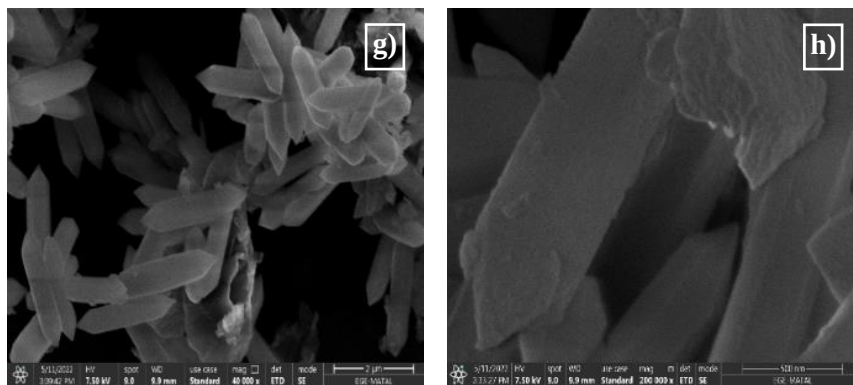


Figure 5.1 SEM images MIL-88A (a,b), g-C₃N₄ (c,d), Ag/AgCl@MIL-88A (e,f), MIL-88A/g-C₃N₄ (g,h).

As seen in Figure 5.1c, and d, g-C₃N₄ possess aggregated morphology with a large size and a typical overloading lamellar structure.

Distribution of Ag/AgCl on MIL-88A can be seen clearly, that cause the relatively rough surface of MIL-88A, see Figure 5.1e, and f. The loading of MIL-88A with Ag/AgCl caused decreased in length of microrods from 1.6 to 1.5 μm . As given in “Catalyst Preparation” Part, MIL-88A/g-C₃N₄ composite was constructed via growth of MIL-88A component on the g-C₃N₄. It is clear that MIL-88A still maintains the hexagonal microrod morphology and was tightly attached on the surface of lamellar g-C₃N₄ structure, see Figure 5.1g, and h (Shao et al., 2019).

The morphology of Ag/AgCl@MIL-88A/g-C₃N₄ prepared with photo-reduction time of 1 h (ACM-gC-2) was given in Figure 5.2 with 1 μm (Figure 5.2a) and 500 nm (Figure 5.2b) magnification. Furthermore, the EDX measurements (Figure 5.3) showed that there were six elements of C, O, N, Fe, Cl, and Ag that existed in the ACM-gC-2 composite. C, O, and N mainly came from melamine that used to synthesize g-C₃N₄ and fumaric acid. Fe and Cl came from the ferric chloride, and Ag came from AgNO₃.

As it was seen that Ag/AgCl was deposited on the surface of MIL-88A and Ag/AgCl@MIL-88A attached on the surface of g-C₃N₄. In the ACM-gC-2 composite, the length of the MIL-88A was 1.2 μm .

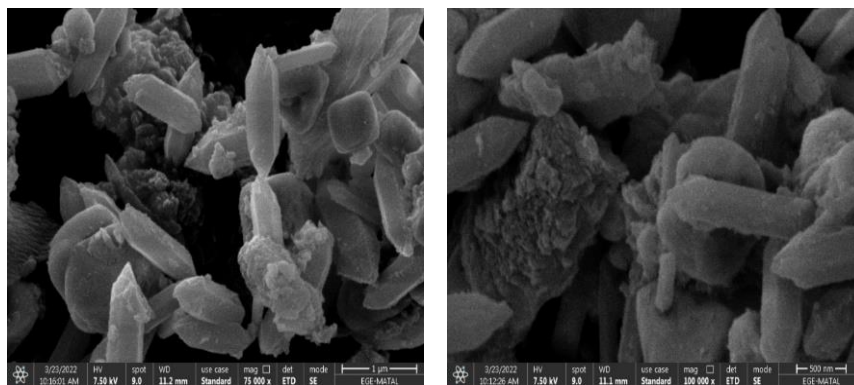


Figure 5.2 SEM images of ACM-gC-2 photocatalyst.

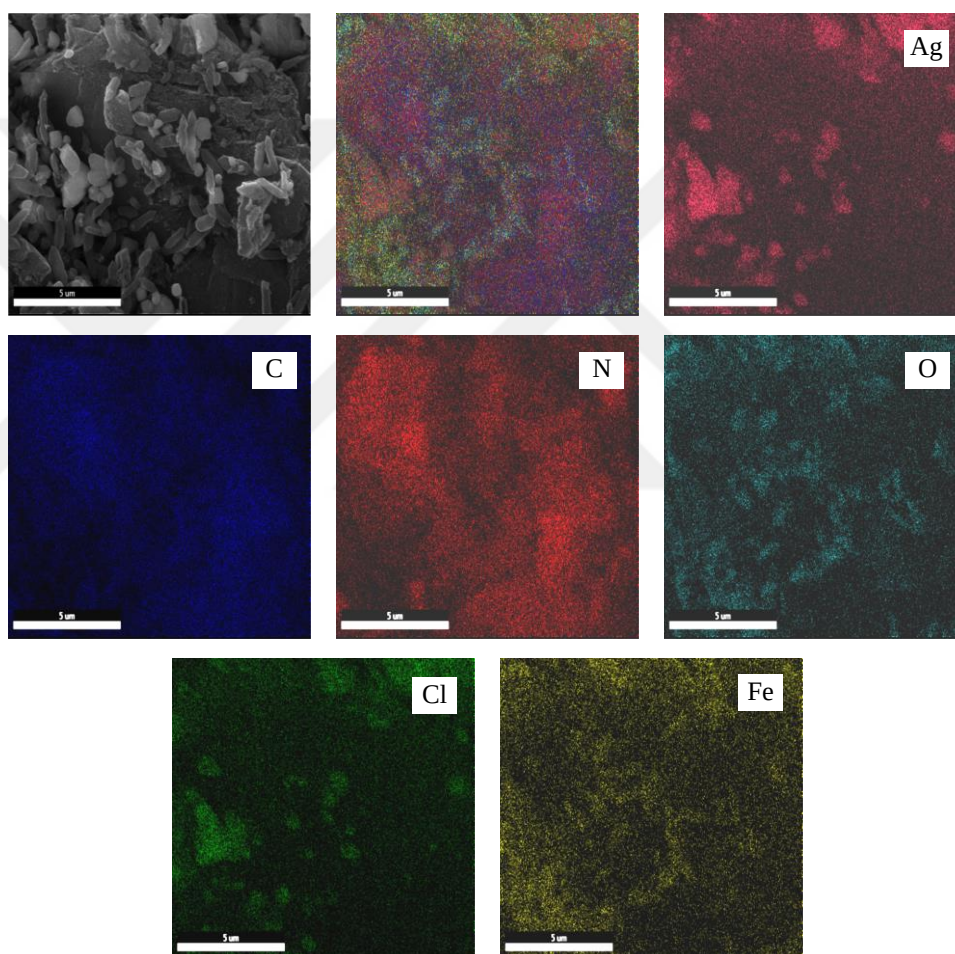


Figure 5.3 SEM-EDX images of ACM-gC-2 photocatalyst.

Figures 5.4a, b and c, d display the SEM images of ACM-gC-1 and ACM-gC-3 photocatalysts that were prepared under the photodeposition time of 30 min and 2 h, in 1 μ m and 500 nm SEM magnification, respectively.

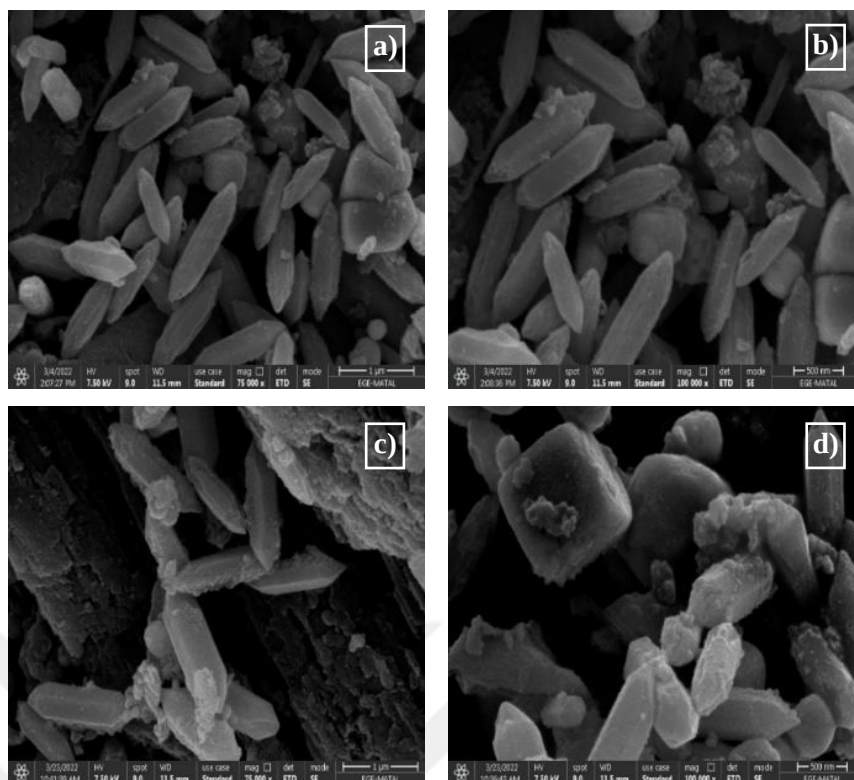


Figure 5.4 SEM images of ACM-gC-1 (a,b) and ACM-gC-3 (c,d) photocatalysts.

As the photo-reduction time was increased, more silver nanoparticles (Ag NPs) formed and attached on the surface of MIL-88A. Photo-reduction time for the ACM-gC photocatalyst preparation plays an important role in the catalytic activity and can be manipulated to bring appropriate distribution and size of metal particles on the support. As the photodeposition time was increased, the Ag NPs continued to grow larger and aggregated. Although larger Ag NPs possessed a stronger plasmonic resonance (SPR) and charge separation, the aggregates of the Ag NPs would be unfavorable due to the low efficiency of the electron transfer (Gholizadeh Khasevani and Gholami, 2019; Shao et al., 2019; Li et al., 2013; Bhardwaj et al., 2019; Bhardwaj et al., 2020; Seh et al., 2012).

Figures 5.5a,b and c,d present the morphology of Ag/AgCl@MIL-88A/g-C₃N₄ prepared with different Fe:Ag ratios of 0.25:0.75 (ACM-gC-4), and 0.75:0.25 (ACM-gC-5) for photodeposition time of 1 h, in magnification 1 μ m and 500 nm, respectively. Figure 5.6 shows the distribution and weight percentage of Ag element in the composites of ACM-gC- 5, ACM-gC-2 and ACM-gC-4, respectively, that were analyzed by SEM-EDX.

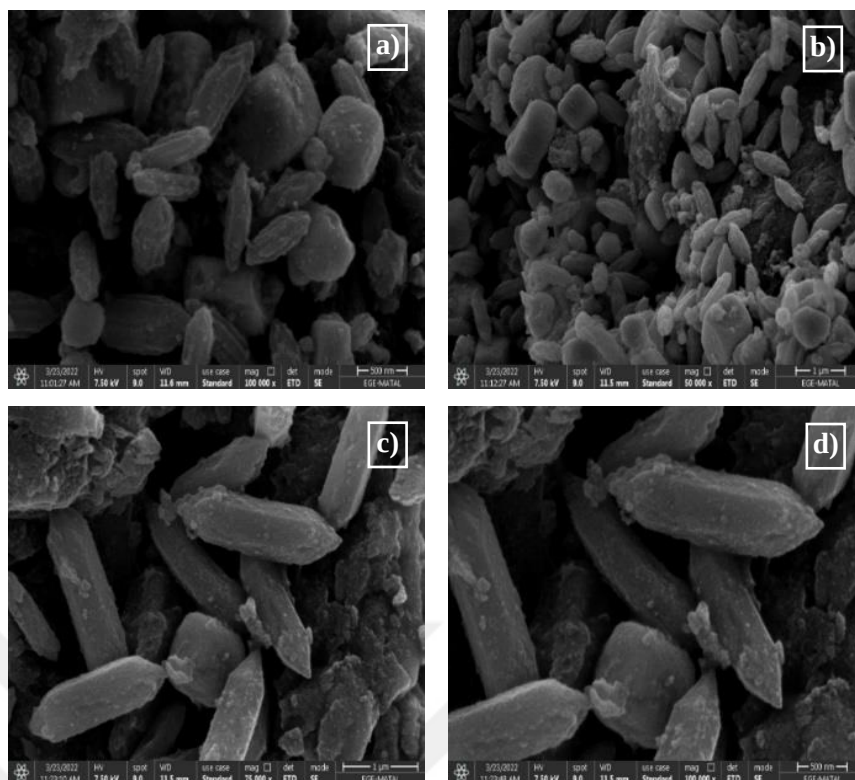


Figure 5.5 SEM images of ACM-gC-4 (a,b) and ACM-gC-5 (c,d) photocatalysts.

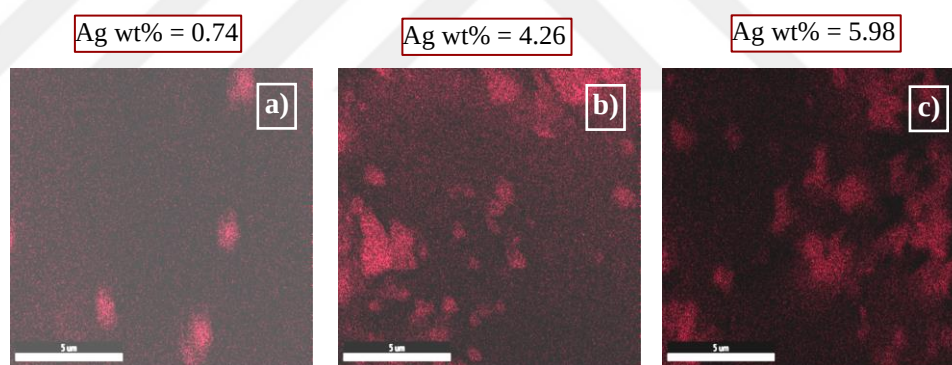


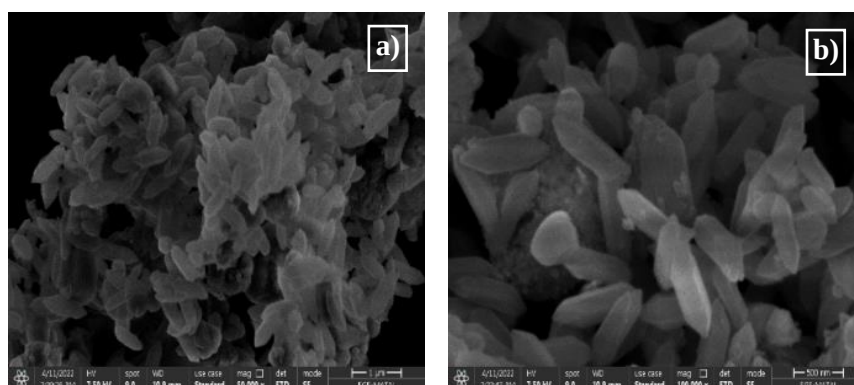
Figure 5.6 Distribution and weight percentage of Ag element in the composites of ACM-gC-5 (a), ACM-gC-2 (b) and ACM-gC-4 (c).

As seen in Figures 5.5a,b, 5.2 and 5.5c,d, the average size of MIL-88A in the composites of ACM-gC-4, ACM-gC-2, and ACM-gC-5 were 770 nm, 1.2 μm , and, 1.5 μm respectively. According to this result, it could be said that the size of the microrods of MIL-88A was affected by the loading amount of co-catalyst Ag/AgCl particles. This could be due to the strong attachment capability of the Ag/AgCl particles, that need more space for the uniform accumulation on MIL-88A with more surface area. The other reason that affect the size of microrods MIL-88A is nucleation rate. Fast nucleation rate lead to formation of a great quantity of crystal

nucleus, which would yield the smaller size particles and shorter stage of crystal growth. On the contrary, slow nucleation rate would produce large microrods. One of the parameter that affect the nucleation rate is the concentration of metal ion. In this context, in the present study, increasing loading amount of co-catalyst Ag/AgCl lead fast nucleation rate, thus the size of microrods decreased with increasing doping amount of Ag/AgCl (Wu et al., 2019; Viswanathan et al., 2021).

Effect of increment in weight percentages of Ag in ACM-gC composites with increasing Ag loading during the catalyst synthesis step can be seen in Figure 5.6. Weight percentages of 0.74%, 4.26% and 5.98% were observed with composites of ACM-gC-5, ACM-gC-2, and ACM-gC-4, those were prepared with Fe : Ag ratios of 0.75:0.25, 0.5:0.5, and 0.25:0.75, respectively.

Figure 5.7 displays the morphology of ACM-gC photocatalysts that were prepared with different sacrificial agents of ethanol (ACM-gC-6) (a,b), no-sacrificial agent (ACM-gC-7) (c,d), and glycerol (ACM-gC-8) (e,f) under photodeposition time of 1 h at the Fe:Ag mole ratio of 0.25:0.75. Here it should be remembered that Figure 5.5a,b presents the morphology of ACM-gC-4 photocatalyst that was prepared with same conditions but with the sacrificial agent of ammonium oxalate. Since the Fe:Ag mole ratio and photo-reduction time were the same for the samples of ACM-gC-4, ACM-gC-6, ACM-gC-7, and ACM-gC-8, their morphologies are also very similar. However, as will be mentioned in “XPS results” the reduction ratio of Ag^+ to Ag^0 was different. The length of the MIL-88A was measured with SEM analysis and it was about 800 nm in the mentioned photocatalysts.



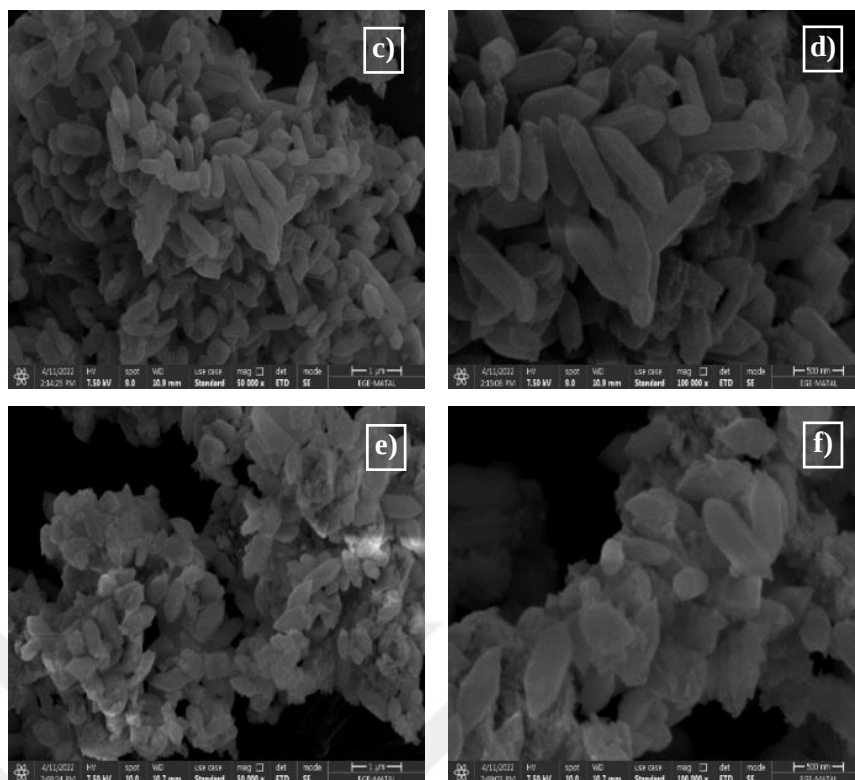


Figure 5.7 SEM images of ACM-gC-6 (a,b), ACM-gC-7 (c,d), and ACM-gC-8 (e,f) photocatalysts.

Figure 5.8 presents the morphology of ACM-gC photocatalyst which was prepared under 1 h of photoreduction with visible high pressure Na lamps, without sacrificial agent and Fe:Ag molar ratio of 0.25:0.75 (ACM-gC-9). Na lamps were also efficient for the reduction of Ag^+ to Ag^0 as visible LED lamps. As the all-synthesis parameters were the same with ACM-gC-7 except light source, there was no difference with the morphologies.

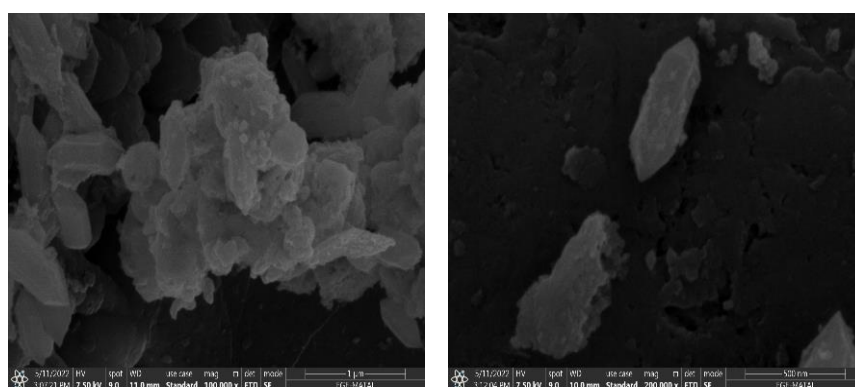


Figure 5.8 SEM images of ACM-gC-9 photocatalyst.

5.1.2 XRD analysis of prepared catalysts

The crystalline phase structures of all prepared samples were characterized using X-Ray Diffraction (XRD) analysis.

Figure 5.9 shows the XRD peaks belong to MIL-88A, g-C₃N₄, MIL-88A, Ag/AgCl@MIL-88A and ACM-gC-2 samples. The main diffraction peak of MIL-88A could be seen at 2θ of 10.4° and 12.9°, that ascribed by (100) and (101) crystal facets, respectively (Huang et al., 2022). They were given as inset in Figure 5.9 for more clear understanding. The characteristic peaks of g-C₃N₄ were observed at $2\theta = 27.40^\circ$ and 13.2° , however the latter was not so obvious in all samples. The diffraction peaks belong to AgCl could be seen at 27.84° , 32.26° , 46.26° , 54.86° , 57.52° , 67.9° , 74.52° and 77.2° (Yentür and Dükkancı, 2020a). The peak belongs to g-C₃N₄ $2\theta = 27.40^\circ$ was not obvious for composite sample due to the coverage of surface by MIL-88A and Ag/AgCl. The peaks near 38.1° , and 44.3° can be represented by the (111) and (200) crystal facets of metallic Ag, however, only the peak at 38.1° was obvious for Ag/AgCl@MIL-88A sample (given as inset). No diffraction peaks related to Ag was determined in the XRD pattern of ACM-gC-2 photocatalyst, which was ascribed to the low loading amount and fine distribution Ag NPs into the structure. Nevertheless, the existence of Ag NPs was confirmed by XPS analysis. The peaks related to MIL-88A was not obvious for Ag/AgCl@MIL-88A sample. This may be due to the coverage of MIL-88A by Ag and AgCl (Huang et al., 2018; Gholizadeh Khasevani and Gholami, 2019; Huang et al., 2022; Yentür and Dükkancı, 2020a).

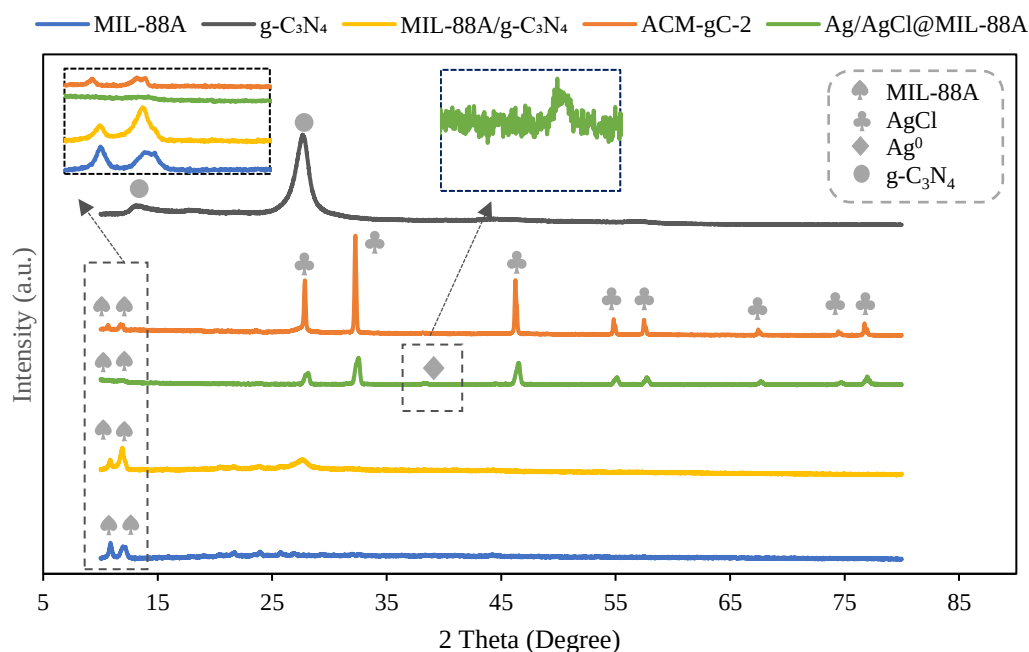


Figure 5.9 XRD patterns of MIL-88A, g-C₃N₄, MIL-88A/g-C₃N₄, Ag/AgCl@MIL-88A and ACM-gC-2 samples.

Figure 5.10 presents the XRD patterns of Ag/AgCl@MIL-88A/g-C₃N₄ catalysts those were prepared with different photodeposition time of 30 min (ACM-gC-1), 1 h (ACM-gC-2) and 2 h (ACM-gC-3). It is clear that the reduction of Ag⁺ to Ag⁰ increased with increasing photodeposition time. The peak belongs to Ag NPs (38.1°) was obvious only for the catalyst that was synthesized by 2 h of photodeposition time. This result was in good agreement with the result obtained from XPS analysis. In addition, it was seen that the peak intensities of MIL-88A at 2θ of 10.4° and 12.9° decreased as the reduction time increases and the peak at 10.4° disappeared for ACM-gC-3 sample. This result may be an indication of photodeposition of Ag/AgCl on (100) and (101) facets of MIL-88A. It was also given in XPS analysis that the reduction Ag⁺ to Ag NPs increased with increasing photo-reduction time.

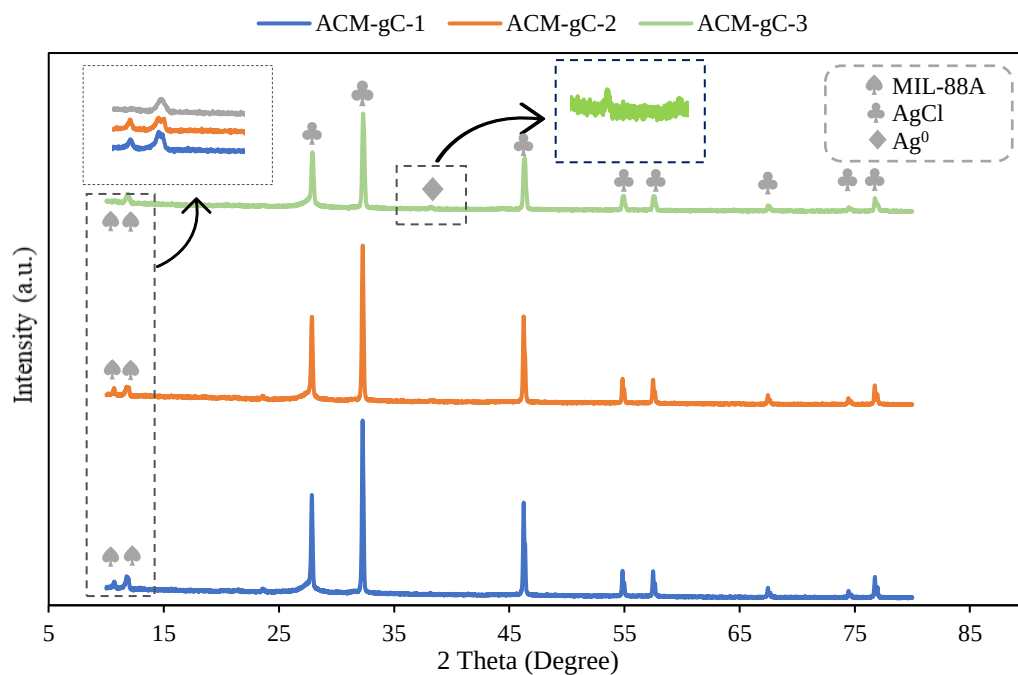


Figure 5.10 XRD patterns of ACM-gC photocatalysts synthesized by photodeposition time of 30 min (ACM-gC-1), 1 h (ACM-gC-2) and (ACM-gC-3) 2 h.

Figure 5.11 gives the XRD patterns of Ag/AgCl@MIL-88A/g-C₃N₄ catalysts those were prepared with different Fe : Ag ratios of 0.75:0.25 (ACM-gC-5), 0.5:0.5 (ACM-gC-2), and 0.25:0.75 (ACM-gC-4) for the photodeposition time of 1 h. It is clear that, main diffraction peaks of MIL-88A at 2θ of 10.4° and 12.9° , decreased with increasing Ag loading amount. That was due to the coverage of MIL-88A surface with Ag and AgCl. The peak belong to Ag NPs at 2θ of 38.1° was only seen for the sample that have the highest Ag loading amount (ACM-gC-4), given as inset.

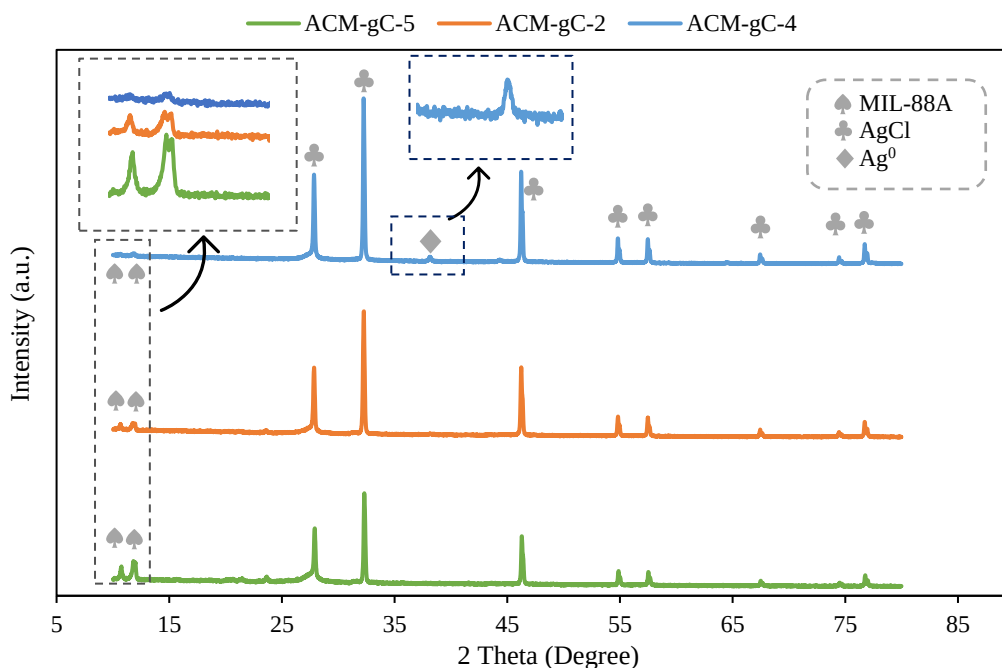


Figure 5.11 XRD patterns of Ag/AgCl@MIL-88A/g-C₃N₄ catalysts prepared with different Fe : Ag ratios of 0.75:0.25 (ACM-gC-5), 0.5:0.5 (ACM-gC-2), and 0.25:0.75 (ACM-gC-4) for the photodeposition time of 1 h.

Figure 5.12 gives the XRD patterns of Ag/AgCl@MIL-88A/g-C₃N₄ catalysts those were prepared with different sacrificial agent of ammonium oxalate (ACM-gC-4), ethanol (ACM-gC-6), glycerol (ACM-gC-8), and with no sacrificial agent (ACM-gC-7). No significant differences in XRD peaks were observed for the samples prepared with different sacrificial agents. However, the peak of Ag NPs at 2θ of 38.1° was observed only for the catalyst prepared with sacrificial agent of ammonium oxalate. This result was due to the insufficient or non-homogenous distribution of Ag NPs on MIL-88A in this sample.

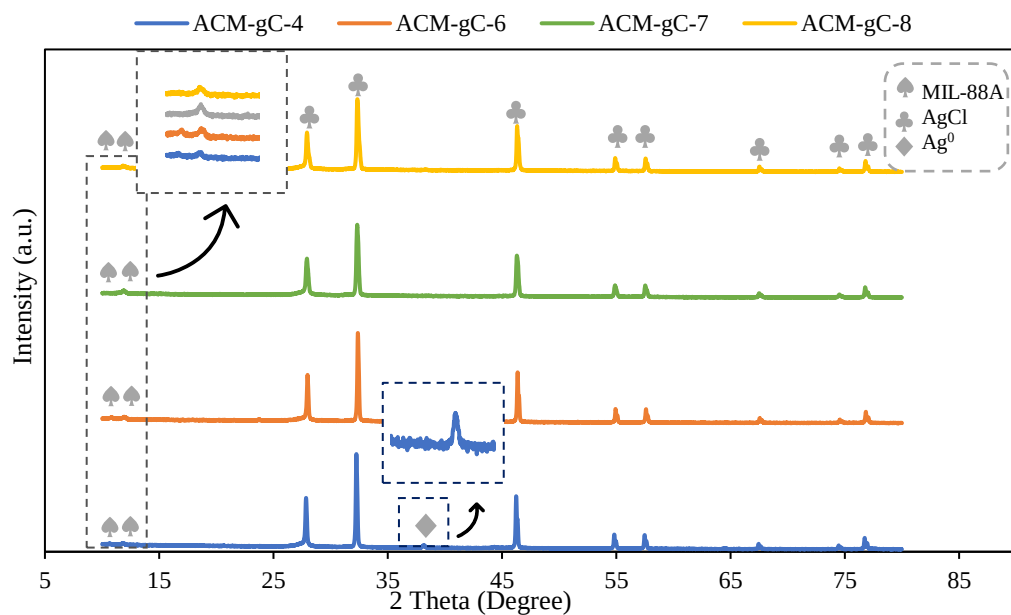


Figure 5.12 XRD patterns of Ag/AgCl@MIL-88A/g-C₃N₄ catalysts those were prepared with different sacrificial agent of ammonium oxalate (ACM-gC-4), ethanol (ACM-gC-6), glycerol (ACM-gC-8), and no-sacrificial agent (ACM-gC-7).

Figure 5.13 shows the XRD peaks of Ag/AgCl@MIL-88A/g-C₃N₄ catalysts synthesized under different light source of visible LED and high-pressure Na Lamps for photoreduction. The peaks belong to MIL-88A can be seen as inset in Figure 5.13. There is no evidence for the presence of Ag NPs that was due to the fine distribution. Sharp diffraction peaks at 27.84°, 32.26°, 46.26°, 54.86°, 57.52° and 74.52° belong to AgCl can be seen clearly for both samples.

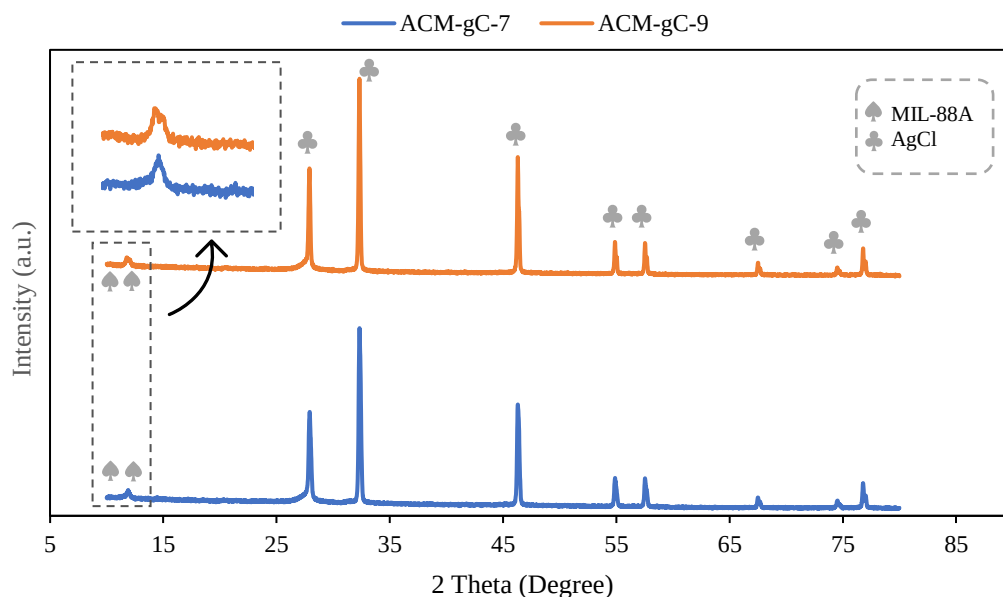


Figure 5.13 XRD patterns of Ag/AgCl@MIL-88A/g-C₃N₄ catalysts synthesized under different light source of visible LED and high-pressure Na Lamps for photoreduction.

5.1.3 XPS analysis of prepared catalysts

The XPS technique was used to examine the surface chemical states and compositions of the MIL-88A, g-C₃N₄, MIL-88A/g-C₃N₄, Ag/AgCl@MIL-88A and all Ag/AgCl@MIL-88A/g-C₃N₄ photocatalysts called as ACM-gC-1, ACM-gC-2, ACM-gC-3, ACM-gC-4, ACM-gC-5, ACM-gC-6, ACM-gC-7, ACM-gC-8 and ACM-gC-9. Figures 5.14-18 represent the results.

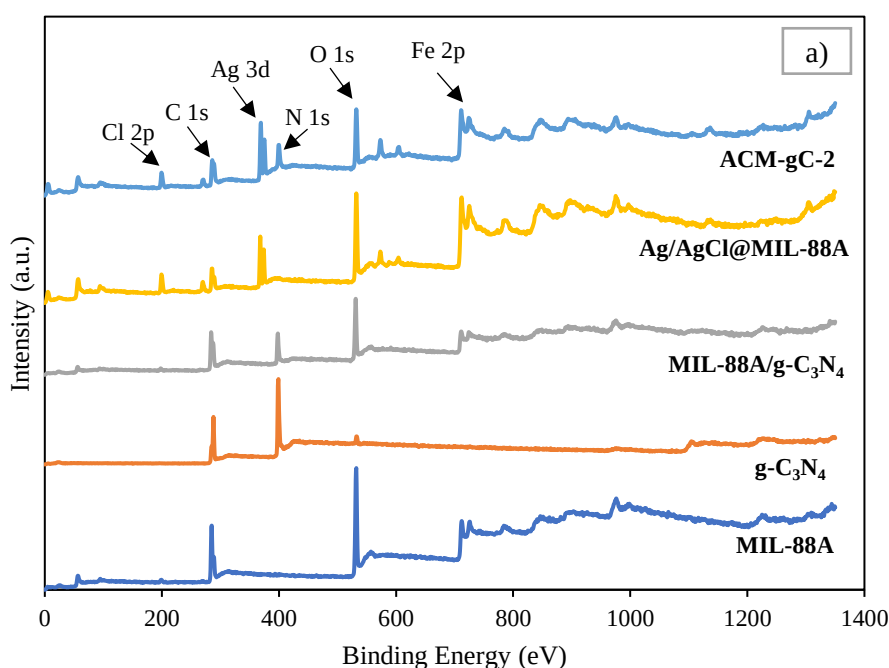
XPS survey spectrum of MIL-88A, g-C₃N₄, MIL-88A/g-C₃N₄, Ag/AgCl@MIL-88A and ACM-gC-2 (that was prepared with Fe : Ag ratio of 0.5:0.5 with AO as sacrificial agent under 1 h of photodeposition time) were given in Figure 5.14a that show the elements of Fe, O, Ag, N, C and Cl exist in the prepared catalysts.

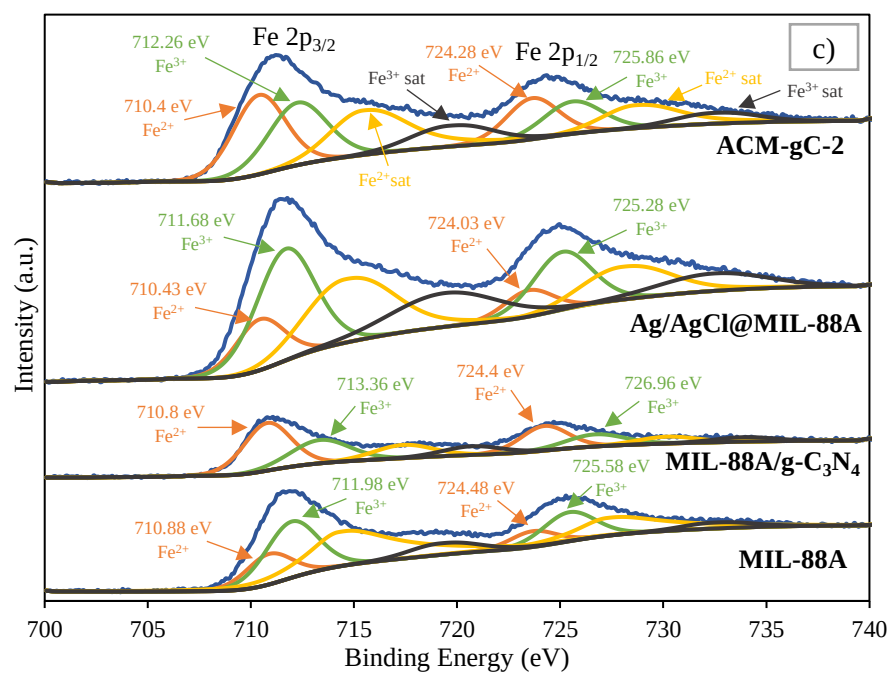
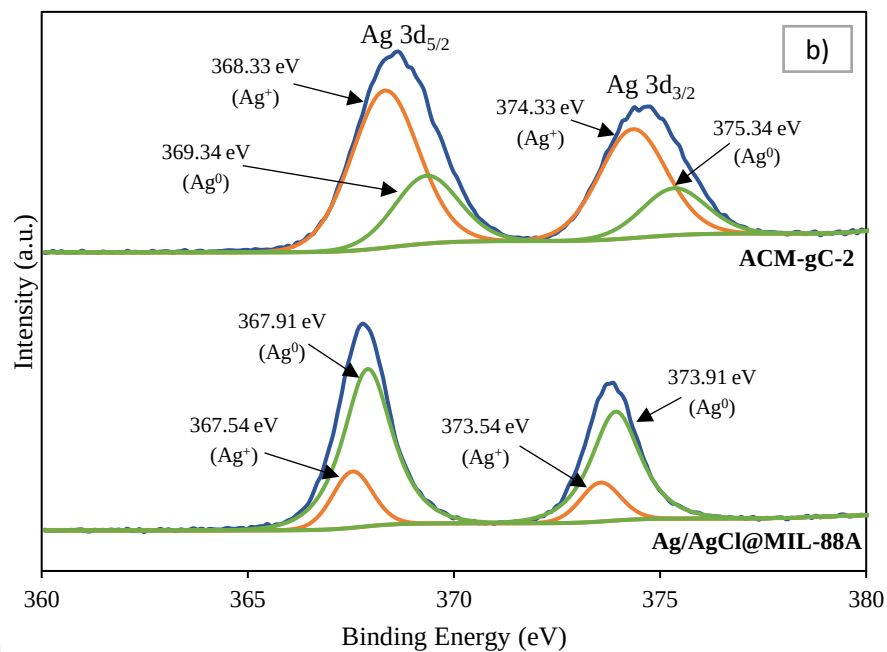
The spectrum of Ag 3d is shown in Figure 5.14b. The binding energies of Ag/AgCl@MIL-88A/g-C₃N₄ (ACM-gC-2) at 368.33 eV and 374.33 eV were attributed to the Ag⁺ in AgCl. Peaks at binding energies of 369.34 eV and 375.34 eV were assigned to metallic Ag in the ACM-gC-2 catalyst.

The XPS spectrum of Fe 2p divided into Fe 2p_{3/2}, Fe 2p_{1/2} and satellite peaks, as illustrated in Figure 5.14c. The binding energy peaks of MIL-88A at 710.88 eV (Fe 2p_{3/2}) and 724.48 eV (Fe 2p_{1/2}) are assigned to Fe²⁺. The peak of Fe 2p at 711.98

eV (Fe 2p_{3/2}) and 725.58 eV (Fe 2p_{1/2}) are consistent with the binding energy of Fe³⁺. The peaks located at 710.4 eV for Fe 2p_{3/2} and 724.28 eV for Fe 2p_{1/2} in ACM-gC-2 photocatalyst were assigned to Fe²⁺. Two peaks for Fe 2p_{3/2} and Fe 2p_{1/2} observed at 712.26 and 725.86 eV, respectively, indicating the presence of Fe³⁺ in ACM-gC-2 photocatalyst (Zheng et al., 2021).

In the O 1s spectrum shown in Figure 5.14d, the MIL-88A has three peaks at 530.05, 531.21, and 532.12 eV, corresponding to C=O, Fe-O, and O-H bonds, respectively. Similarly, the MIL-88A/g-C₃N₄ catalyst showed three characteristic peaks at 529.86, 531.4 and 532.48 eV. It could be said that the low-binding-energy peak belongs to lattice oxygen (O_L) (529 – 531 eV), while the higher-binding-energy peak (532 eV) corresponds to surface adsorbed oxygen (O_H) on oxygen vacancies (Jin et al., 2022). In Ag/AgCl@MIL-88A, O 1s displayed two peaks with binding energies of 530.93 eV and 532.57 eV that represent the lattice and adsorbed oxygen group on the surface, respectively. The ACM-gC-2 photocatalyst demonstrated two peaks at binding energies of 530.96 eV and 532.55 eV, similar to the Ag/AgCl@MIL-88A catalyst. In the former samples the C=O and Fe-O bands overlap thus these were called as lattice oxygen.





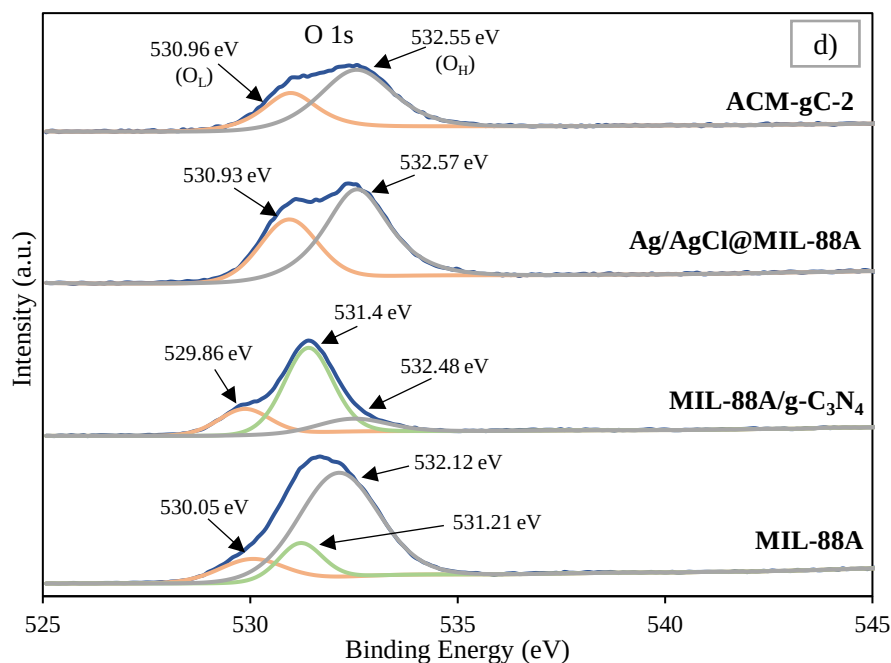


Figure 5.14 XPS spectra of MIL-88A, g-C₃N₄, MIL-88A/g-C₃N₄, Ag/AgCl@MIL-88A, Ag/AgCl@MIL-88A/g-C₃N₄, a) XPS survey, b) Ag 3d c) Fe 2p d) O 1s.

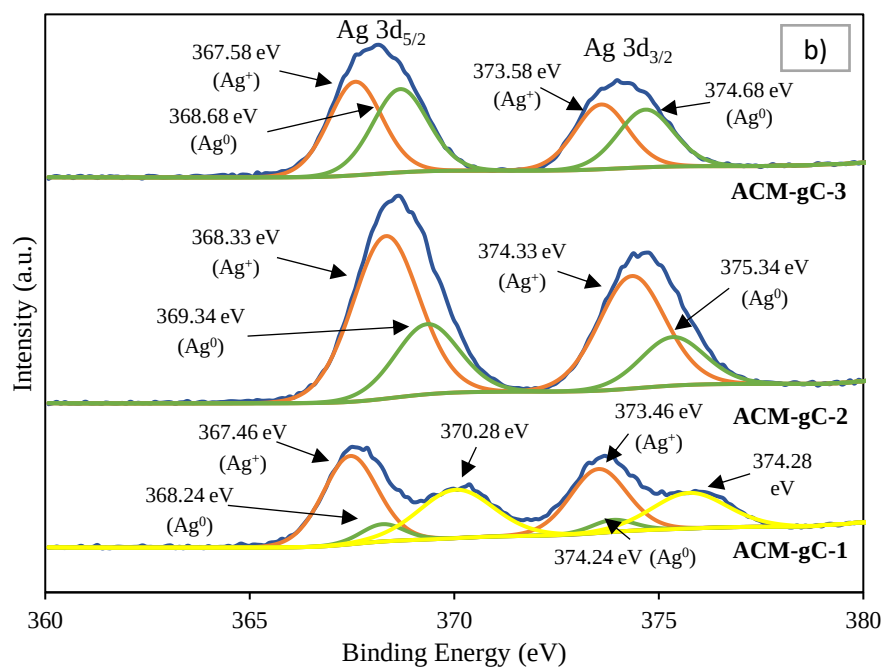
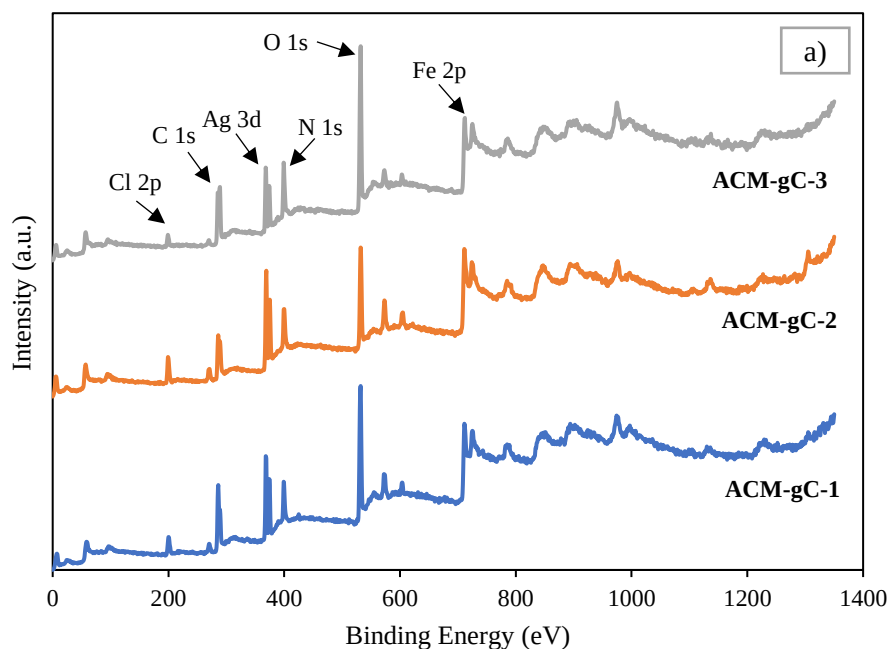
XPS survey spectrum of the ACM-gC samples that were prepared with different photodeposition time of 30 min (ACM-gC-1), 1 h (ACM-gC-2), and 2 h (ACM-gC-3) (prepared with Fe : Ag ratio of 0.5:0.5 with AO as sacrificial agent) revealed that Fe, N, O, Ag, C and Cl elements coexisted in the catalyst, Figure 5.15a.

Table 5.1 presents the Ag^0/Ag^+ , $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{O}_\text{H}/\text{O}_\text{L}$ ratios of all prepared ACM-gC samples obtained from the XPS peak areas.

The binding energies of Ag 3d_{5/2} and Ag 3d_{3/2} those were splinting into Ag⁰ and Ag⁺, Fe 2p_{3/2} and Fe 2p_{1/2} with satellite peaks and the peaks belongs to O 1s were given in Figures 5.15b, c, and d, respectively.

As seen in Figure 5.15b, the peak intensities of Ag⁰ increased with increasing photodeposition time. As the photodeposition time increased from 30 min to 1 h and then 2 h, Ag^0/Ag^+ ratios increased from 0.16 to 0.42 and then 0.93, respectively, Table 5.1. Increase in photodeposition time has positive effect also in reduction of Fe³⁺ to Fe²⁺ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios increased from 1.03 to 1.13 and then 2.15, respectively. In general, the oxygen species adsorbed to the surface have a higher mobility than the lattice oxygen, thus they can actively participate in the photocatalytic reaction (Yang et al., 2021; Yalçın and Dükkancı, 2022; Zhang et al.,

2013). So it is important to investigate O_H/O_L ratios in the samples. In this context, the highest O_H/O_L ratio (5.47) was observed for ACM-gC-3 photocatalyst that was prepared under 2 h of photodeposition time.



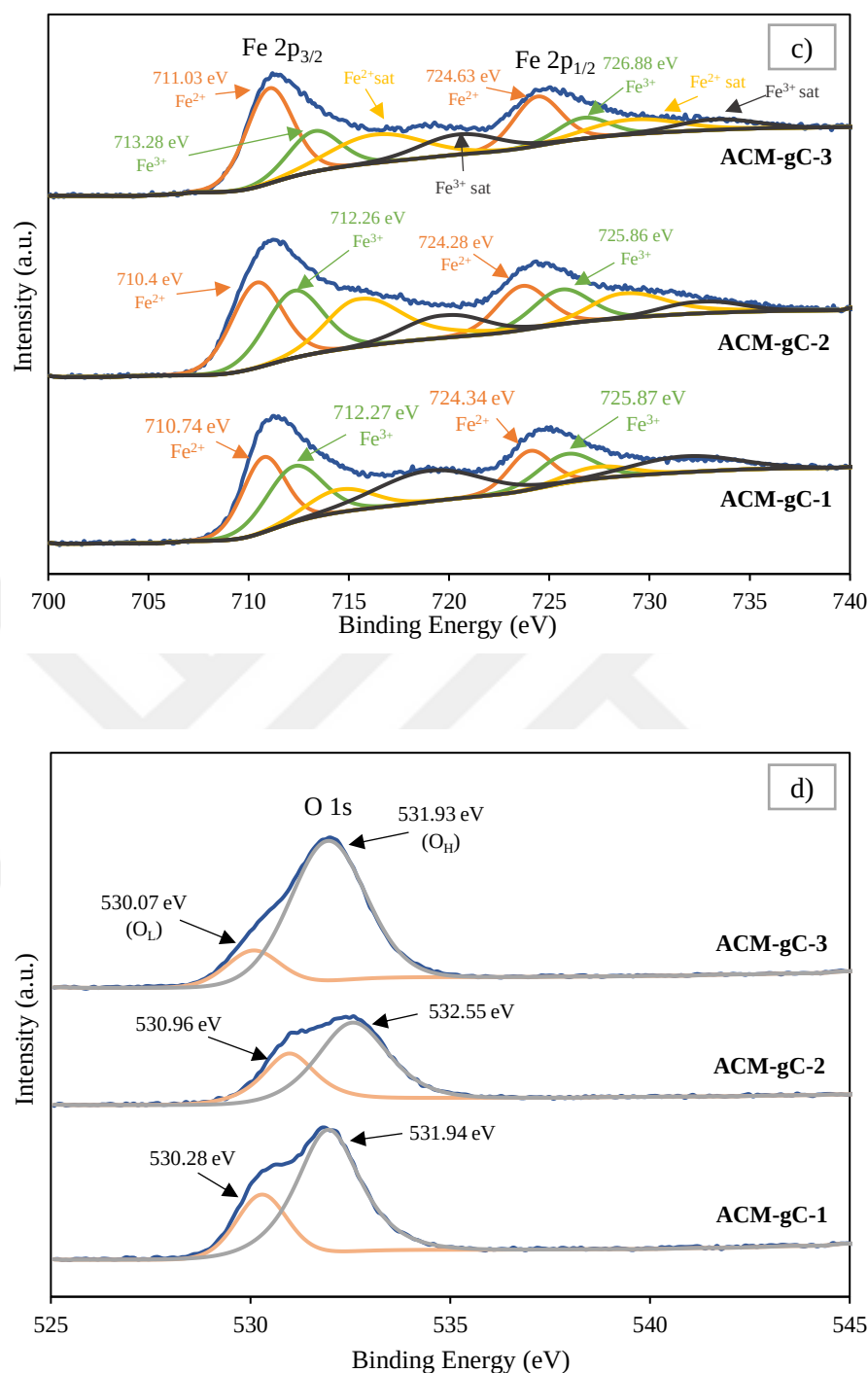


Figure 5.15 XPS spectra of ACM-gC photocatalysts synthesized by photodeposition time of 30 min (ACM-gC-1), 1 h (ACM-gC-2) and 2 h (ACM-gC-3), a) XPS survey, b) Ag 3d c) Fe 2p d) O 1s.

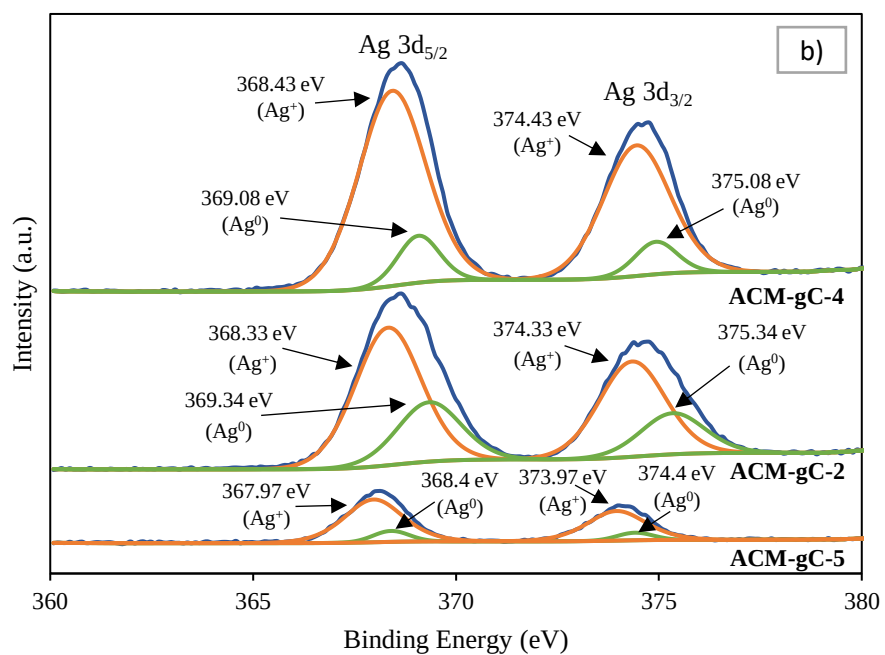
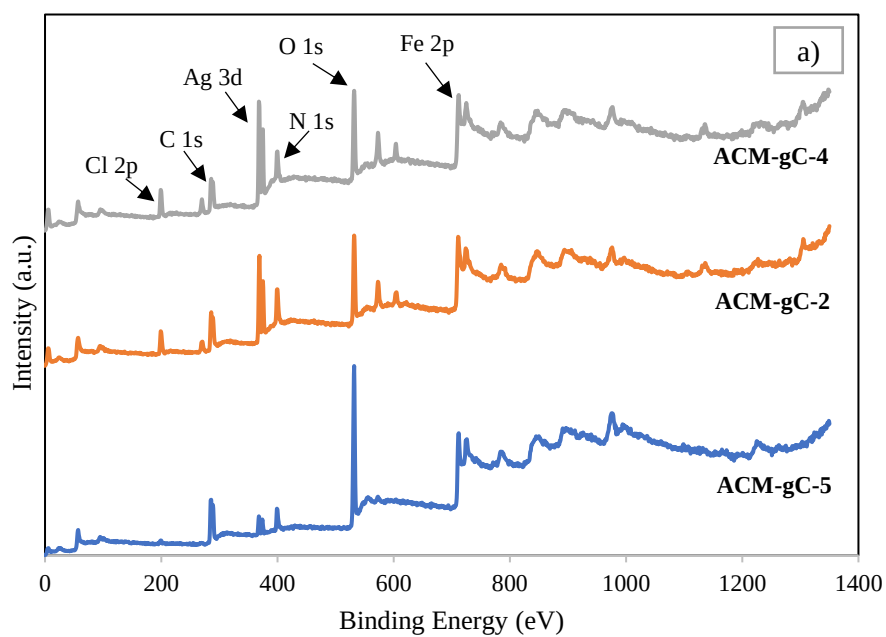
XPS survey spectrum of the ACM-gC photocatalysts that were prepared with different Fe:Ag ratios of 0.25:0.75 (ACM-gC-4), 0.5:0.5 (ACM-gC-2), and 0.75:0.25 (ACM-gC-5) (prepared with AO as sacrificial agent under 1 h of

photodeposition time) is presented in Figure 5.16a, and spectrum confirmed that Fe, N, O, Ag, C, and Cl elements coexist in the catalyst.

The peaks correspond to Ag 3d_{5/2} and Ag 3d_{3/2} of Ag⁺ in AgCl and Ag NPs were given in Figure 5.16b (Huang et al., 2018; Viswanathan et al., 2021; Wu et al., 2019; Yang et al., 2021).

The XPS spectra of Fe 2p was separated into Fe 2p_{3/2}, Fe 2p_{1/2}, and satellite peaks, as illustrated in Figure 5.16c. As depicted in Figure 5.16d, O 1s exhibits two peaks with binding energies around 530 eV and 532 eV, that shows the lattice oxygen (O_L) and surface adsorbed oxygen (O_H) on oxygen vacancies in ACM-gC-4 and ACM-gC-2 samples, respectively. However, in ACM-gC-5 sample, three peaks at 530.44 eV, 531.69 eV, and 532.26 eV correspond the C=O and Fe-O bands and adsorbed surface oxygen, respectively.

As given in Figure 5.16b, the peak intensities of Ag 3d_{5/2} and Ag 3d_{3/2} increased with increasing Ag loading amount. As expected the lowest peak intensities for Fe 2p_{3/2} and Fe 2p_{1/2} was observed with ACM-gC-4 composite that has the lowest Fe amount (Fe:Ag mole ratio of 0.25:0.75). The Ag⁰/Ag⁺, Fe²⁺/Fe³⁺ and O_H/O_L ratios were compared for ACM-gC-5, ACM-gC-2 and ACM-gC-4 photocatalysts to investigate the effect Ag loading amount, see Table 5.1. The highest Ag⁰/Ag⁺ ratio was measured for ACM-gC-2 sample that has the same mole of Fe and Ag (Fe: Ag molar ratio = 0.5:0.5). However, the same value of Ag⁰/Ag⁺ ratio of 0.15 was measured for ACM-gC-4 and ACM-gC-5 samples. The highest Fe²⁺/Fe³⁺ value of 1.84 was measured for ACM-gC-4 sample that has the Fe:Ag molar ratio of 0.25:0.75. It may say that, although ACM-gC-4 has the lowest Fe mole ratio, most of the present Fe³⁺ reduced to Fe²⁺.



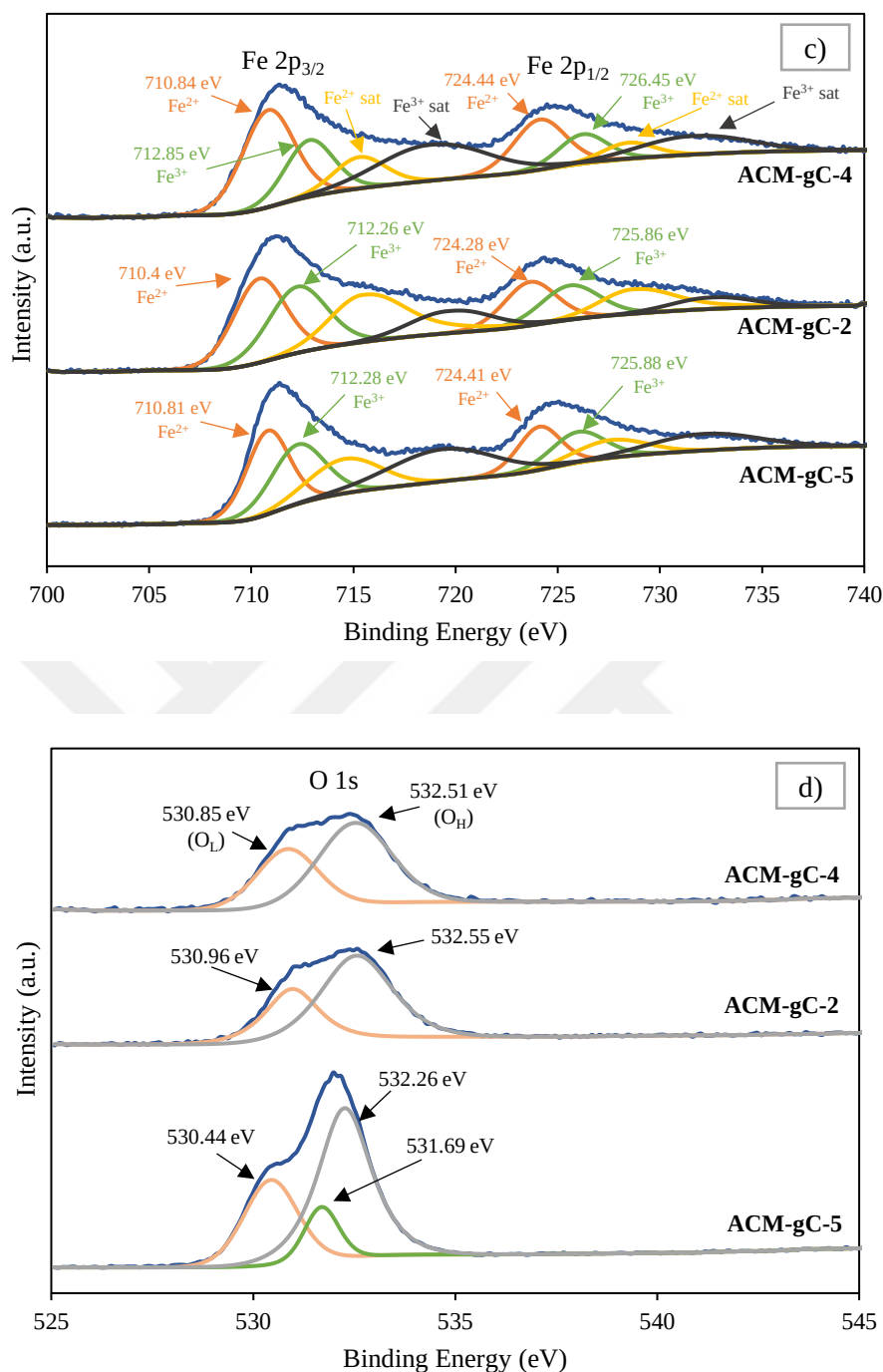
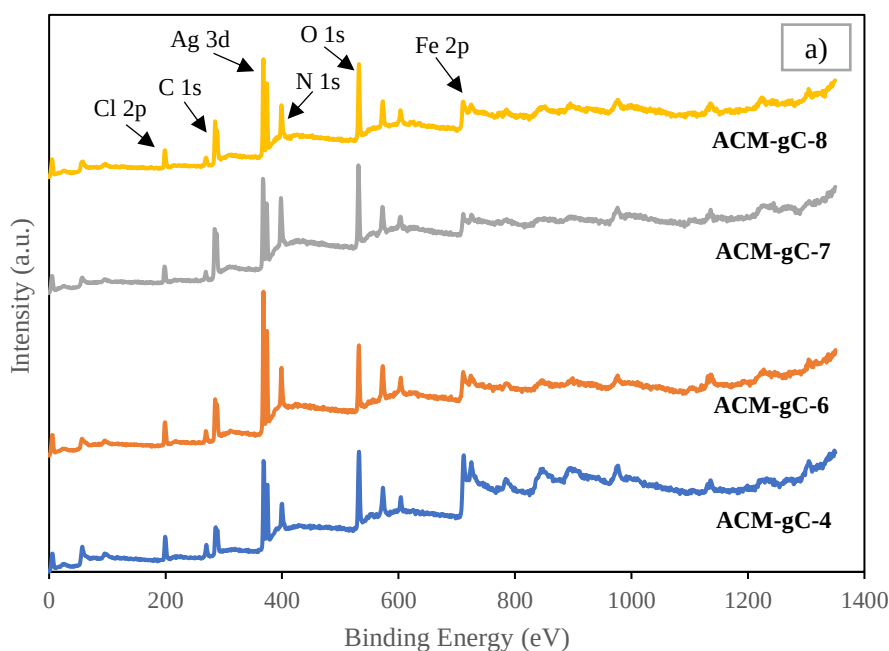


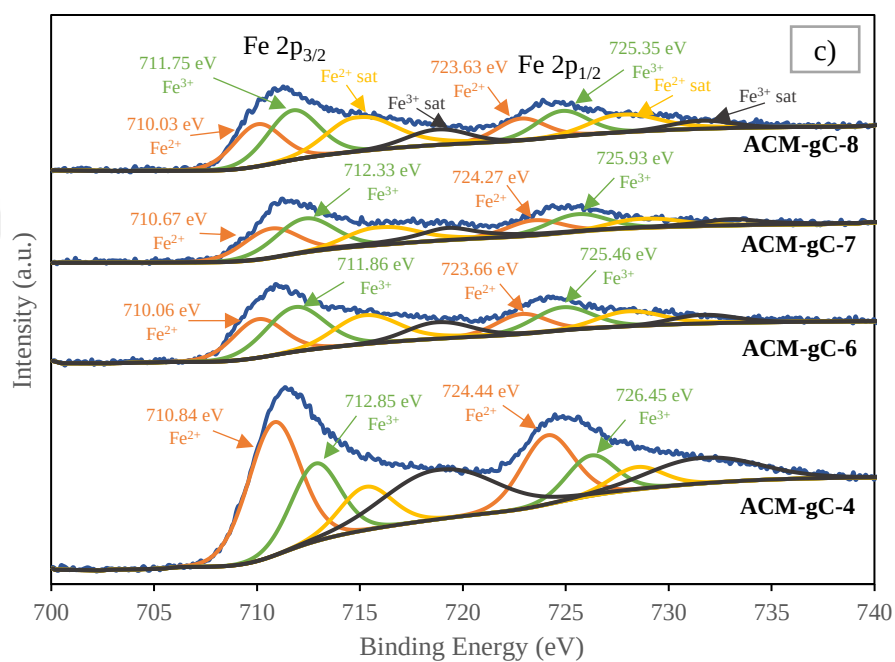
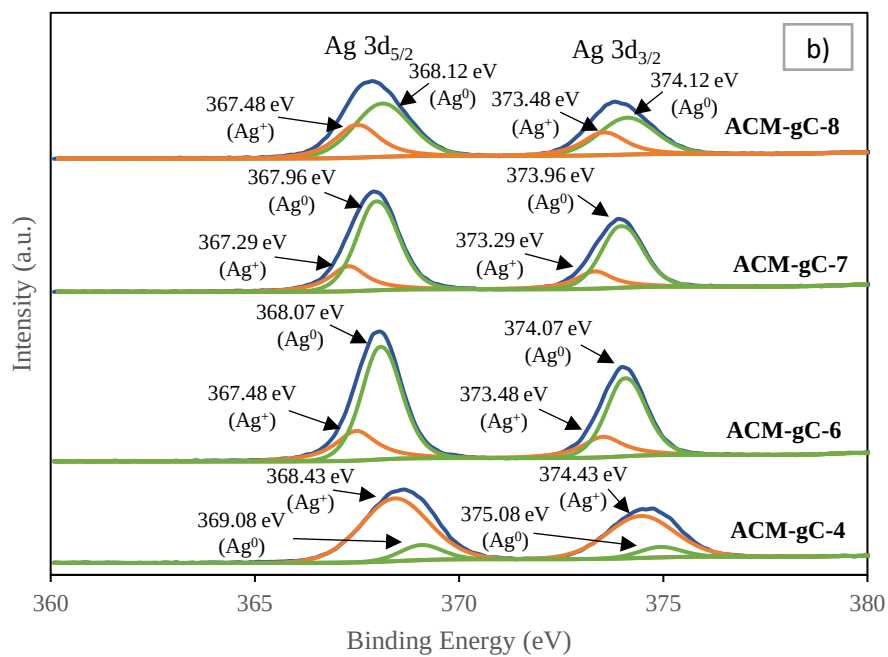
Figure 5.16 XPS spectra of ACM-gC photocatalysts prepared with different Fe:Ag ratios of 0.75:0.25 (ACM-gC-5), 0.5:0.5 (ACM-gC-2), and 0.25:0.75 (ACM-gC-4) for the photodeposition time of 1 h, a) XPS survey, b) Ag 3d c) Fe 2p d) O 1s.

XPS spectra of the ACM-gC catalysts prepared with different sacrificial agents of ammonium oxalate (ACM-gC-4), ethanol (ACM-gC-6), and glycerol (ACM-gC-8) and without sacrificial agent (ACM-gC-7) (with Fe : Ag ratio of

0.25:0.75 under 1 h of photodeposition time) show that sample consists of Fe, N, O, Ag, C and Cl elements (Figure 5.17a).

The Ag^0/Ag^+ , $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{O}_\text{H}/\text{O}_\text{L}$ ratios were compared for ACM-gC-4, ACM-gC-6, ACM-gC-7, and ACM-gC-8 samples to investigate the effect of sacrificial agent, see Table 5.1. The Ag^0/Ag^+ ratio measured for ACM-gC-4 sample was much lower than that of ACM-gC-6, ACM-gC-7, and ACM-gC-8 samples. It could be said that, ammonium oxalate as sacrificial agent has the lowest ability to reduced the Ag^+ in AgCl to Ag^0 . The highest $\text{Fe}^{2+}/\text{Fe}^{3+}$ value of 1.84 was measured for ACM-gC-4 and it was followed by ACM-gC-7 (0.80), ACM-gC-8 (0.79), and ACM-gC-6 (0.74). The highest $\text{O}_\text{H}/\text{O}_\text{L}$ ratio of 18.37 was measured for ACM-gC-6 sample that was prepared with ethanol as sacrificial agent. According to this result, it may say that, the OH group in ethanol promote the production of more adsorb oxygen in the structure.





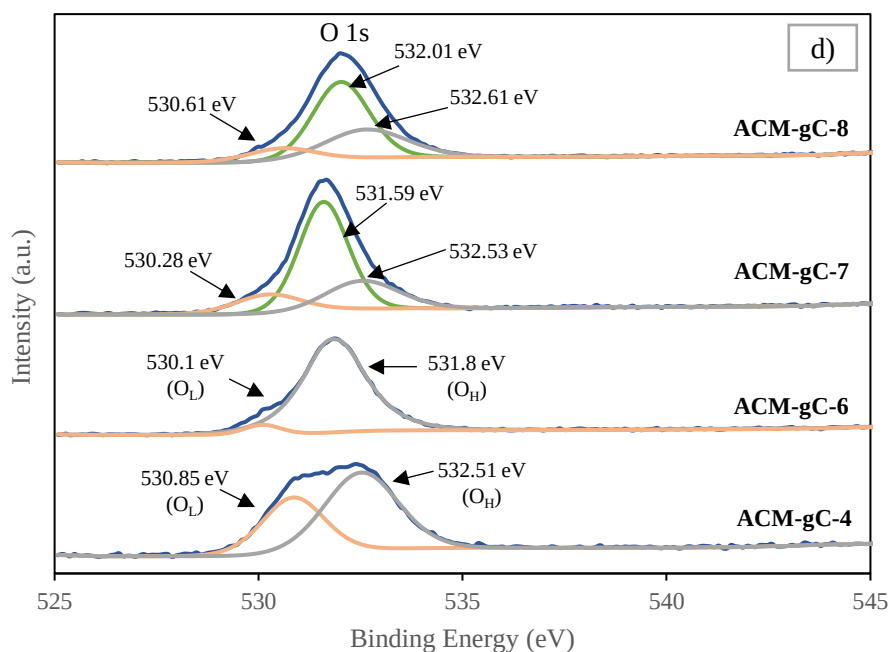
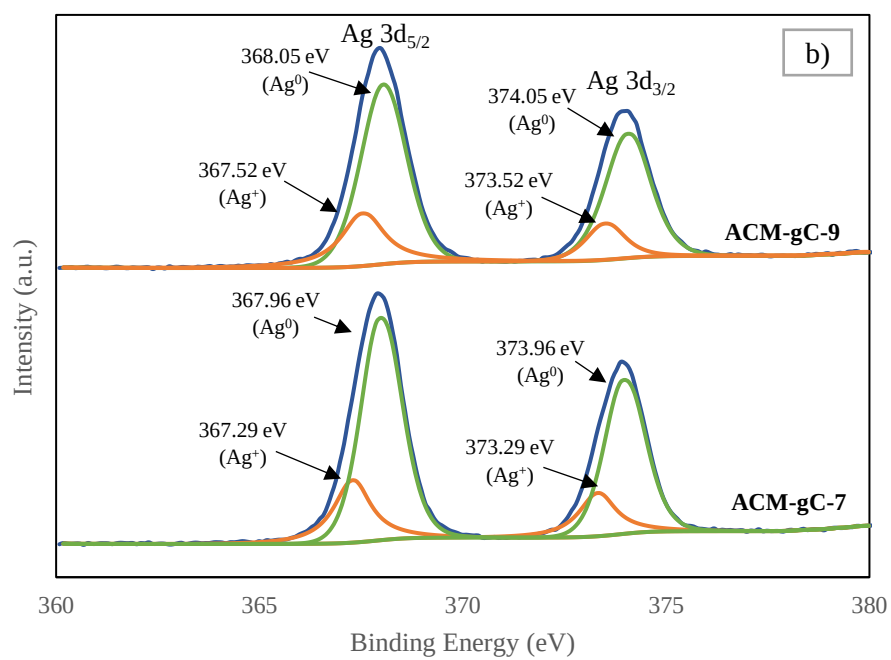
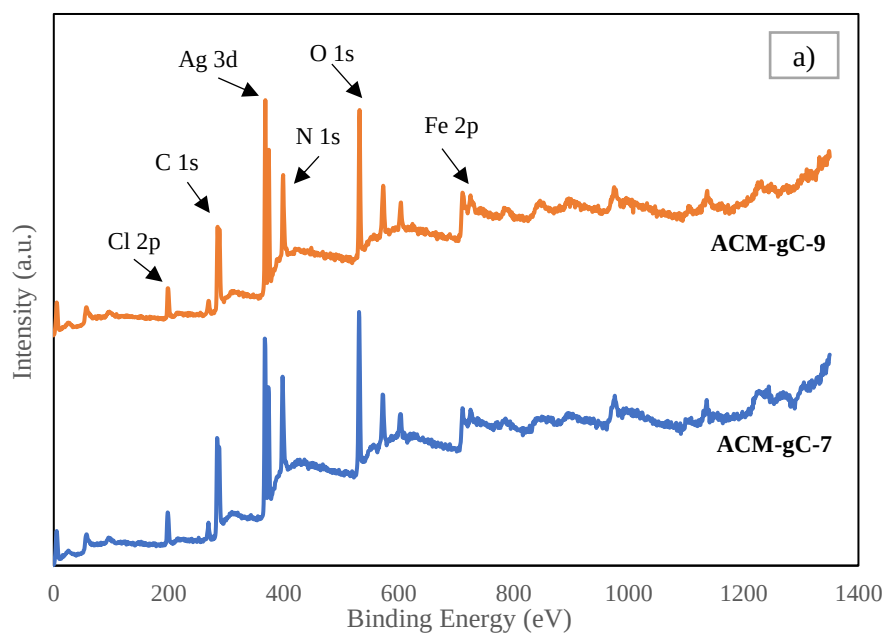


Figure 5.17 XPS spectra of ACM-gC photocatalysts prepared with different sacrificial agent of ammonium oxalate (ACM-gC-4), ethanol (ACM-gC-6), glycerol (ACM-gC-8), and with no sacrificial agent (ACM-gC-7), a) XPS survey, b) Ag 3d c) Fe 2p d) O 1s.

XPS survey spectrum of the ACM-gC photocatalysts that were prepared with different light source of visible LED (ACM-gC-7) and high-pressure Na Lamps (ACM-gC-9) for photoreduction (prepared with Fe : Ag ratio of 0.25:0.75 without sacrificial agent under 1h of photodeposition time) indicates the coexistence of Fe, N, O, Ag, C, and Cl elements in the structure, see in Figure 5.18a.

The Ag^0/Ag^+ , $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{O}_\text{H}/\text{O}_\text{L}$ ratios were compared for ACM-gC-7, and ACM-gC-9 samples to investigate the effect of light type in photodeposition process, see Table 5.1. As seen, the high-pressure Na lamps is as effective in Ag reduction as LED lamp. The Ag^0/Ag^+ ratio measured for ACM-gC-7 sample was 3.31 and it was 2.83 for ACM-gC-9 samples. However, same effect is not valid for the reduction of Fe^{3+} to Fe^{2+} . The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio was much lower for ACM-gC-9 than that of ACM-gC-7. Almost the same $\text{O}_\text{H}/\text{O}_\text{L}$ ratio was measured for ACM-gC-7 and ACM-gC-9 samples that was prepared without sacrificial agent.



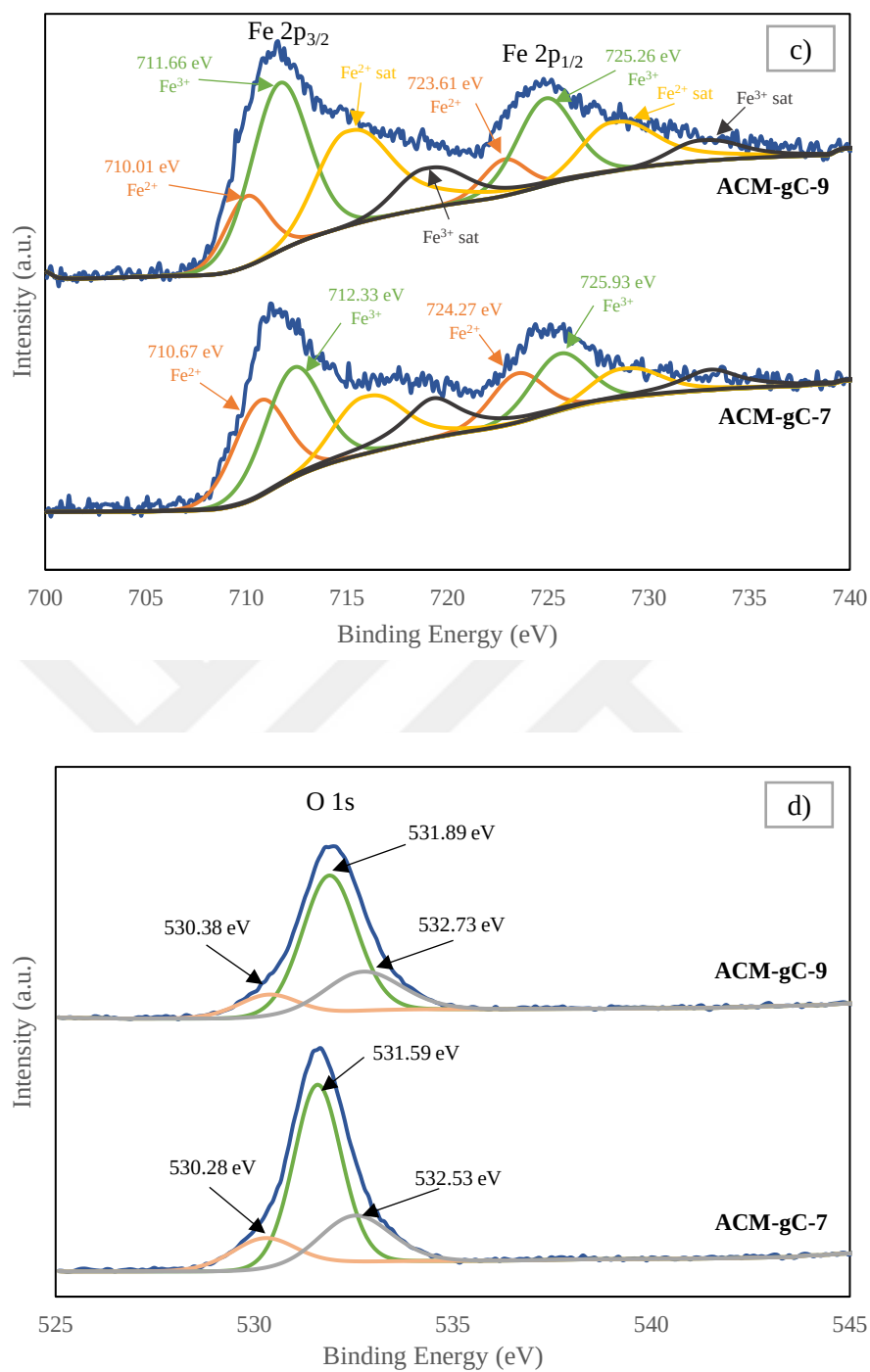


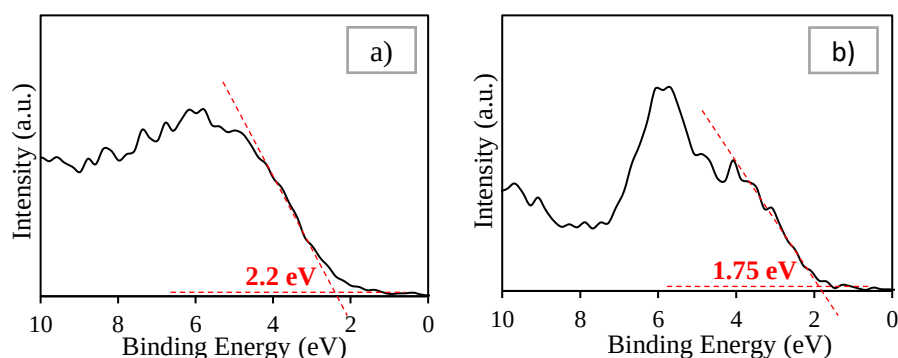
Figure 5.18 XPS spectra of ACM-gC photocatalysts synthesized under different light source of visible LED (ACM-gC-7) and high-pressure Na Lamps (ACM-gC-9) for photoreduction, a) XPS survey, b) Ag 3d c) Fe 2p d) O 1s.

Table 5.1 Ag^0/Ag^+ , $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{O}_\text{H}/\text{O}_\text{L}$ ratios for prepared samples.

Catalyst	$\text{Fe}^{2+}/\text{Fe}^{3+}$	Ag^0/Ag^+	$\text{O}_\text{H}/\text{O}_\text{L}$
ACM-gC-1	1.03	0.16	2.65
ACM-gC-2	1.13	0.42	1.97
ACM-gC-3	2.15	0.93	5.47
ACM-gC-4	1.84	0.15	1.63
ACM-gC-5	1.13	0.15	1.34
ACM-gC-6	0.74	3.12	18.37
ACM-gC-7	0.80	3.31	0.31
ACM-gC-8	0.79	1.86	1.31
ACM-gC-9	0.32	2.83	0.34

5.1.4 XPS-VB spectrum analysis

In order to explain photodegradation mechanism of DRN over MIL-88A/g- C_3N_4 and Ag/AgCl@MIL-88A/g- C_3N_4 composites, valance band energies should be measured. Valance band energies of MIL-88A and g- C_3N_4 were measured from XPS-VB spectrum analysis. Figure 5.19 shows the Valance Band position of samples MIL-88A (Figure 5.19a) and g- C_3N_4 (Figure 5.19b). Intercept of peak intensity with x-axis gives valance band energy. According to result, valance band energies of MIL-88A and g- C_3N_4 were 2.2 eV and 1.75 eV, respectively.

**Figure 5.19** XPS-VB spectrum, a) MIL-88A, b) g- C_3N_4 .

5.1.5 UV-Vis DRS analysis of prepared catalysts

To determine the electronic behavior of prepared samples, UV-Vis DRS analysis was performed. Band Theory is a theory, which described with terms defined for the valence and conduction bands of semiconductor materials: HOMO (π -orbitals) and LUMO (π^* -orbitals). The band gap of the material can be defined

by the energy difference between HOMO and LUMO. The band gap of the as-prepared samples was measured using the Tauc model as given in Eq. 20.

$$(F(R) * hv) = C (hv - E_g)^n \quad (20)$$

where h is the Plank's constant, v is the light frequency, $hv = (1240/\lambda)$ eV, C is a parameter that depends on the transition probability, $F(R) = (1-R)^2/2R$, R is reflectance, E_g is the band gap energy and n is a number that refers to the transition process:

$n = 1/2$: Direct allowed transitions

$n = 2$: Indirect allowed transitions

The Tauc plots for the samples were obtained at $n=2$, which shows that the prepared samples have indirect band gap (Wu et al., 2019; Huang et al., 2022). The band gap energy of samples was estimated by the x-axis intercept at $(F(R)*hv)^{1/2} = 0$ (Bagherzadeh et al., 2022, Landi et al., 2022). Figure 5.20 shows the reflectance values of all samples, and Figure 5.21 gives $(F(R)*hv)^{1/2} - hv$ relationship for measurement of band gap energy.

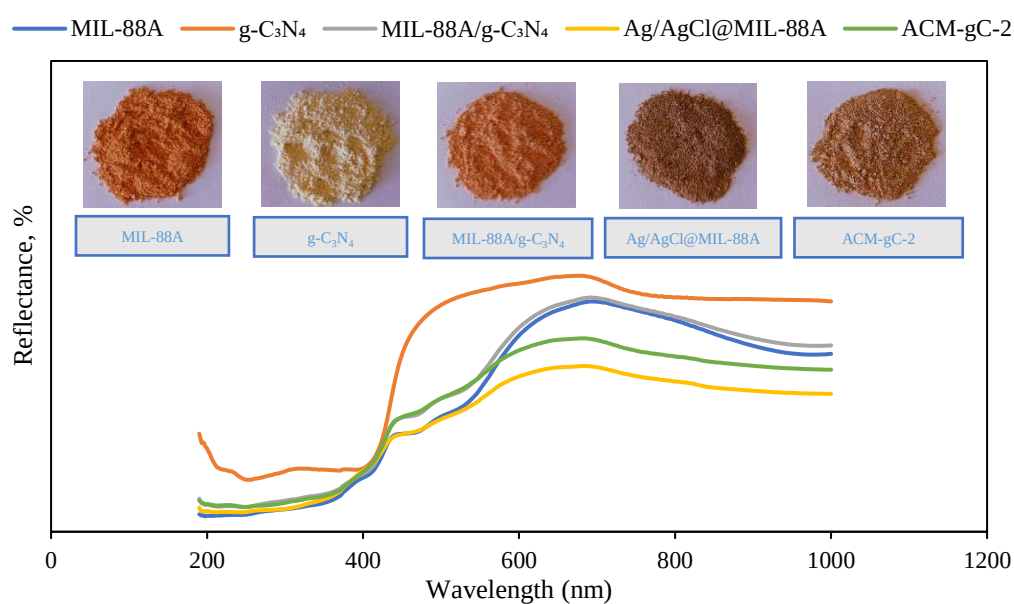


Figure 5.20 Reflectance, % values of the samples measured from UV-Vis DRS analysis.

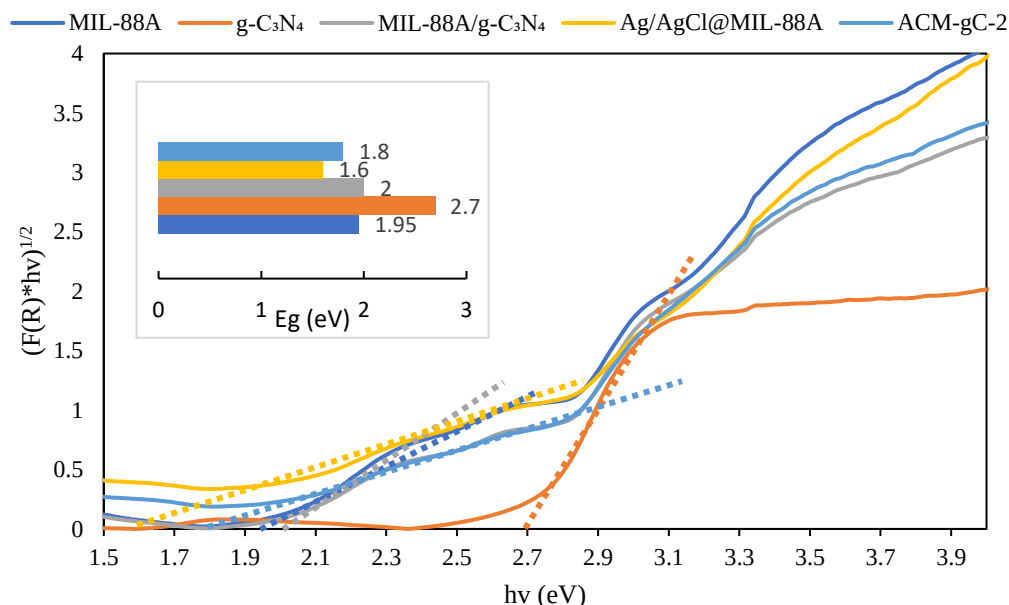


Figure 5.21 Calculated band gap energies of the MIL-88A, g-C₃N₄, MIL-88A/g-C₃N₄, Ag/AgCl@MIL-88A, and ACM-gC-2 catalyst.

The measured band gap energy was 1.95 eV for MIL-88A. Addition of Ag/AgCl decreased the band gap energy from 1.95 eV to 1.6 eV due to the surface plasmon resonance effect of Ag NPs. The band gap energy of bare g-C₃N₄ was 2.7 eV, however, as expected the band gap energy of MIL-88A/g-C₃N₄ was between the MIL-88A and g-C₃N₄ and measured as 2.0 eV. The ACM-gC-2 photocatalyst, which was synthesized with Ag:Fe mole ratio of 0.5:0.5, with ammonium oxalate as sacrificial agent and under 1 h of photodeposition, had the band gap energy of 1.8 eV. Based on the measured band gap energies, it may have said that all the sample would give photocatalytic activity under visible light irradiation.

Mesaurement of band gap energies of samples is especially important to examine the formation of electron-hole pairs under light irradiation. However, separation and migration efficiency of induced electrons and holes is another important issue in photocatalytic system in the presence of heterostructured catalysts. Huang et al. (2018) investigated the photocurrent responses of Ag/AgCl loaded MIL-88A and the pure MIL-88A(Fe). They observed that, the photocurrent response of Ag/AgCl@MIL-88A was much more higher than that of the MIL-88A(Fe) under several on–off visible light irradiation cycles. As it is known that a larger photocurrent density means a more efficient charge transfer and a lower

recombination tendency of photoinduced charge carriers, it could be said that Ag/AgCl@MIL-88A had more efficient separation and transfer efficiency of photogenerated charge carriers. Similarly, the photocurrent intensity of binary composite MIL-88A/g-C₃N₄ was more than that of bare g-C₃N₄, MIL-88A and that showed the MIL-88A/g-C₃N₄ interface improved the rapid charge separation and transfer (Gholizadeh Khasevani and Gholami, 2019). Shao et al. 2019 synthesized several MIL-88A/g-C₃N₄ composites and it was obvious that the composites had higher photocurrent density than that of bare MIL-88A and g-C₃N₄.

5.1.6 Nitrogen Adsorption studies

The specific surface area and pore volume of MIL-88A, g-C₃N₄, MIL-88A/g-C₃N₄, Ag/AgCl@MIL-88A, and ACM-gC-2 samples were evaluated by BET and results are summarized in Table 5.2. The isotherms of all prepared samples indicated a type IV according to IUPAC classification, see Figure 5.22. Type IV represents the presence of mesopores in the samples. MIL-88A has the highest surface area of 105.13 m²/g. Incorporation of Ag/AgCl or g-C₃N₄ caused a decrease in BET surface area to 17.35 m²/g and 21.88 m²/g, respectively. The decrease in BET surface area may due to the coverage of MIL-88A porosity by Ag/AgCl and g-C₃N₄. This was also confirmed by the pore volume of samples. Pore volume of MIL-88A was dropped from 0.0638 cm³/g to 0.0445 cm³/g and 0.0422 cm³/g, respectively. ACM-gC-2 triple composite photocatalyst has very low surface area according to bare MIL-88A, probably due to the g-C₃N₄ flakes that cover the MIL-88A surface, thereby reducing the specific surface area.

Table 5.2 Physico-chemical properties of prepared MIL-88A, g-C₃N₄, MIL-88A/g-C₃N₄, Ag/AgCl@MIL-88A, and ACM-gC-2 samples.

Photocatalyst	S _{BET} (m ² /g)	Pore volume (cm ³ /g)
MIL-88A	105.13	0.0638
g-C ₃ N ₄	15.04	0.0855
MIL-88A/g-C ₃ N ₄	21.88	0.0422
Ag/AgCl@MIL-88A	17.35	0.0445
ACM-gC-2	13.02	0.0471

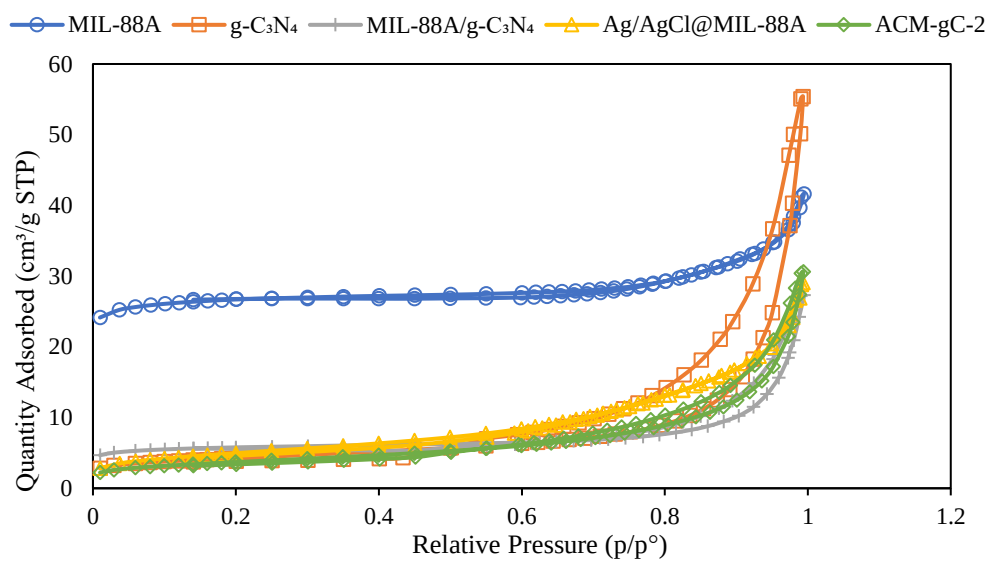
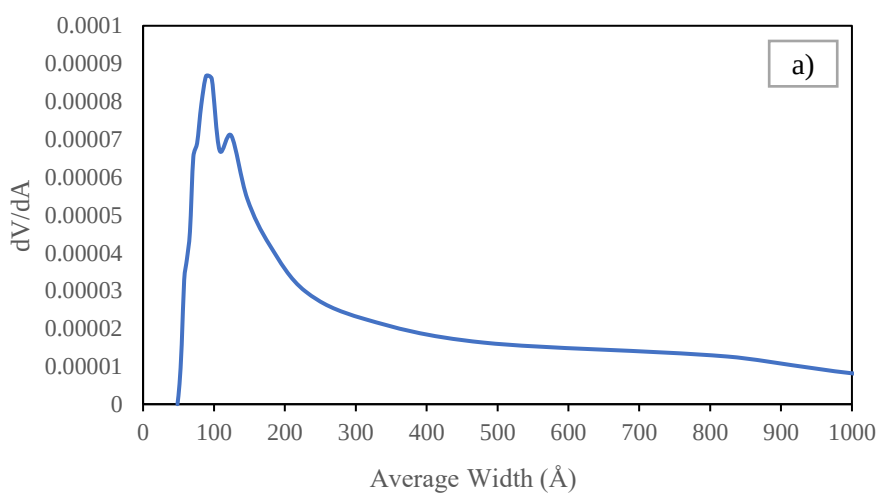
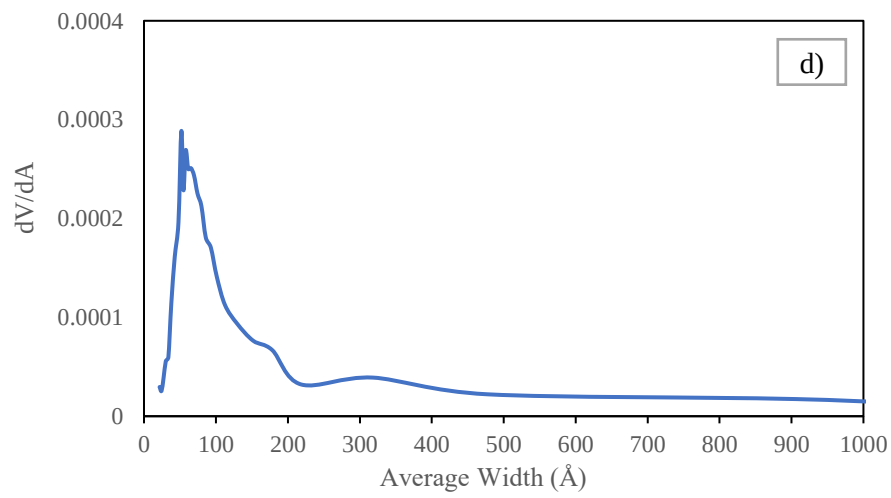
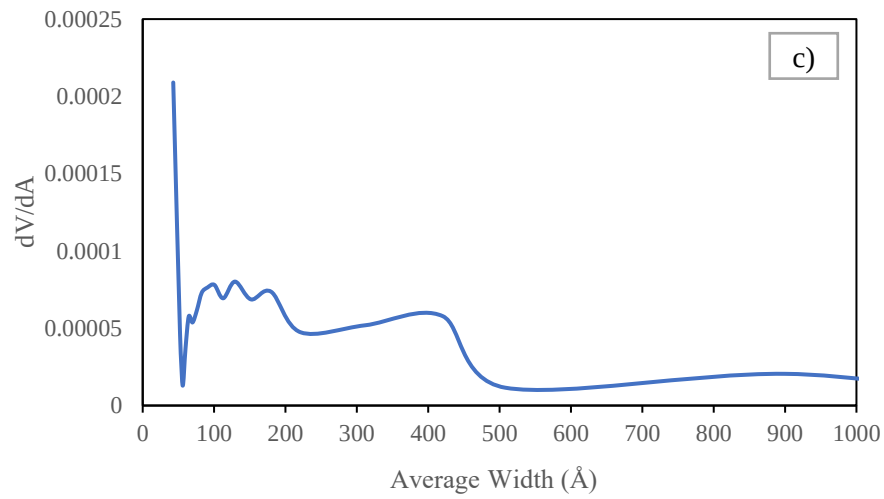
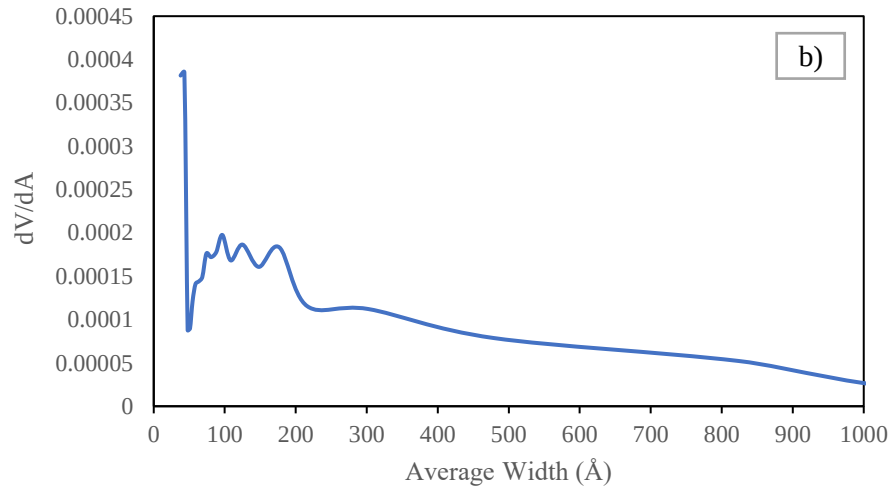


Figure 5.22 Nitrogen adsorption-desorption isotherms.

Pore size distribution curves were given in Figure 5.23. The pore size distribution curves provides the isotherms, pores are distributed between 2 nm – 20 nm.





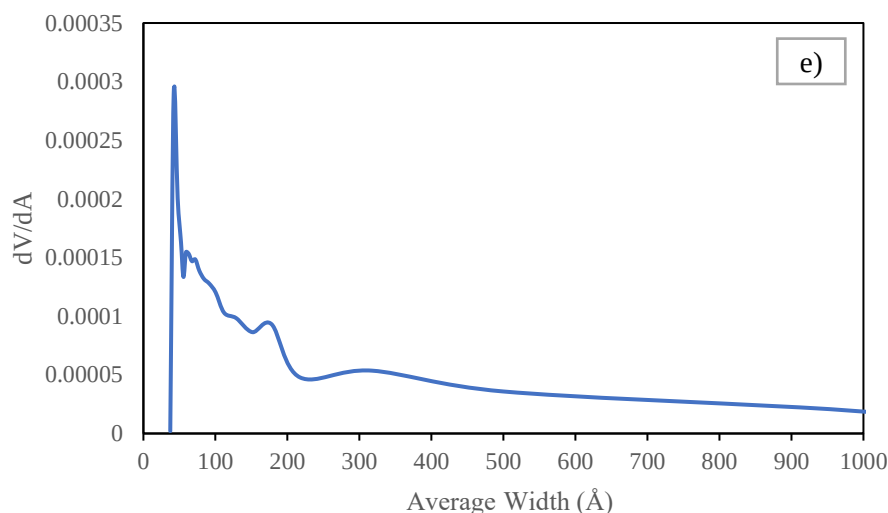


Figure 5.23 Pore size distribution curves of a) MIL-88A, b) g-C₃N₄, c) MIL-88A/g-C₃N₄, d) Ag/AgCl@MIL-88A, e) ACM-gC-2.

5.1.7 FT- IR Analysis of prepared composites

In order to further verify the structure of all prepared Ag/AgCl@MIL-88A/g-C₃N₄ photocatalysts, all samples were investigated by FT-IR spectroscopy, see Figure 5.24. The transmittance % values were calculated from absorbance values via Eqs. 21 and 22 (Song et al., 2022).

$$\text{Absorbance} = -\log (\text{transmittance}) \quad (41)$$

$$A = 2 - \log (T\%) \quad (22)$$

As observed for all ACM-gC photocatalysts, the broad absorption band at around 3000 – 3500 cm⁻¹ are ascribed to the O – H stretching vibrations of surface adsorbed water (Gholizadeh Khasevani and Gholami, 2018). The band at 418 cm⁻¹ can be assigned to vibration mode of Fe – O in MIL-88A structure. The bands at 1398 and 1635 cm⁻¹ can be attributed to the symmetric and asymmetric vibration of the carboxyl group (-COOH) in fumaric acid, respectively. The peak at 672 cm⁻¹ is attributable the carbonyl group. The MIL-88A/g-C₃N₄ heterocomposite formation was confirmed through the bands at 805 cm⁻¹, and 1200 – 1635 cm⁻¹ related to the triazine phase and the stretching vibration of C – N mode, respectively (Gholizadeh Khasevani and Gholami, 2018; Gholizadeh Khasevani and Gholami, 2019; Fu et al., 2020; Viswanathan et al., 2021).

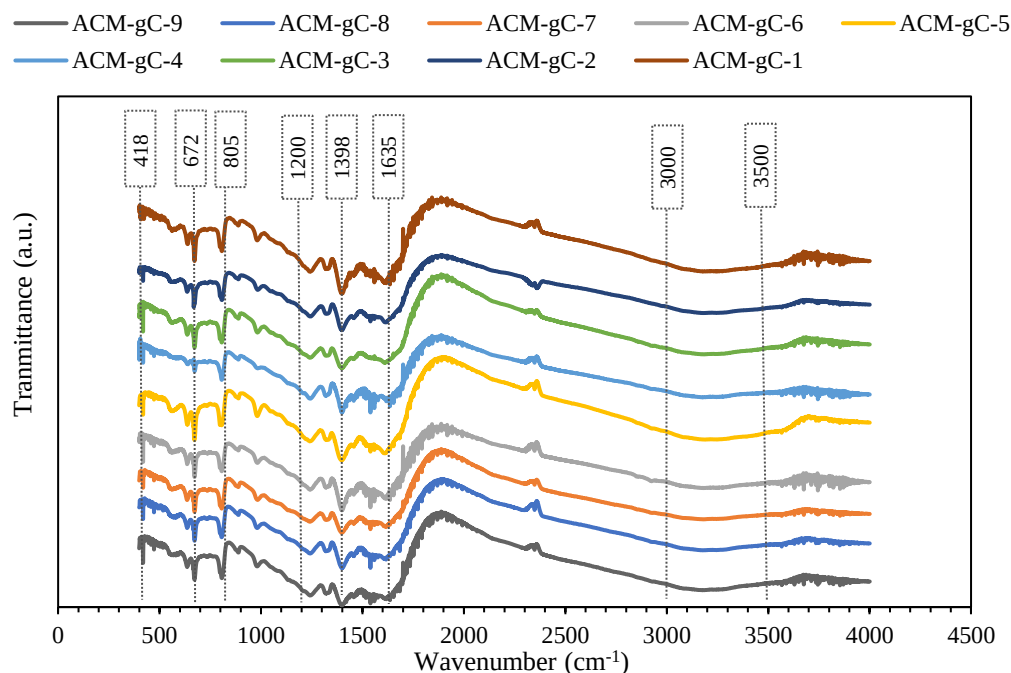


Figure 5.24 FT-IR spectra of all the prepared ACM-gC photocatalysts.

5.2 Photodegradation of Diuron

5.2.1 Photodegradation of Diuron over different photocatalysts

The photodegradation of Diuron (DRN) was performed over MIL-88A, g-C₃N₄, MIL-88A/g-C₃N₄, Ag/AgCl@MIL-88A, and Ag/AgCl@MIL-88A/g-C₃N₄ (ACM-gC-2) photocatalysts. Experiments were conducted under visible LED light irradiation under following conditions: DRN initial concentration of 10 ppm, catalyst loading of 1g/L with DRN solution of 150 mL and at a temperature of 298K (Figure 5.25). In all experiments, adsorption-desorption equilibrium was performed in the dark for 30 min and shown on the related Figures. The adsorption of DRN on different samples was very low and change in the range of 0.95% - 9%. Therefore, although the DRN concentration is 10 ppm at the beginning of each experiment, it changes not more than 10% for each sample after 30 minutes of adsorption. The duration of photo-oxidation was 2 h. Each run was repeated at least three times and mostly two times, and standard deviations were in the range of ± 0.0006 - ± 0.064 .

Figure 5.25a exhibits changes of concentration of DRN with time, and Figure 5.25b shows degradation percentage of DRN over MIL-88A, g-C₃N₄, MIL-88A/g-

C_3N_4 , $Ag/AgCl@MIL-88A$, $Ag/AgCl@MIL-88A/g-C_3N_4$ (ACM-gC-2) photocatalysts within 2 h of irradiation.

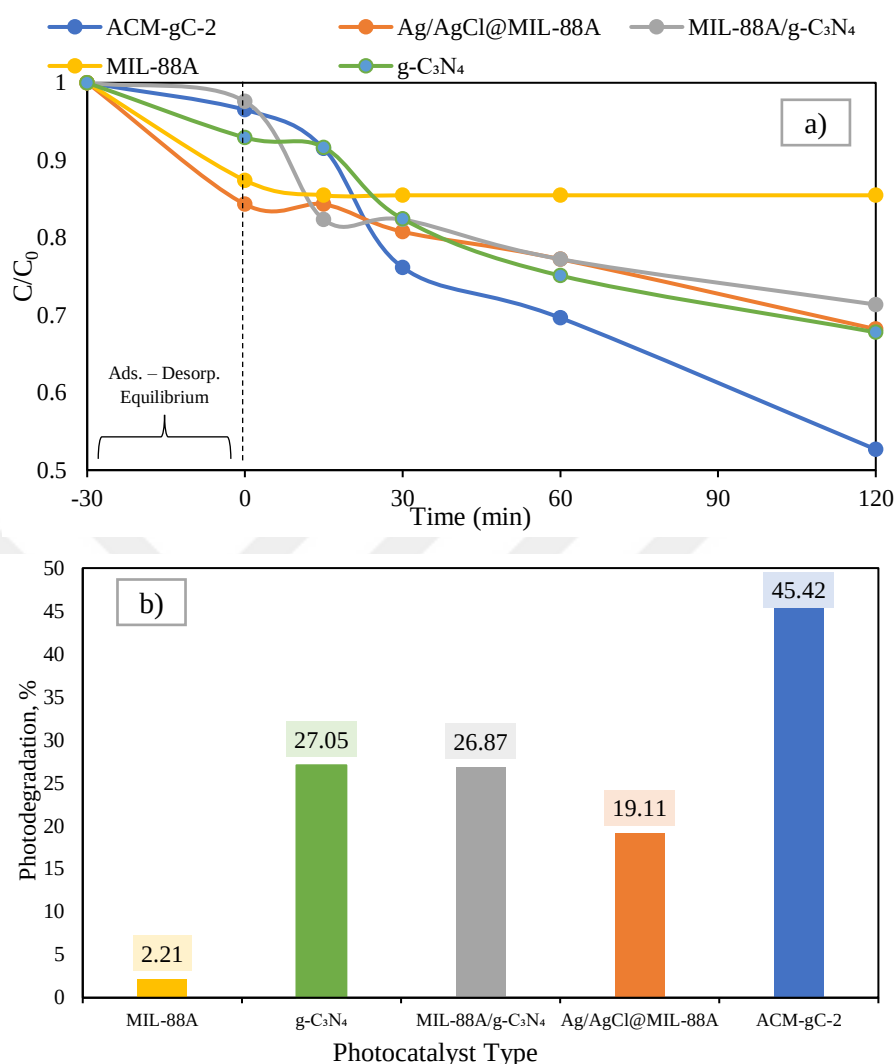


Figure 5.25 Photodegradation of DRN over MIL-88A, $g-C_3N_4$, MIL-88A/ $g-C_3N_4$, $Ag/AgCl@MIL-88A$, and ACM-gC-2, a) change of DRN concentration with time, b) photodegradation % after 2 h of reaction ($[DRN]_0 = 10$ ppm, catalyst loading = 1 g/L, $T = 298K$).

As seen in Figures 5.25a and b, 27.05% and 2.21% of photodegradations were observed over bare $g-C_3N_4$ and MIL-88A, respectively. In the presence of binary MIL-88/ $g-C_3N_4$, a degradation of 26.87% was achieved. However, loading of co-catalyst, $Ag/AgCl$, increased the efficiency of MIL-88A from 2.21% to 19.11%. The highest degradation of 45.42% was achieved over ACM-gC-2 photocatalyst.

Kinetic studies were also performed over the each photocatalysts, and it was observed that photocatalytic oxidation of DRN was obeyed pseudo-first order

kinetics. Calculated rate constants gave the similar trend with photodegradation results and they were in the following order: ACM-gC-2 ($k = 0.0052 \text{ min}^{-1}$) > MIL-88A/g-C₃N₄ ($k = 0.0031 \text{ min}^{-1}$) > g-C₃N₄ ($k = 0.0028 \text{ min}^{-1}$) > Ag/AgCl@MIL-88A ($k = 0.0017 \text{ min}^{-1}$), and MIL-88A ($k = 0.0015 \text{ min}^{-1}$).

As known well, like other single-component photocatalysts, bare MIL-88A MOFs exhibit fast recombination of conduction band electrons and valance band holes during the photocatalytic process that caused a low catalytic efficiency (2.21% after 2 h of irradiation). Plasmonic metals, including platinum (Pt), silver (Ag), and gold (Au), are responsible for conducting electrons by exploiting local surface plasmon resonance (LSPR), which is preferred for improving the catalytic performance of MOFs. LSPR is a natural frequency of oscillation of valence band electrons against the restoring force of the positively charged nuclei. If the frequency of the photon reaching the semiconductor matches the natural oscillation frequency of the valence band electrons, a strong electric field is produced around the metal surface, resulting in oscillations of the electrons. The light absorption is greatly enhanced by LSPR excitation and the resonance typically occurs in the visible region (Li et al., 2021; Wang et al., 2019). Among several plasmonic metals, silver (Ag) is preferable due to the high conductivity and particularly low cost. Generally, AgCl is accompanied with the presence of Ag to modify MOFs. By this way, the lifetime of photogenerated electrons is extended by a good match of the energy band structure of MOFs and AgCl and the LSPR effect of Ag (Chen et al., 2022; Zheng et al., 2021). Thus, photodegradation of DRN increased significantly (from 2.2% to 19.1%) over Ag/AgCl@MIL-88A.

Coupling of MIL-88A with g-C₃N₄ (MIL-88A/g-C₃N₄) caused an increment in photodegradation performance of DRN from 2.21% to 26.87% due to the separation and migration efficiency of photoinduced electron-hole pairs. This enhancement could be explained with Type II heterojunction mechanism (Z-scheme mechanism) that achieved the keeping of electrons and holes on separate semiconductors (Shao et al., 2019; Gholizadeh Khasevani and Gholami, 2018). The mechanism of MIL-88A/g-C₃N₄ was discussed and explained in detail in Part “5.2.12”.

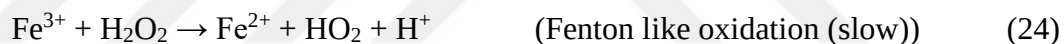
As seen clearly, the highest photodegradation of DRN of 45.42% was achieved over ACM-gC-2 composite after 2 h of irradiation. This enhancement

was due to the great LSPR effect of metallic Ag (Ag^0) that rapidly forms electron-hole pairs under visible light (Yentür and Dükkancı, 2020a; Yang et al., 2014). Here, the role of Ag^0 is not only to improve the utilization of visible light and provide electrons for other semiconductor, but also to serve as the recombination center of CB electrons and the valence band holes on its surface. The mechanism of triple $\text{Ag}/\text{AgCl}/\text{MIL-88A/g-C}_3\text{N}_4$ was discussed and explained in detail in Part “5.2.12”. This mechanism improved the photodegradation performance.

In addition to all these, as MIL-88A(Fe) constructed from Fe^{3+} and fumaric acid, MIL-88A MOFs are visible-light-driven photocatalysts which can achieve improved photo-Fenton oxidation activity. Due to the abundant Fe–O clusters and slow recombination of photo-induced electron-hole pairs via the reactions given below: Due to the abundant Fe–O clusters they drive the Fenton reactions given below.



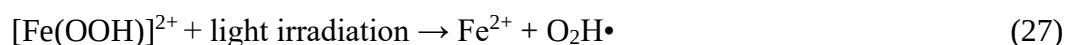
Reaction mentioned in Eq. 23 is propagated from Fe^{2+} regeneration that takes place mainly by reduction of Fe^{3+} by the following reaction called Fenton-like oxidation (Eq. 24):



The slow regeneration of iron(II) is due to the formation of stable hydroxo-iron(III) complexes such as $[\text{Fe}(\text{OOH})]^{2+}$ and $[\text{Fe}(\text{OH})]^{2+}$ by the reaction of iron(III) ions with H_2O_2 and OH^- as shown by the following reactions (Eqs. 25 and 26):



The rate of regeneration of iron(II) that will contribute the Fenton reaction to produce $\text{OH}\cdot$ radicals could be increased in the presence of light irradiation. The advantage of light irradiation is related to the photo-reduction of iron(III) to iron(II) that produces greater amounts of $\text{OH}\cdot$ radicals. The regeneration of iron(II) in the presence of light irradiation of iron(III) complexes can be represented by reactions (Ahmed et al., 2011) (Eqs. 27 and 28):



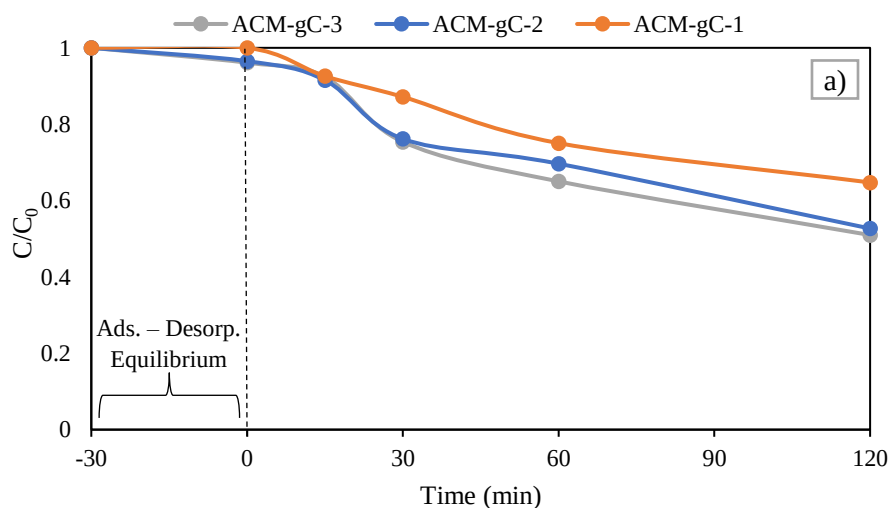
Thus, it could be said that light irradiation helps the decomposition of hydroxo-iron(III) complexes and $[\text{Fe}(\text{OH})]^{2+}$ to $\text{O}_2\text{H}\cdot$ and $\text{OH}\cdot$ radicals that will oxidize DRN. In this part of the study, there was no additional H_2O_2 in the reaction system. The utilized H_2O_2 in the photo-Fenton reaction came from the reaction of abundant $\text{OH}\cdot$ radicals with each other ($\text{OH}\cdot + \text{OH}\cdot \rightarrow \text{H}_2\text{O}_2$). In the presence of additional H_2O_2 the rate of reaction and thus photodegradation is expected to increase.

5.2.2 Effect of Photo-reduction Time on Photodegradation of DRN

In the photocatalytic reaction, amount of Ag NPs, size, growth and distribution of them on MIL-88A are very important and should be investigated.

In the content of this study, firstly photocatalytic activities of Ag/AgCl@MIL-88A/g- C_3N_4 that was prepared with different photodeposition time of 30 min, 1 h, and 2 h (ACM-gC-1, ACM-gC-2, and ACM-gC-3 photocatalysts) was investigated. Experiments were conducted under the following conditions: $[\text{DRN}]_0$: 10ppm, Catalyst loading= 1g/L, $T=298\text{K}$, LED light power= 93.4W, see Figure 5.26.

Runs were repeated two times and the observed standard deviations were in the range of ± 0.014 - ± 0.1 .



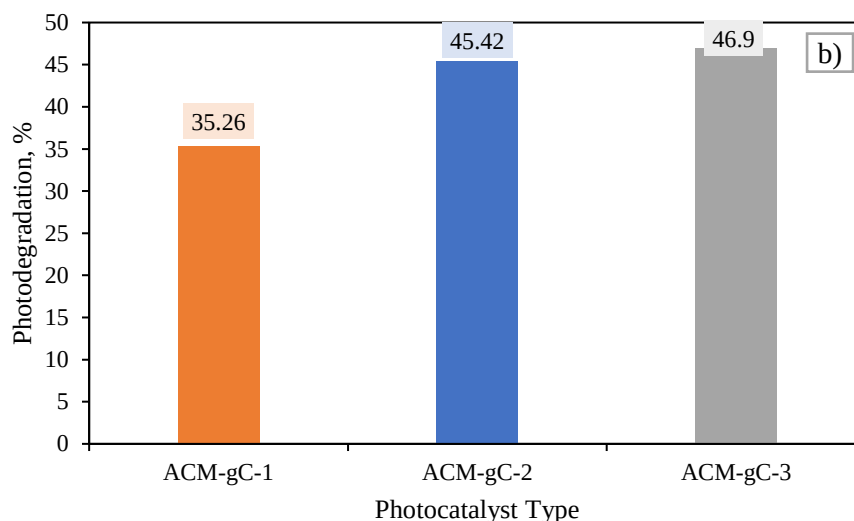


Figure 5.26 Effect of photodeposition time on photodegradation of DRN a) change of DRN concentration with time, b) photodegradation% after 2 h of reaction ($[DRN]_0 = 10$ ppm, catalyst loading = 1g/L, $T = 298K$).

Photo-reduction time for the catalyst preparation plays an important role for distribution and loading amount of co-catalyst, Ag NPs (Bhardwaj et al., 2020). Longer photodeposition times offer greater number of Ag NPs over MIL-88A surface that induced decreased in recombination rate of generated charge carriers. Longer photodeposition times generate stronger optical properties, in other words stronger surface plasmon resonance effect. Because longer photodeposition time lead to continuous growth of Ag NPs. Larger particles lead to enhanced charge transfer due to have larger interfacial contact area. Stronger LSPR effect of plasmonic particles with relative larger particle size was also mentioned in the study done by Seh et al. (2012) and Zhou et al. (2014). Larger Ag NPs in size will contact with MIL-88A and AgCl, thus larger amount of electrons are flow from MIL-88A to Ag NPs to provide the equilibrium Fermi level (Yu et al., 2006). As a consequence, it may say that, higher loading amount and photo-deposition time cause stronger optical properties, and to growth the deposited NPs more thereby resulting in stronger photocatalytic efficiencies.

As seen in Figure 5.26, as the photodeposition time increased from 30 min to 1 h, the photocatalytic degradation of DRN increased from 35.26% to 45.42% after a reaction time of 2 h. However further increase in the photodeposition time during the catalyst preparation step, from 1 h to 2 h, the degradation of DRN increased slightly (from 45.42% to 46.9%).

The first order reaction rate constants for ACM-gC-2 and ACM-gC-3 are closed the each other (0.0052 and 0.0056 min^{-1} , respectively), however, as expected, the rate constant obtained for ACM-gC-1 (0.0039 min^{-1}) was much lower than both.

As explained well above, photodeposition time increased the loading amount of Ag NPs. This result was confirmed by XPS analysis. XPS results verified the presence of more Ag NPs on MIL-88A. Ag^0/Ag^+ ratio was increased along with the increase in photo-reduction time. Ag^0/Ag^+ ratios were 0.16, 0.42 and 0.93 in the Ag/AgCl@MIL-88A/g- C_3N_4 that was prepared with photodeposition time of 30 min (ACM-gC-1 photocatalyst), 1 h (ACM-gC-2 photocatalyst), and 2 h (ACM-gC-3 photocatalyst), respectively. Due to the larger amount of Ag NPs and larger hydrodynamic size, thus greater LSPR effect, higher optical absorption, and efficient charge carrier, photodegradation of DRN increased significantly with increasing the photo-deposition time in the catalyst preparation step from 30 min to 1 h. However, when the photo-deposition time increased from 1 h (ACM-gC-2 photocatalyst) to 2 h (ACM-gC-3 photocatalyst), photodegradation increased slightly (from 45.42% to 46.9%) within the reaction time of 2 h. This may due to the formation of many aggregates of Ag NPs that influenced the photodegradation negatively. In addition to this, further increase in the Ag NPs amount in the Ag/AgCl@MIL-88A/g- C_3N_4 composite with increasing photodeposition time, composite photocatalyst may act as a recombination center for valance band electrons, instead of hindering the recombination of electron-hole pairs. It could be concluded that, although larger amount of Ag NPs have crucial effect on the efficiency of photodegradation, there should be optimum amount in the photocatalytic activities. In the present study 1 h of photodeposition time was selected as optimum time and kept constant for investigating other parameters of loading amount of Ag, and type of sacrificial agents.

Similar results were obtained in the photocatalytic oxidation of tetracycline over $\text{BiVO}_4/\text{NiS}/\text{Au}$ photocatalyst. $\text{BiVO}_4/\text{NiS}/\text{Au}$ photocatalyst was prepared with three different photodeposition time of 60, 90, and 120 min, and the highest degradation of tetracycline (TC) was observed in the presence of photocatalyst that was prepared with 90 min of photodeposition time (Zhang et al., 2019). In the study done by Xue et al. (2019) $\text{BiVO}_4\text{-Ag@CdS}$ ternary composite was prepared with

the photodeposition of 1 h, 2 h, and 3 h, and the tetracycline hydrochloride degradation of 100% was achieved with the photodeposition time of 2 h. Gomes et al. (2021) investigated the effect of photo-reduction time on the activity of BiVO₄/Pt/PtOx photocatalyst. They observed that, with increasing the photo-reduction time from 90 min to 480 min, the peak area of metallic Pt increased from 10.43% to 72.39% according to XPS analysis, however, they reported that the activity was negatively affected by this increase.

Besides all these, the Fe²⁺/Fe³⁺ ratios that was measured from the XPS analysis (Table 5.1) increased from 1.03 to 1.13 and then to 2.15 with increasing photodeposition time from 30 min to 1 h and then to 2 h, respectively. This result showed that higher deposition time lead to reduction of Fe³⁺ to Fe²⁺. More Fe²⁺ may contribute the photo-Fenton process to produce more OH• radicals via the reaction mentioned in Eq. 23.

Another parameter that may affect the photocatalytic efficiency is the ratio of O_H/O_L. In general, the oxygen species adsorbed to the surface (O_H) have a higher mobility than the lattice oxygen (O_L), thus they can actively participate in the photocatalytic reaction and increased the photocatalytic efficiency (Yalçın and Dükkancı, 2022). The highest O_H/O_L ratio was observed for ACM-gC-3 photocatalyst that was prepared with 2 h of photodeposition time, and the highest degradation of 46.9% was achieved over that catalyst.

5.2.3 Effect of Ag Loading Amount on Photodegradation of DRN

In this part of the study, the effect of Ag loading amount on photocatalytic activities of Ag/AgCl@MIL-88A/g-C₃N₄ that was prepared with changing Fe:Ag mole ratios (Fe:Ag mole ratio of 0.25:0.75 (ACM-gC-4), 0.5:0.5 (ACM-gC-2); and 0.75:0.25 (ACM-gC-5)) keeping the fumaric acid mole constant that equal to metal (Fe+Ag) moles was investigated. For these photocatalysts the photodeposition time was 1 h that was decided at optimum time in the previous part. Experiments were performed at [DRN]₀ of 10ppm, catalyst loading of 1g/L, at a temperature of T=298K, see Figure 5.27.

Each experiments were repeated with two times and standard deviations were in the range of ±0.006 - ± 0.06.

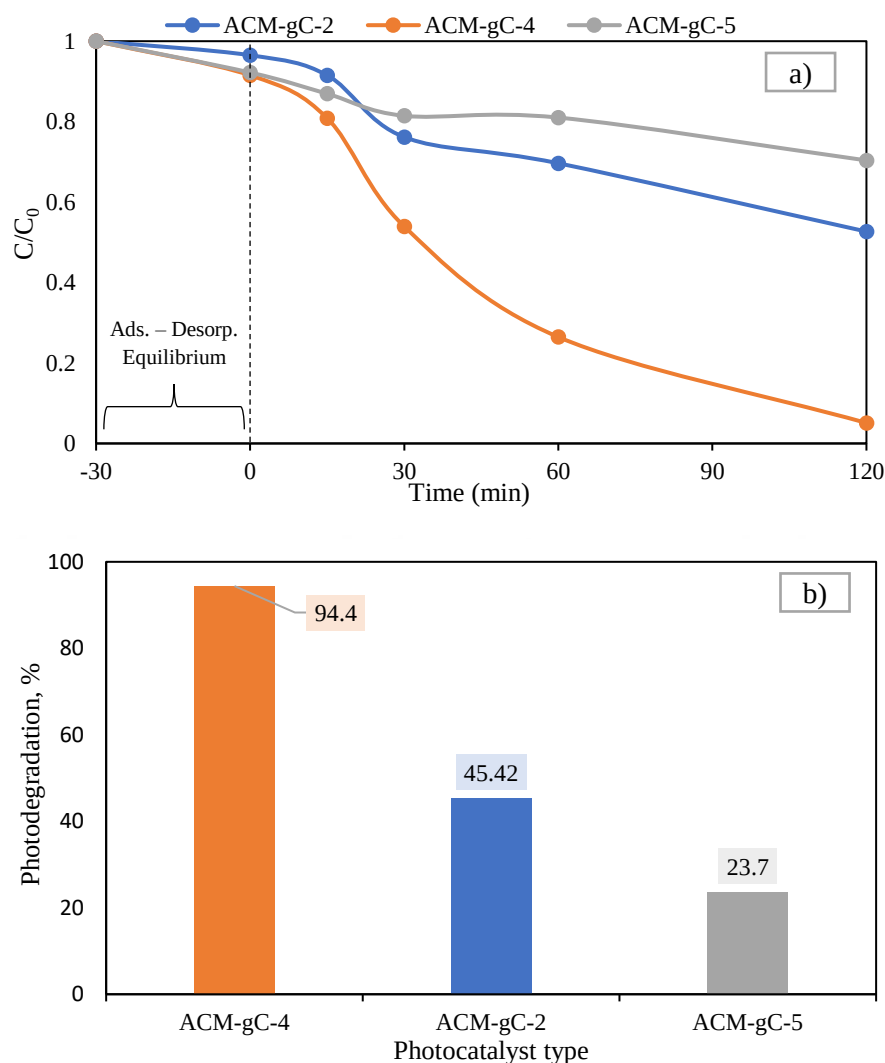


Figure 5.27 Effect of Ag loading on photodegradation of DRN a) change of DRN concentration with time, b) photodegradation% after 2 h of reaction ($[DRN]_0 = 10$ ppm, catalyst loading = 1g/L, $T = 298K$).

As seen in Figure 5.27, at the Fe:Ag mole ratios of 0.25:0.75, 0.5:0.5, and 0.75:0.25 (ACM-gC-4, ACM-gC-2, and ACM-gC-5, respectively), the obtained photodegradations were 94.4%, 45.42%, and 23.7%, respectively within the reaction time of 2 h. Increasing Ag loading caused a significant increase in photodegradation also in rate constants. The highest rate constant of 0.0229 min^{-1} was measured for ACM-gC-4, and it was followed by ACM-gC-2 (0.0052 min^{-1}), and ACM-gC-5 (0.0023 min^{-1}).

As mentioned in SEM Characterization part, weight% of Ag was greatly increased from 0.74 to 4.26 and then 5.98 with increasing Ag loading from 0.25 to

0.5 and then 0.75 mole in Fe:Ag mole ratios, respectively. Higher Ag loading induce effective charge carrier separation with more effective LSPR effect. In addition to these, higher Ag loading caused a change in morphology, see Figures 5.2 and 5.4a,b,c, and d. Average size of microrods decreased from 1.5 μm to 1.2 μm , and to 770 nm at the Fe:Ag mole ratios of 0.75:0.25, 0.5:0.5, and 0.25: 0.75, respectively. This could be due to the strong attachment capability of the Ag/AgCl particles, that need more space for the uniform accumulation on MIL-88A with more surface area and thus cause highly effective photodegradation. Addition of more Ag/AgCl as cocatalyst enhanced the nucleation rate that induce the formation of shorter microrods (Wu et al., 2019; Viswanathan et al., 2021).

As the highest photodegradation of 94.4% was achieved with ACM-gC-4 photocatalyst (prepared with Fe:Ag molar ratio of 0.25:0.75 under 1 h of photo-reduction), this Fe:Ag molar ratio was selected for further investigation.

5.2.4 Effect of Sacrificial Agent on Photodegradation of DRN

Sacrificial agents that used in the photodeposition of Ag NPs in the catalyst preparation step affect the loading amount, particle size, position and distribution of Ag NPs on the surface of MIL-88A.

Ammonium oxalate (ACM-gC-4), glycerol (ACM-gC-8), ethanol (ACM-gC-6) were used as sacrificial agents keeping the photodeposition time and Fe:Ag mole ratio constant at 1 h and of 0.25:0.75, respectively. Photodeposition was also carried out in the absence of sacrificial agent (in the presence of only water (ACM-gC-7)) for comparison.

Experiments were carried out with $[\text{DRN}]_0$ of 10 ppm, catalyst loading of 1g/L, at a temperature of 298K under 2 h of irradiation. Figure 5.28a presents the change of concentration of DRN with time, and Figure 5.28b presents the photodegradation of DRN after a reaction of 2 h.

All the experiments were repeated twice and extremely low standard deviation values were measured as $\pm 0.006 - \pm 0.15$.

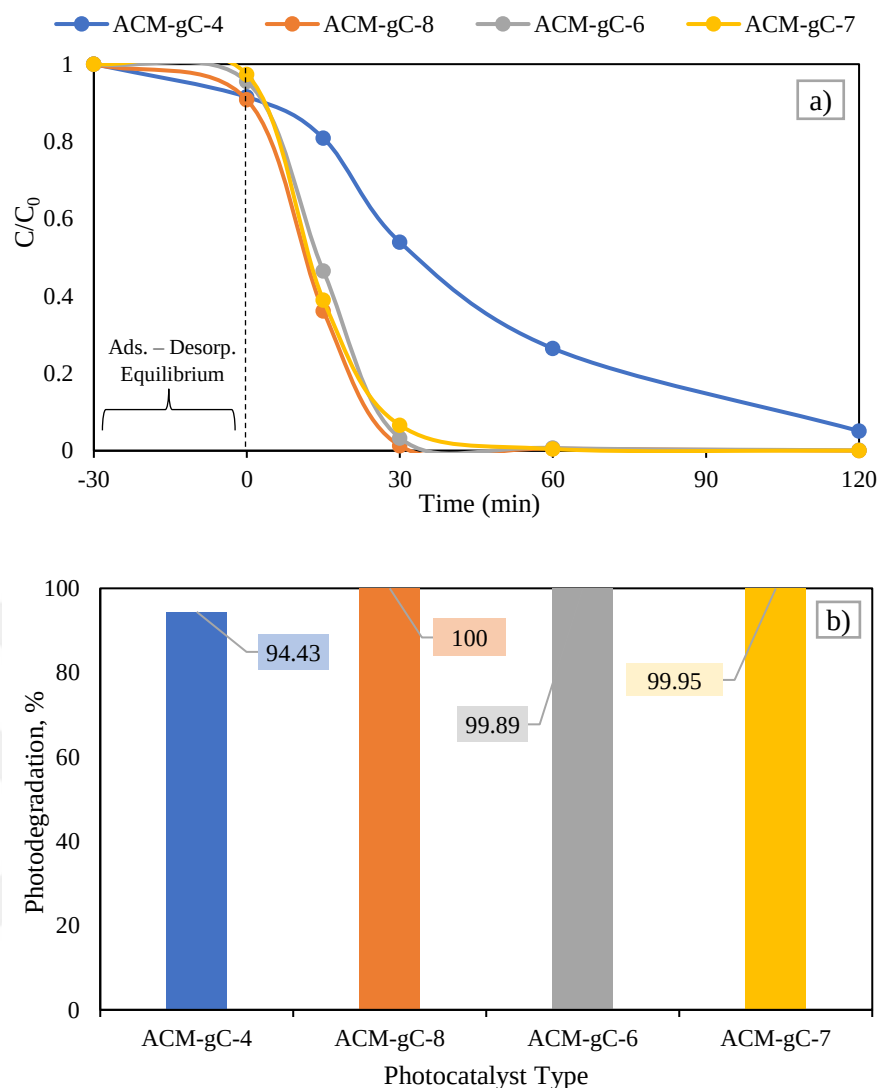


Figure 5.28 Effect of sacrificial agent on photodegradation of DRN a) change of DRN concentration with time, b) photodegradation% after 2 h of reaction ($[DRN]_0 = 10$ ppm, catalyst loading = 1 g/L, $T = 298K$).

As seen in Figure 5.28, complete degradation of DRN was achieved for photocatalysts of ACM-gC-6 (prepared with EtOH), ACM-gC-8 (prepared with glycerol), and ACM-gC-7 (prepared with only water) within the reaction time of 2 h. However, the photodegradation of DRN with ACM-gC-4 photocatalyst (94.4%) was a little bit lower than that of others. In addition, initial photodegradation rate for photocatalysts of ACM-gC-6, ACM-gC-8, and ACM-gC-7 were higher than that of ACM-gC-4. Similar trend was observed for reaction rate constants. The rate constant of 0.0229 min^{-1} was measured for ACM-gC-4, that was much lower than that of ACM-gC-6 (0.0641 min^{-1}), ACM-gC-7 (0.0702 min^{-1}), and ACM-gC-8 (0.168 min^{-1}).

As mentioned in the previous part of the study, the Ag component of ACM-gC heterostructures plays a crucial role in the visible light driven photocatalytic reactions, therefore the quantity, hydrodynamic size and dispersion of Ag nanostructures have a considerable effect on the photocatalytic performance of ACM-gC heterostructures.

The higher photocatalytic efficiencies of ACM-gC-6, ACM-gC-7, and ACM-gC-8 than that of ACM-gC-4 is largely related to the favorable Ag distribution with relatively large number on the heterostructures. Large number of Ag NPs were confirmed with XPS analysis of the samples. According to XPS result, the Ag^0/Ag^+ ratios were 3.12, 3.31, and 1.86 for ACM-gC-6, ACM-gC-7, and ACM-gC-8, respectively, whereas it was 0.15 for ACM-gC-4. High amount of Ag NPs allow the LSPR to happen on the surface of ACM-gC heterostructures, providing a large number of active sites for photocatalytic process of DRN. It could be said that as compared to ethanol and glycerol, the presence of ammonium oxalate (AO) make against the photodeposition of Ag cocatalyst by occupying the surface adsorption sites of MIL-88A which has the negative effect on the adsorption of metal NPs for subsequent deposition (Seh et al., 2012; Zhou et al., 2014; Cao et al., 2018; Huang et al., 2015; Liu et al., 2015).

ACM-gC-7 heterostructure that was prepared without using sacrificial agent for photoreduction of Ag^+ to Ag^0 was chosen for further investigation of the photodegradation of DRN.

There are some studies in literature that investigate the role of sacrificial agent (hole scavenger) on photodeposition of metal NPs over different semiconductors. Liu et al. (2015) decorated ZnO by Ag NPs with using different sacrificial agents of water, water+ethanol and air. They observed that type of sacrificial agent influence the amount, dispersion and position of Ag NPs significantly. The highest RhB degradation of 82% was achieved over Ag/ZnO sample that was prepared with only water (Ag loading of 7.68%). Although Ag/ZnO prepared with water+ethanol had the highest Ag loading amount of 26.1%, the lowest degradation of 27.3% was achieved with this catalyst. In the other study conducted by Huang et al. (2015) photodeposition of Ag NPs on ZnO was managed with several sacrificial agent of water+ethanol, water+glycol, and only water. Ag loading amount and photocatalytic performance was found to be in good agreement. The highest

removal rate of RhB (100%) was obtained with the catalyst prepared with water+glycol that had the highest Ag loading amount (35.03%). The authors explained the result with enlarging of interface between Ag and ZnO by glycol. Cao et al. (2018) managed the photodeposition of Pt or Au on g-C₃N₄ surface by methanol or triethanolamine as sacrificial agents. They observed that, while methanol was more successful in Platinum loading, triethanolamine is more successful in Au loading in H₂ production rate. In the present study, the composite photocatalyst that prepared with ethanol (ACM-gC-6), glycerol (ACM-gC-8) and water (ACM-gC-7) gave the similar photocatalytic efficiency. Although sacrificial agents serve as the hole scavenger and thus reduce the electron-hole recombination, it is possible to obtain enough Ag NPs for photodegradation in the case of absence of sacrificial agent. Here in addition to amount of Ag NPs, the distribution, position and size are the other important parameters.

5.2.5 Effect of Light Type on Photodegradation of DRN

In this part of the study, the activities of composite photocatalysts that were synthesized with different light sources, visible LED (ACM-gC-7) and high pressure Na Lamps (ACM-gC-9) for the reduction of Ag⁺ to Ag⁰ were compared with each other. The power and the light intensity of LED lamps were 93.4 W and 200 W/m², for high pressure Na Lamps the power and the light intensity were 300 W and 314 W/m², respectively.

Experiments were carried out with [DRN]₀ of 10 ppm, catalyst loading of 1g/L, at a temperature of 298K under 2 h of irradiation under visible LED light. Figure 5.29a presents the change of concentration of DRN with time, and Figure 5.29b presents the photodegradation of DRN after a reaction of 2 h.

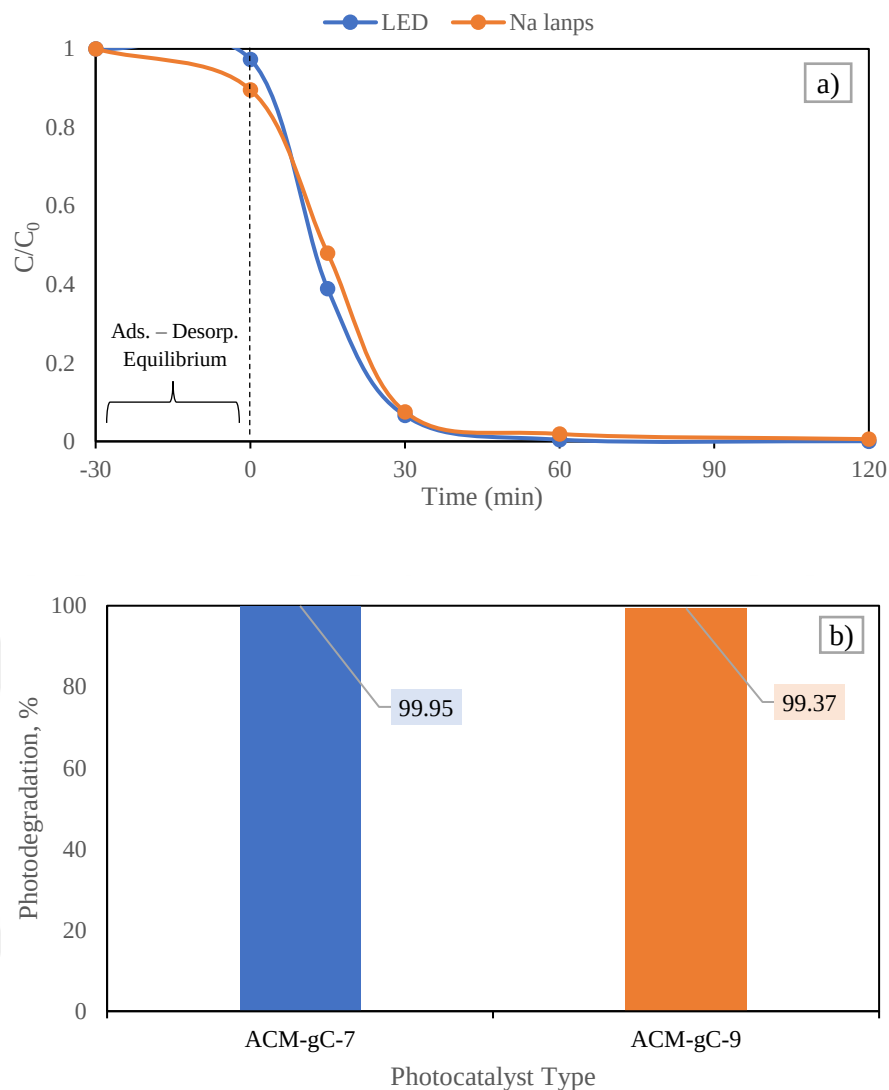


Figure 5.29 Effect of light type on photodegradation of DRN a) change of DRN concentration with time, b) photodegradation% after 2 h of reaction ($[DRN]_0 = 10$ ppm, catalyst loading = 1g/L, $T = 298K$).

As seen in Figure 5.29, both of the catalysts gave similar photodegradation (>99%) of DRN after a reaction time of 2h. Thus, it could be said that the high pressure Na lamp was as efficient as the LED lamps in reducing Fe^{3+} and Ag^+ . However, as the power of the LED lamps were lower than that of visible Na lamps, due to its energy saving feature, the catalyst that was synthesized under visible LED light was chosen for further investigation.

5.2.6 Surface – Performance Relationship in terms of Turn-Over Frequency (TOF)

It is reasonable to say that the total DRN removal efficiency was related with Ag concentration, and catalytic ability of each active site. Therefore, surface –

performance relationship was performed in terms of turn over frequency (TOF) of the prepared samples. TOF values were estimated by considering the number of DRN molecules degraded (mmol) per silver atoms (mmol) in the required time to achieve 30% DRN degradation (Martin et al., 2011; Liao et al., 2019; Lv et al., 2015). The exposed Ag NPs surface species was quantified by XPS analysis. The TOF values were given in Table 5.3. For reminder purposes, percentage photodegradation values over prepared samples at 15 and 120 min were also given in Table 5.3.

As seen in Table 5.3, ACM-gC-8 photocatalyst showed the highest TOF value (1.58 h^{-1}), suggesting the introduced Ag NPs favored oxidation ability of photodegradation reaction by the help of local surface resonance effect of them. It was followed by ACM-gC-7 photocatalyst with TOF value of 1.54 h^{-1} . TOF results were in good agreement with photodegradation, as the highest photodegradation of 63.85% and 100% were achieved over ACM-gC-8 photocatalyst, and it was followed by the ACM-gC-7 photocatalyst with 61.06% and 99.9% photodegradations at 15 and 120 min, respectively.

Table 5.3 The turn-over frequency (TOF) for the different catalysts determined at 30% DRN removal, and photodegradation at 15 and 120 min.

Photocatalysts	Photodegradation, % at 15 min	Photodegradation, % at 120 min	TOF (1/h)
Ag/AgCl@MIL-88A	15.68	19.11	0.04
ACM-gC-1	7.41	35.26	0.93
ACM-gC-2	8.49	45.42	0.19
ACM-gC-3	7.59	46.9	0.21
ACM-gC-4	19.16	94.43	0.59
ACM-gC-5	13.06	23.7	0.86
ACM-gC-6	53.53	99.9	0.86
ACM-gC-7	61.06	99.9	1.54
ACM-gC-8	63.85	100	1.58
ACM-gC-9	52.03	99.4	1.44

As there were no significant differences with TOF values and photodegradations over ACM-gC-8 (prepared with glycerol) and ACM-gC-7 (prepared without sacrificial agent), ACM-gC-7 was chosen as the most effective photocatalyst in the degradation of DRN.

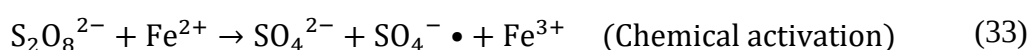
5.2.7 Effect of addition of oxidants on photocatalytic oxidation of DRN over Ag/AgCl@MIL-88A/g-C₃N₄ (ACM-gC-7) photocatalyst

The effect of various oxidants such as hydrogen peroxide (H₂O₂) and persulfate (PS) on photocatalytic oxidation of DRN over most active Ag/AgCl@MIL-88A/g-C₃N₄ photocatalyst (ACM-gC-7) was examined in this part of the study.

UV radiation can produce hydroxyl radicals (OH•) from H₂O₂ via Eq. 29 (Chen et al., 2018).



Due to their higher standard redox potential and longer lifetime, sulfate radical (SO₄•) based AOPs have also gained importance in recent years (Zhang et al., 2020; Vela et al., 2019). PS can be activated and converted to sulfate radicals via physical processes like UV irradiation (Eq. 30), ultrasonication (Eq. 31), and heating (Eq. 32), or chemical ways like homogeneous and heterogeneous metal catalysis (Eq. 33) (El Asmar et al., 2021; Vela et al., 2019; Lin et al., 2015).



Through formation of those strong oxidative radicals, recalcitrant contaminants in wastewaters, including many pesticides, are degraded into small molecules, which are ultimately mineralized into carbon dioxide and water molecules (Sun et al., 2022; Vela et al., 2019).

It is well known that visible light (> 400 nm) has not enough energy to activate H₂O₂ or persulfate to produce active radicals. However, in the presence of visible light and heterogeneous catalyst together, they can be activated under visible light by capturing the conduction band electrons and produce active radicals via Eqs 34-36 (Zhang et al., 2020; Fu et al., 2020). This capturing property also prevent the recombination of valence band holes and conduction band electrons.



In this part of the present study, blank experiments were carried out before evaluating the effect of addition of oxidants. Figure 5.30 depicts the degradation of DRN in the presence of only visible light (Vis), only H_2O_2 , only PS, H_2O_2 +Vis, PS+Vis, and ACM-gC-7+Vis.

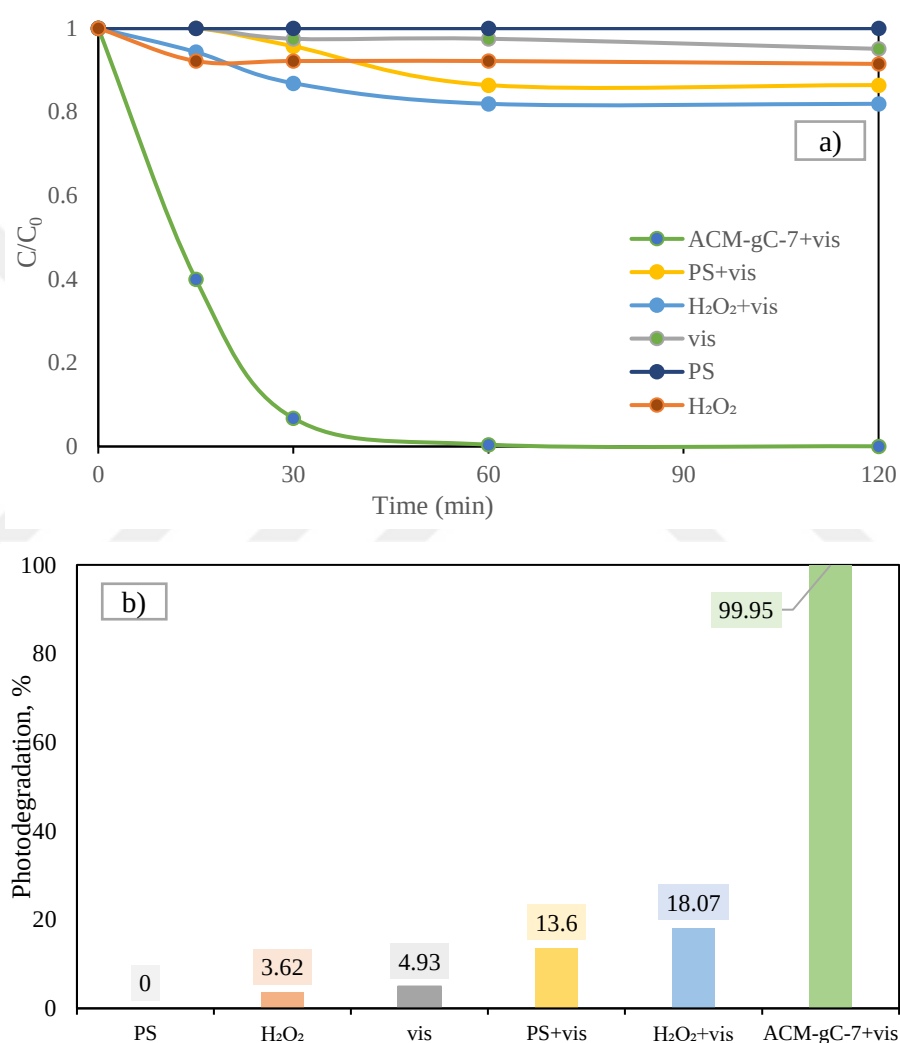


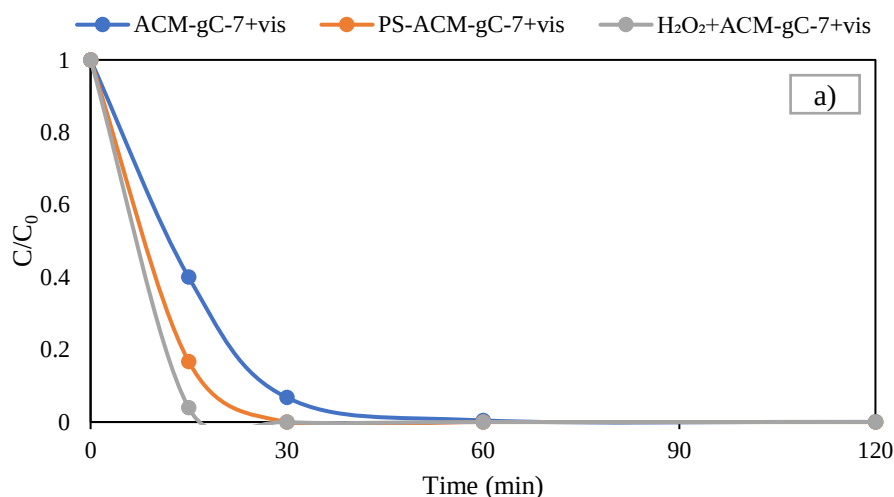
Figure 5.30 Photodegradation of DRN in various degradation processes a) change of concentration with time, b) photodegradation of DRN within 2 h ($[\text{DRN}]_0$: 10ppm, $[\text{PS}]_0$ or $[\text{H}_2\text{O}_2]_0$ =1mM, Catalyst loading= 1g/L, T =298K, LED light power= 93.4W).

As shown in Figure 5.30, in the absence of photocatalyst and visible light irradiation when PS was applied alone, no degradation of DRN was observed after

120 min of reaction time. When H_2O_2 was used alone, the obtained degradation was 3.62%. In the presence of only visible light, 4.93% degradation of DRN was obtained. The degradation percentage of DRN increased to 13.6% when the PS was irradiated with visible light. Similarly, in the presence of H_2O_2 under LED light, the degradation of DRN was observed as 18.07%. Under visible light irradiation, in the absence of oxidants, DRN degradation was 99.95% over ACM-gC-7 photocatalyst. The performed blank experiments showed that only oxidants or only visible light could not achieve DRN photodegradation. It was clear that visible light has not enough energy to degrade $\text{H}_2\text{O}_2/\text{PS}$ to produce active radicals of $\text{OH}^\bullet$ and $\text{SO}_4^{\bullet-}$. Because only 13.6% and 18.1% degradations of DRN were obtained in the combined process of PS+Vis, and H_2O_2 +Vis, respectively. Photocatalyst of ACM-gC-7 and visible light should be together for satisfactory photodegradation.

After blank experiment, photocatalytic oxidation of DRN over ACM-gC-7 catalyst was carried out in the presence of PS and H_2O_2 under the following conditions: $[\text{DRN}]_0 = 10\text{ppm}$, $[\text{PS}]_0$ or $[\text{H}_2\text{O}_2]_0 = 1\text{mM}$, Catalyst loading = 1g/L , $T = 298\text{K}$, LED light power = 93.4W .

Figure 5.31 indicates DRN photodegradation over ACM-gC-7 photocatalyst in the presence and absence of H_2O_2 and PS.



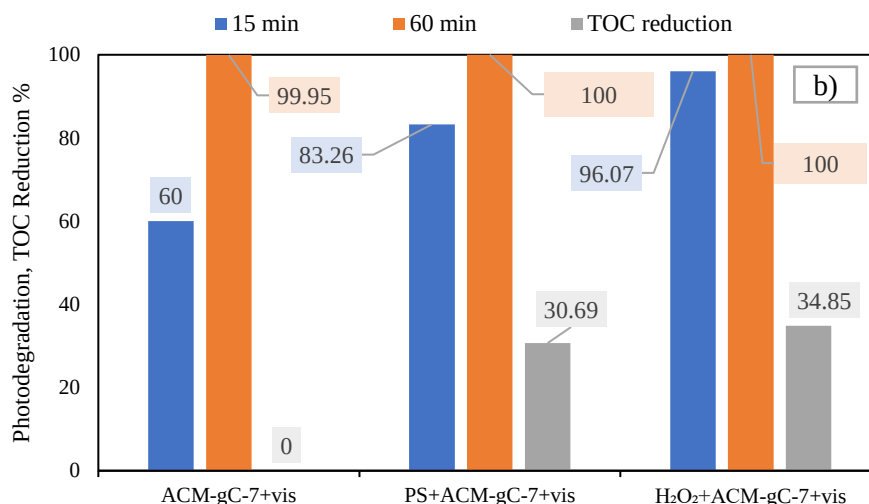


Figure 5.31 Effect of addition of PS and H₂O₂ on photocatalytic oxidation of DRN over ACM-gC-7 photocatalyst a) change of concentration with time, b) photodegradation of DRN within 2 h ([DRN]₀: 10ppm, [PS]₀ or [H₂O₂]₀=1mM, Catalyst loading= 1g/L, T=298K, LED light power= 93.4W).

As seen in Figure 5.31, complete degradation of DRN was achieved in the photocatalytic oxidation of DRN over ACM-gC-7 photocatalyst in the absence of oxidants after a reaction time of 60 min. However, considering the initial degradation rates up to the 15th min, degradation values of 60%, 83.26% and 96.07% were achieved for ACM-gC-7+Vis, PS+ACM-gC-7+Vis, H₂O₂+ ACM-gC-7+Vis, respectively. It could be said that addition of oxidants accelerated the initial degradation rate and shortened the degradation time.

ACM-gC-7 photocatalyst could be activated by a visible light, thus photogenerated electrons (e⁻) on the conduction band (CB) of ACM-gC-7 was trapped by H₂O₂ and PS to produce OH• and SO₄• radicals, respectively, Eqs. 34-36. In addition to production of OH• and SO₄• radicals, H₂O₂ and PS served as electron acceptors in this process, and electron/hole recombination was reduced, resulting in increased photocatalytic efficiency.

It is important to say that addition of oxidants has positive effect on mineralization of DRN. There was no TOC reduction in the absence of oxidants, however, TOC reduction of 30.69% and 34.85% were achieved in the presence of PS and H₂O₂, respectively, within the reaction time of 2 h.

According to mineralization results, it was clear that DRN degraded into oxidation resistance by-products rather than CO_2 and H_2O , in the absence of oxidants. To confirm this, 3D HPLC chromatogram was taken. In the 3D HPLC chromatogram, the retention time of DRN was 7 min (Figure 5.32a) and at the end of 2 h of photooxidation (Figure 5.32b) the peaks belong to DRN disappeared but new peaks that have the retention time lower than DRN appeared. As the retention time of formed by-products are lower than the DRN retention time of 7 min, it could be said that the hydrophilicity of the formed by-products is stronger than DRN molecule.

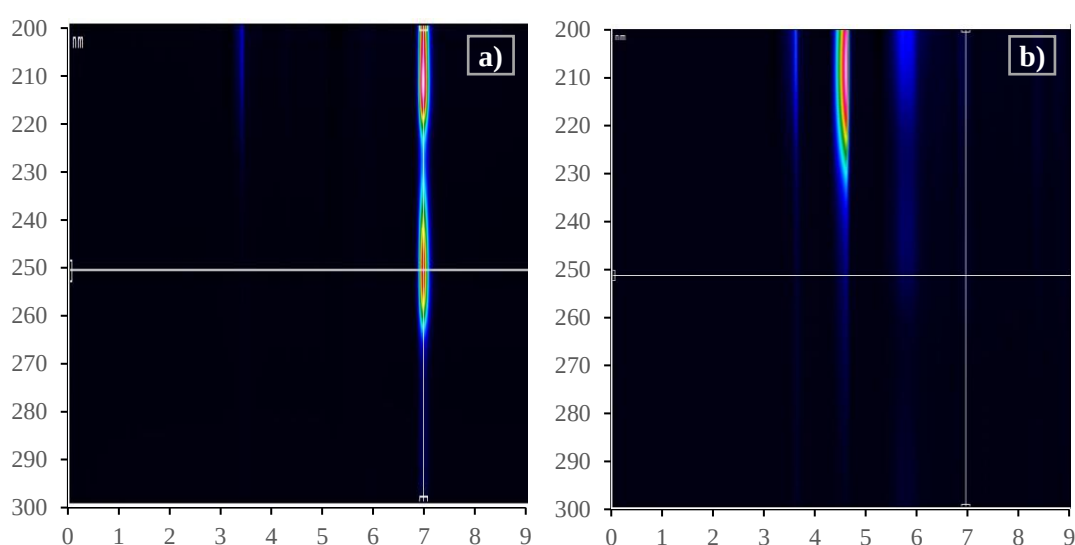
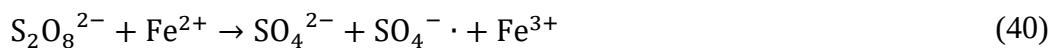


Figure 5.32 3D HPLC chromatogram for DRN at the initial (a), and at the end of 2 h (b) ($[\text{DRN}]_0 = 10$ ppm, ACM-gC-7 catalyst loading = 1g/L, $T = 298\text{K}$, LED light power = 93.4W).

Furthermore, Fe-based MOFs can be employed as a heterogeneous Fenton catalyst to activate PS or H_2O_2 in AOPs by converting Fe^{3+} to Fe^{2+} that maintains the continuity of the Fenton reaction cycle (Eqs. 23-28) (Zhang et al., 2020; Fu et al., 2020; El Asmar et al., 2021; Liao et al., 2019; Lin et al., 2015). The produced $\text{SO}_4^{\cdot -}$ and $\text{OH}^{\cdot}$ contributed the degradation of DRN under studied experimental conditions, Eqs. 37-41.





There are several studies in literature that proved the positive effect of H_2O_2 and PS on photocatalytic oxidation of several organic pollutants over MOF catalysts. These are some examples;

In the study of Gholizadeh Khasevani and Gholami (2019), the photocatalytic performance of MIL-88A/g- C_3N_4 composite was investigated by decomposition of Methylene Blue (MB) under visible light. After 120 min of reaction time, 75% photocatalytic degradation of MB was observed, however, presence of H_2O_2 increased the degradation to 85%.

In the study by Fu et al. (2020), MIL-88A was synthesized in various sizes (MIL-88A-1 and MIL-88A-2) at room temperature. Under visible light, 21% Rhodamine B (RhB) and 17% bisphenol A (BPA) degradations were observed for the MIL-88A-2 in the absence of H_2O_2 within 120 min. However, both MIL-88A-1 and MIL-88A-2 catalysts showed almost complete degradation towards RhB and BPA in the presence of H_2O_2 after 80 min of visible light irradiation.

Kamandi et al. (2021) synthesized g- C_3N_4 , MIL-101(Fe), and MIL-101(Fe)/g- C_3N_4 binary composites and tested their catalytic activity on the photodegradation of Rhodamine B dye in the presence of H_2O_2 as oxidant. The decolorization efficiency of bare g- C_3N_4 was 40% and MIL-101(Fe) was 73%, the decolorization efficiency of MIL-101(Fe)/g- C_3N_4 photocatalyst was 99.3% under visible light in the presence of H_2O_2 .

Viswanathan et al. (2020) fabricated three distinct morphologies of MIL-88A(Fe), such as rod, diamond, and spindle, and tested their photocatalytic activity to degrade RhB in the presence of H_2O_2 under sunlight. Using the catalysts d-MIL-88A(Fe) and s-MIL-88A(Fe), the percentage of RhB degradation was 72% and 51%, respectively. When utilizing r-MIL-88A(Fe), it was established that RhB was degraded by 98% in 50 min in the presence of H_2O_2 .

In the work done by Zhang et al. (2019), MIL-88A was synthesized and employed as a high-efficiency photocatalyst in the combination with sulfate radical-

based advanced oxidation processes (SR-AOPs) to degrade tetracycline hydrochloride (TC-HCl) under visible light irradiation. When only MIL-88A was used, 10% degradation was achieved in 80 min; however, after PS was added, the degradation reached to 99.8%.

The catalytic activity of MIL-53(Fe) for the degradation of tetracycline hydrochloride (TC-HCl) was investigated under visible light irradiation by Zhang et al. (2020). Only 17.1 percent TC degradation was observed over MIL-53(Fe) in the absence of PS while 99.7% TC degradation was accomplished in 80 min using sulfate radical-based advanced oxidation processes (SR-AOPs) combined with photocatalysis processes.

5.2.8 Effect of aqueous matrix species on Photodegradation of DRN

Many inorganic anions and organic substances commonly found in real aqueous environments can affect the efficiency of UV based advanced oxidation processes (Chen et al., 2018; Sun et al., 2022) and the efficiency/stability of MOFs (Wang et al., 2022). Therefore, chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}) and carbonate (CO_3^{2-}) inorganic anions and fulvic acid (FA) as natural organic material were used to examine the effect of those components in aqueous environments on the photodegradation of DRN over Ag/AgCl@MIL-88A/g- C_3N_4 (ACM-gC-7) photocatalyst, see Figure 5.33. Sodium salts were used as an anion source in this study. In addition, to investigate realistic conditions, photocatalytic oxidation of DRN that was prepared with tap water was studied using the same catalyst of ACM-gC-7.

The following parameters were used at the experiments: catalyst loading of 1g/L, DRN solution of 10 ppm and 150 mL, and temperature of 298K. The additional anion ion concentration was all set at 2 mM.

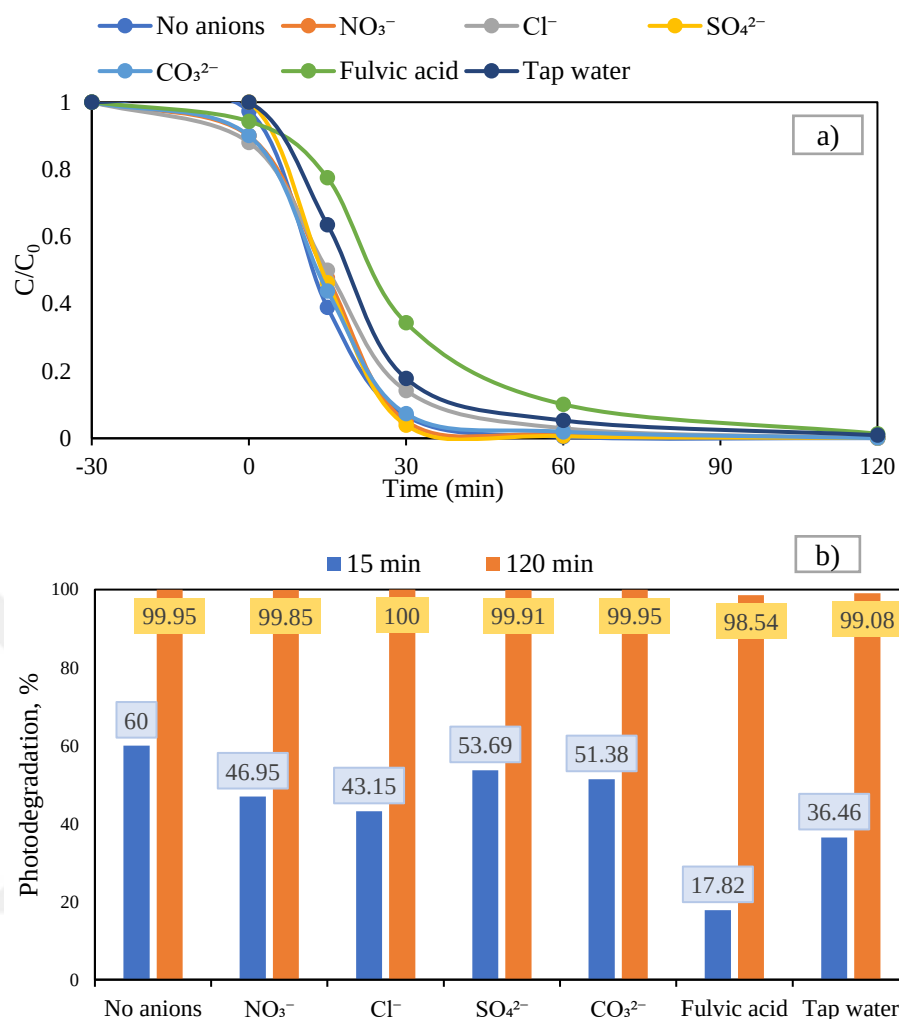


Figure 5.33 Photodegradation of DRN in different aqueous matrix, a) change of DRN concentration with time, b) photodegradation % after 15 min and 2 h of reaction ($[\text{DRN}]_0 = 10$ ppm, catalyst loading = 1 g/L, $T = 298\text{K}$, $[\text{Inorganic anions}] = 2\text{mM}$, LED light power = 93.4W).

As shown in Figure 5.33, after the reaction time of 120 minutes, all prepared simulated water samples had a negligible effect on the degradation of DRN. This indicates that ACM-gC-7 has good catalytic activity under the applied environmental conditions. However, considering the initial degradation rates up to the 15th min, the upsetting impact of the used anions was in the following order: no anions (60%) > SO_4^{2-} (53.69%) > CO_3^{2-} (51.38%) > NO_3^- (46.95%) > Cl^- (43.15%) > tap water (36.46%) > FA (17.82%).

As seen, FA showed the highest inhibitory effect, photodegradation of DRN decreased from 60% to 17.82% within the reaction time of 15 min. The inhibitory

effect of FA on the photocatalytic reaction can be explained by three aspects. FA could compete with DRN molecules for the limited reaction site in the photocatalytic process, reducing the quantity of reaction sites available for DRN degradation and hence reducing the removal efficiency. FA can also directly absorb light photons, leading in a decrease in the incident light energy absorbed by ACM-gC-7 and cause production of less reactive oxygen species on the ACM-gC-7 surface. The last one is the scavenging effect of active radicals those play crucial role in photodegradation of all organic pollutants present in water (Chen et al., 2018; Wang et al., 2021).

When the reaction solution was prepared with tap water, the percentage of DRN degradation decreased from 60% to 36.46% at the initial reaction time of 15 min, indicating that ions in tap water inhibits the degradation process of DRN.

The results demonstrated that the presence of different inorganic anions showed no obvious decrease in photodegradation, but it retarded the photodegradation of DRN over ACM-gC-7. Since inorganic ions have negative charge, the reaction between inorganic anions and positive holes /OH• radicals produce less reactive radicals (radical quenching effect), thus cause a decrease in photodegradation (Eqs. 42-51) (Cheng et al., 2022; Luna-Sanguino et al., 2021; Saleh et al., 2019; Sang et al., 2021).



Some studies on MOF-based catalysts to investigate the effect of aqueous matrix species during the degradation of different organic pollutants are as follows.

In the study by He et al. (2021), Cu-EDTA was used as the target pollutant. It was found that, in the presence of MIL-53(Fe) photocatalyst, about 91% of Cu-EDTA degraded after 60 min under ultraviolet irradiation. CO_3^{2-} , NO_3^- , Cl^- , and humic acid were employed to evaluate the effects of inorganic ions and organic matter on Cu-EDTA degradation. Cu-EDTA degradation was inhibited by humic acid and CO_3^{2-} , while Cl^- and the optimum NO_3^- have adverse effect. After 120 min of photocatalytic degradation, 80% of Cu-EDTA was degraded when the concentration of humic acid was 20 mg L⁻¹. The presence of CO_3^{2-} similarly inhibited the degradation of Cu-EDTA. With the addition of 2.5 mmol L⁻¹ CO_3^{2-} , there was a 10% reduction in the Cu-EDTA removal efficiency. However, Cu-EDTA degradation efficiency improved to about 99% during 120 minutes of treatment when NO_3^- and Cl^- concentration was 0.1 mmol L⁻¹.

In the work done by Zhang et al. (2021), MIL-88A(Fe) particles were adsorbed onto the commercial porous block substrate (PBS) to produce MIL-88A/PBS, which was then calcined at high temperatures like 400, 500, 600, and 700 °C to produce $\text{Fe}_3\text{O}_4@\text{PBS}$ (M- $\text{Fe}_3\text{O}_4\text{-T}@\text{PBS}$). Tetracycline hydrochloride (TC) degradation was achieved in the simulated wastewater by activating peroxodisulfate (PDS) over the M- $\text{Fe}_3\text{O}_4\text{-T}@\text{PBS}$ in the presence of white light. The results showed that, under white light and real sunlight irradiation, respectively, 97.5% and 92.8% of TC could be degraded after 40 minutes via PDS activation over the best catalyst M- $\text{Fe}_3\text{O}_4\text{-600}@\text{PBS}$. Aqueous solutions containing various inorganic ions, such as H_2PO_4 , Cl , HCO_3 , and NO_3 , were used to prepare simulated wastewater samples in order to examine the practical uses of the M- $\text{Fe}_3\text{O}_4\text{-600}@\text{PBS}$ /light/PDS system. The sequence of the effects of inorganic anions on TC degradation was as follows: no anions (97.5%) > NO_3^- (94.7%) > H_2PO_4 (91.4%) > HCO_3 (84.7%) > Cl (82.0%). The inorganic anions have an inhibitory effect because they can serve as reactants to change more active radicals into less active ones or as scavengers to reduce these radicals. According to the results, the Cl^- anion showed the highest inhibition effect.

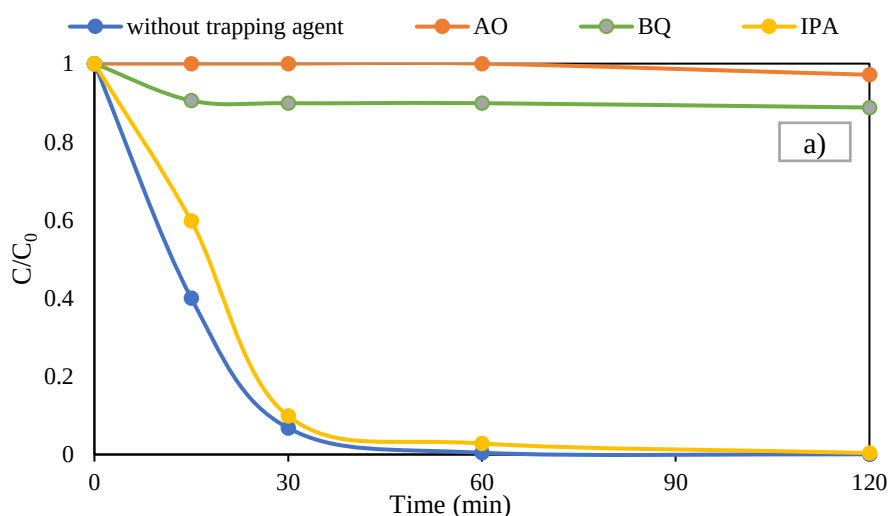
Sun et al. (2022) synthesized a Fe-based MOF group using formic acid as a modulator. Fe-MOFs-2, the sample with the highest catalytic activity, can degrade sulfamethoxazole (SMX) via PS activation with a removal efficiency over 95% in

120 min. Phosphate (PO_4^-), nitrate (NO_3^-), chloride (Cl^-), bicarbonate (HCO_3^-), and humic acid (HA) were chosen to investigate the practical treatment capacity of Fe-MOFs-2/PS. The little influence of NO_3^- , Cl^- , and HA on the degradation of SMX demonstrates that Fe-MOFs-2/PS have excellent catalytic capability and environmental applicability. On the other hand, when PO_4^- and HCO_3^- are introduced, the rate of SMX degradation rapidly decreased to 15.96% and 22.55%, respectively, showing strong inhibition.

5.2.9 Effect of trapping agents on Photodegradation of DRN

Different trapping agents such as ammonium oxalate (He et al., 2021; Tan et al., 2022; Wang et al., 2022), p-Benzoquinone (Gholizadeh Khasevani and Gholami 2018; Huang et al., 2022; Wu et al., 2019), and isopropyl alcohol (Huang et al., 2018; Shao et al., 2019; Viswanathan et al., 2021) were used to identify the main active species on the photodegradation of DRN over Ag/AgCl@MIL-88A/g- C_3N_4 (ACM-gC-7) photocatalyst. Experiments were conducted under following conditions: DRN initial concentration of 10 ppm, catalyst loading of 1g/L with DRN solution of 150 mL and at a temperature of 298K. Furthermore, a 1 mM trapping agent concentration was utilized.

Ammonium oxalate (AO), benzoquinone (BQ), and isopropyl alcohol (IPA) were used to trap holes (h^+), $\text{O}_2^{\bullet-}$ radicals, and $\text{OH}^\bullet$ radicals, respectively. Figure 5.34 illustrates the effects of adding AO, BQ, and IPA on the photodegradation of DRN over ACM-gC-7 photocatalyst.



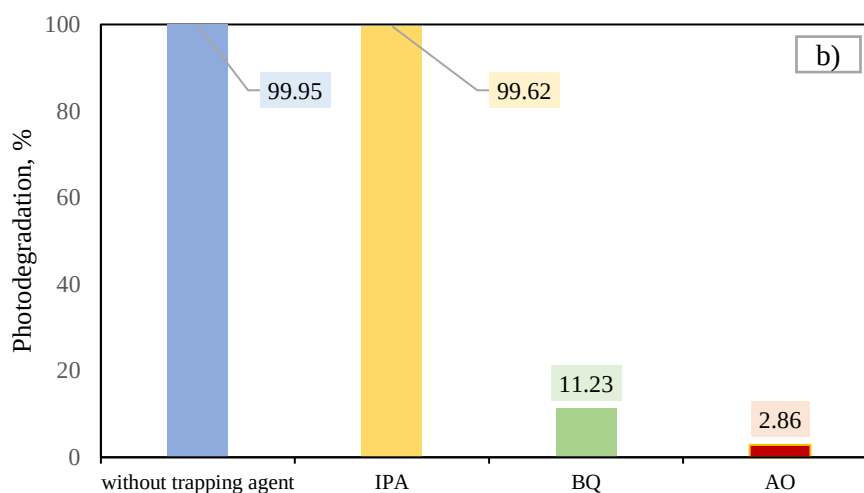


Figure 5.34 Effect of trapping agents on photodegradation of DRN a) change of DRN concentration with time, b) photodegradation % after 2 h of reaction ($[DRN]_0 = 10$ ppm, catalyst loading = 1g/L, $T = 298K$, [Trapping agents] = 1mM, LED light power = 93.4W).

The degradation of DRN over ACM-gC-7 photocatalyst without addition of trapping agent was 99.95%. After addition of IPA, the photocatalytic activity of ACM-gC-7 remained almost the same (99.62%), as depicted in Figure 5.34. However, with the addition of BQ and AO, the photodegradation percent of DRN over ACM-gC-7 decreased significantly to 11.23% and 2.86%, respectively. This dramatic reduction showed that $O\cdot_2^-$ and h^+ were the main oxidative species and play a significant role in the photocatalytic activity.

As mentioned in part “5.2.7 Effect of addition of oxidants on photocatalytic oxidation of DRN over Ag/AgCl@MIL-88A/g-C₃N₄ (ACM-gC-7) photocatalyst” addition of PS or H₂O₂ shortened the time needed for complete degradation. According to the results obtained from trapping agent experiments, it is clear that, the addition of oxidant was more effective in supporting the separation of the electron - hole pairs rather than contributing to the production of hydroxyl radicals.

Some studies from literature that clarify the active species effect on photocatalytic degradation of various organic pollutants on MOF-based photocatalysts are given below.

In the study of Tan et al., (2022) the photocatalytic performance of MIL-88A/g-C₃N₄ composite was investigated by decomposition of Acid Red 1 (AR1) dye. The MIL-88A/g-C₃N₄ composite demonstrated 100% decomposition efficiency within 30 min for AR1 dye degradation under simulated sunlight

irradiation. The major oxidizing species in the photocatalytic reaction system was confirmed via a trapping test on the MIL-88A/g-C₃N₄. Hydroxide radicals (OH•), photogenerated holes (h⁺), and superoxide radicals (O₂•⁻) were all trapped by isopropanol (IPA), ammonium oxalate (AO), and nitrogen (N₂). With the addition of AO, the decomposition efficiency of the MIL-88A/g-C₃N₄ was reduced to 66.7%. Tests conducted in the nitrogen atmosphere revealed a 92% decomposition efficiency for the MIL-88A/g-C₃N₄. The photocatalytic effectiveness of MIL-88A/g-C₃N₄ was unaffected by the addition of IPA. According to the results, h⁺ was the primary oxidizing species in the photocatalytic reaction, while O₂•⁻ was the secondary oxidizing species.

Wang et al. (2022) studied the catalytic activity of a MIL-53(Fe)/polyaniline (PANI) composite for the simultaneous elimination of rhodamine B (RhB) and Cr(VI). Both RhB and Cr(VI) were eliminated with an efficiency above 98%. Reactive species trapping experiments were conducted to better understand the effectiveness of main active species in photocatalytic process. In order to trap the hydroxyl radical (OH•), superoxyg radicals (O₂•⁻), and holes (h⁺) in the solution of RhB/Cr(VI), the trapping agents of isopropanol (IPA), p-benzoquinone (PBQ), and ammonium oxalate (AO) were used. The degradation efficiency of RhB was reduced to 64% and 10%, respectively, with the addition of IPA and BQ. Furthermore, after the addition of AO, the degrading efficiency of RhB was identical to that obtained without the trapping agent. The findings indicated that the primary species involved in the photocatalytic decomposition of RhB were O₂•⁻ and OH• radicals. Additionally, the efficiency of the reduction of Cr(VI) only decreased with the addition of BQ, demonstrating that the superoxide radical is the primary active species in the reduction of Cr (VI).

Wu et al., (2019) were synthesized several Ag/AgCl@MIL-88A (ACML) composites using variously shaped MIL-88A supports. Rhodamine B (RhB) was used to determine the photocatalytic activity of ACML composites under simulated sunlight and visible light irradiation. The s-ACML composite achieved degradation efficiencies of 99.1% and 98.3% for simulated sunlight and visible light irradiation, respectively. In the trapping tests, OH•, h⁺, and O₂•⁻ were trapped using isopropyl alcohol, EDTA, and benzoquinone, respectively. The degradation of RhB decreased from 98.3% to 83%, 67%, and 31%, respectively, with the addition of EDTA,

benzoquinone, and isopropyl alcohol as trapping agents under visible light irradiation. The results indicated that the major species involved in the photocatalytic degradation of RhB over s-ACML are h^+ and $O_2^{\bullet-}$.

MIL-88A(Fe)/Bi₂WO₆ (M88/BWO) heterojunction photocatalyst was fabricated using hydrothermal technique in the study of Li et al. (2021). Under visible light illumination, the degradation of rhodamine B (96% within 50 min) and tetracycline (71% within 80 min) was used to assess the photocatalytic activity of the M88/BWO. In that study ethylenediamine tetra acetic acid disodium salt (EDTA-2Na), p-benzoquinone (BQ) and isopropanol (IPA) were used to trap h^+ , $O_2^{\bullet-}$, $OH^{\bullet}$, respectively. According to trapping experiments, the degradation degrees of rhodamine B were 77.99%, 45.87% and 39.18% in the presence of IPA, EDTA-2Na, and BQ, respectively. This shows that $O_2^{\bullet-}$ and h^+ were the main active species in the photodegradation of RhB.

Ethylenediaminetetraacetic acid complexed copper pollutant (Cu-EDTA) was chosen as the target pollutant in the investigation by He et al., (2021) and it was discovered that, in the presence of MIL-53(Fe) photocatalyst, nearly 91% of Cu-EDTA decomposed within 60 min under ultraviolet irradiation. To trap h^+ , $O_2^{\bullet-}$, $OH^{\bullet}$, $^1O_2$, and e^- , the trapping agents AO, p-BQ, IPA, DABCO, and KBrO₃ were utilized, respectively. In the presence of KBrO₃, AO, IPA, p-BQ, and DABCO, the Cu-EDTA elimination efficiency decreased to 63%, 54%, 67%, 74% and 66%, respectively. This shows that h^+ , $O_2^{\bullet-}$, $OH^{\bullet}$, $^1O_2$, and e^- play important roles in the decomposition of Cu-EDTA.

5.2.10 Reusability and Stability of ACM-gC-7 photocatalyst

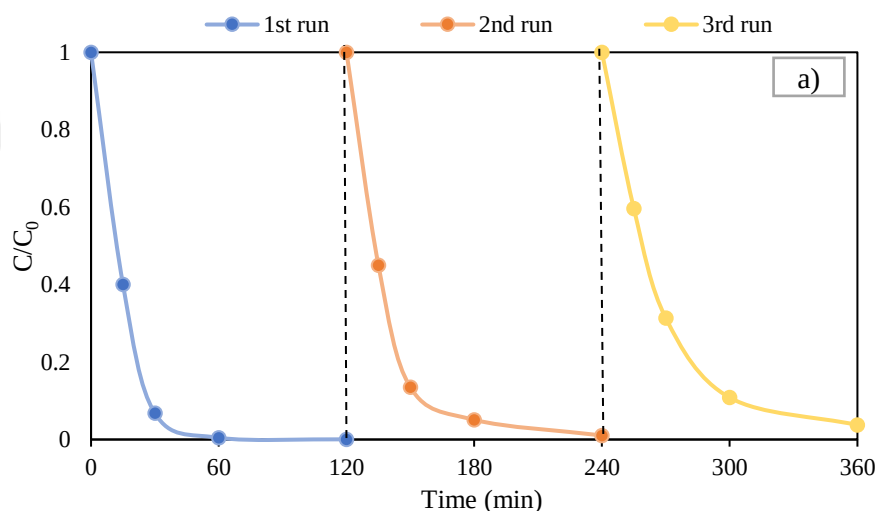
The reusability and stable structure of photocatalysts are an indication of whether the catalyst can be used in practical applications. To assess the reusability of the ACM-gC-7, three-cycle experiments were performed in photocatalytic degradation of DRN. During the cyclic experiments, ACM-gC-7 photocatalyst was separated from the solution by the help of filtration paper, and washed three times by water and then ethanol, after drying in the oven at 65°C for 6 h, it was continued to be used in the degradation of fresh DRN solution.

As displayed in Figure 5.35, ACM-gC-7 photocatalyst still remains a relatively high photodegradation ability of DRN during three cycling times,

suggesting that the ACM-gC-7 possesses high stability and can be used for repeated treatment of DRN.

The stability of the catalyst was also tested in terms of iron leaching from the catalyst to the solution. For this purpose, iron concentration in the treated DRN solution after each cycling was determined using Atomic Adsorption Spectroscopy. Iron concentration was less than 1ppm ($< 5\%$), implying the high stability of ACM-gC-7 photocatalyst.

Additionally, crystal structure of fresh ACM-gC-7 and recycled sample was compared using XRD analysis (Figure 5.36), and it presents no obvious changes in the position of the characteristic peaks, demonstrating that the crystal form of the composite did not change before and after the reaction. However, in the XRD spectrum of recycled ACM-gC-7 sample, a new peak at 38.2° was appeared that belongs to Ag NPs and besides the peaks intensities of AgCl decreased. This may due to the inevitable photo-reduction of some AgCl particles by photogenerated electrons to form Ag^0 during visible light irradiation in the reaction.



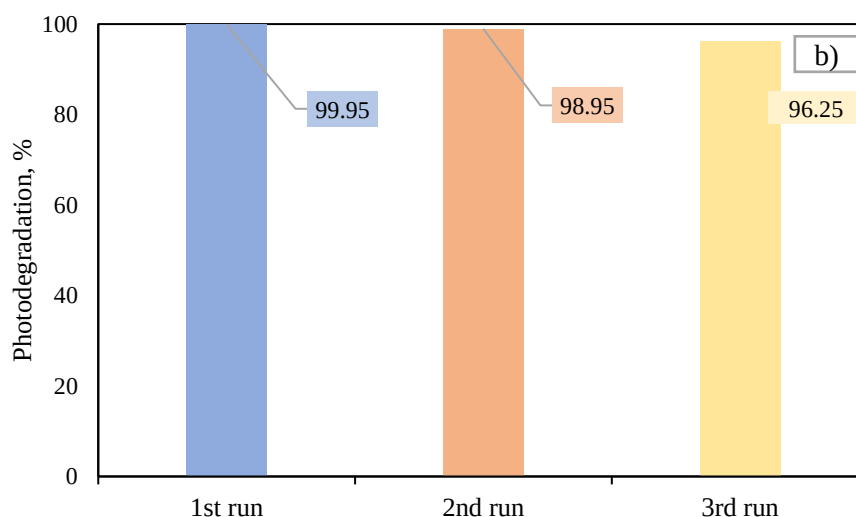


Figure 5.35 Three-cycle photodegradation experiments a) change of DRN concentration with time, b) photodegradation % after 2 h of reaction ($[DRN]_0 = 10$ ppm, catalyst loading = 1g/L, $T = 298K$).

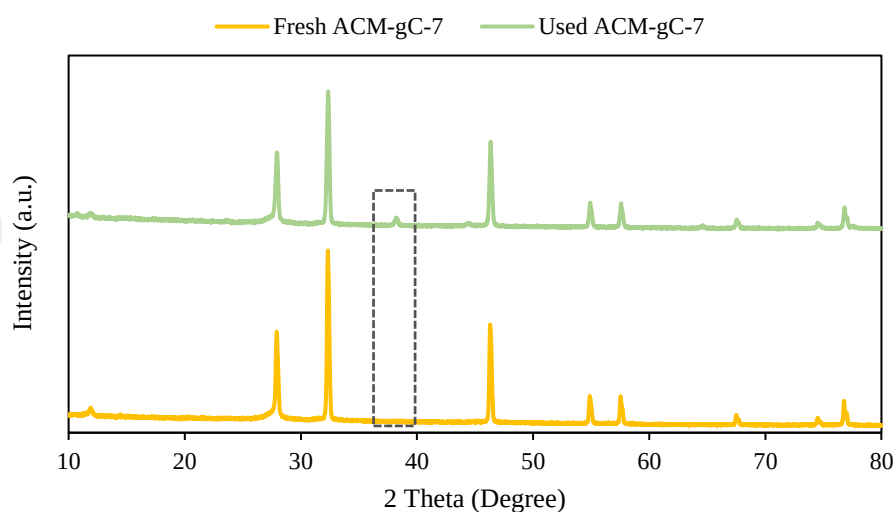


Figure 5.36 Comparison of crystal structure of fresh ACM-gC-7 and recycled sample using XRD analysis.

5.2.11 Toxicity measurements

Toxicity tests were carried out to understand whether the hydrophilic intermediates formed during the photocatalytic oxidation of DRN were more toxic than DRN. In toxicity tests, the root lengths of the cress seeds (*Lepidium Sativum* L.) were measured. For this purpose 15 numbers of seeds were homogeneously distributed on the filter papers placed in two different petri dishes. One of the petri dish was moisture with 5 mL of treated DRN and the other was moisture with the

same amount of untreated DRN solution. Then petri dishes were placed in dark cabinet for 5 days. At the end of fifth day, cress seeds were collected and the root lengths of them were measured and average values were calculated (Petrie et al., 2015; Ayodhya et al., 2016; Shekoohiyan et al., 2020, Yalçın and Dükkancı, 2022; Yentür and Dükkancı, 2020b). The photocatalytic treatment test was performed at the conditions of 10 ppm DRN initial concentration, ACM-gC-7 photocatalyst loading of 1 gL⁻¹, temperature of 25 °C, and DRN neutral pH under 2 h of visible LED light irradiation.

For calculation of inhibition % following equation (Eq. 52) was used:

$$\text{Inhibition, \%} = \frac{\text{Root Length}_{\text{treatedDRN}} - \text{Root Length}_{\text{untreatedDRN}}}{\text{Root Length}_{\text{treatedDRN}}} \quad (52)$$

Inhibition, % value was measured as 48.5%. As seen in Figure 5.37, the treated DRN solution allowed elongation of the root length more. It could be said that, although complete mineralization of DRN was not achieved in the photocatalytic oxidation of DRN over most active ACM-gC-7 photocatalyst, the formed intermediates were less toxic than DRN molecule.

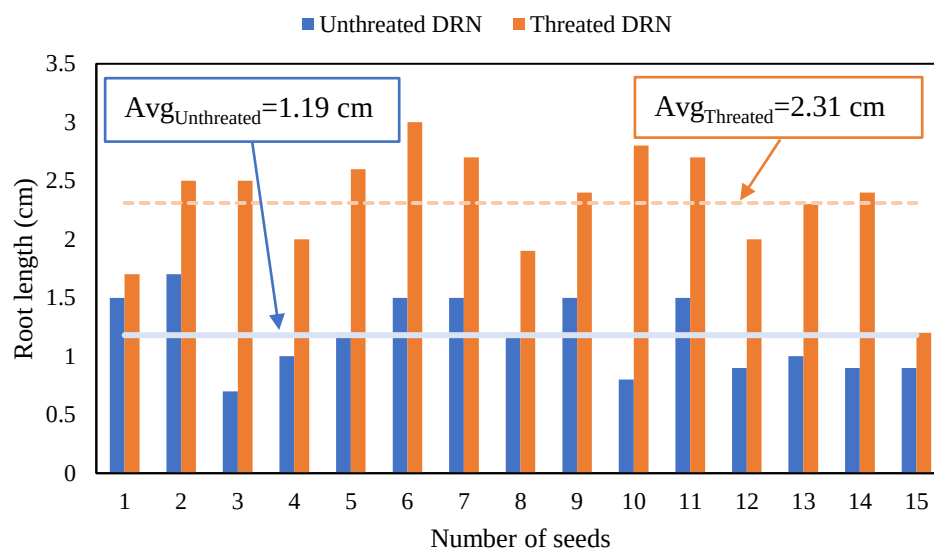


Figure 5.37 Seed root lengths for treated and untreated DRN solutions.

5.2.12 Photocatalytic degradation mechanism over MIL-88A/g-C₃N₄ and Ag/AgCl@MIL-88A/g-C₃N₄ photocatalysts

In order to explain the mechanisms of MIL-88A/g-C₃N₄ and Ag/AgCl@MIL-88A/g-C₃N₄ catalysts in photocatalytic reactions, the valence band (VB) and conduction band (CB) energies of semiconductors are need to know. The valence band energies of MIL-88A and g-C₃N₄ were measured as 2.2 eV and 1.75 eV, respectively, with the XPS-VB spectrum. The band gap energies for MIL-88A and g-C₃N₄ were determined using UV-Vis DRS analysis as 1.95 eV and 2.7 eV, respectively. The conduction band energies of semiconductors can be found using Eq. 53 (Tan et al., 2022).

$$E_{CB} = E_{VB} - E_g \quad (53)$$

The conduction band potential, valence band potential, and energy gap of the semiconductor are denoted by E_{CB} , E_{VB} , and E_g , respectively.

According to Eq. 53, the conduction band energies of MIL-88A and g-C₃N₄ were found to be 0.25 eV and -0.95 eV, respectively.

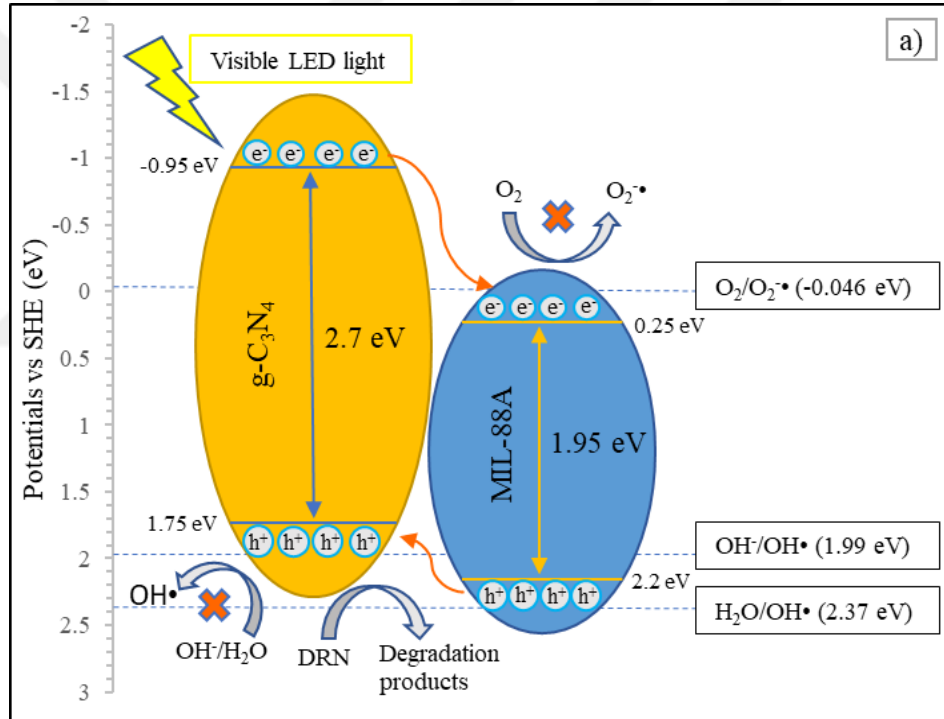
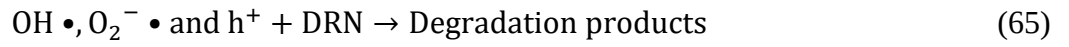
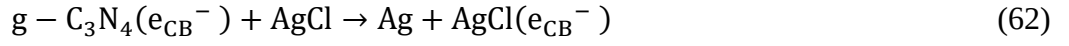
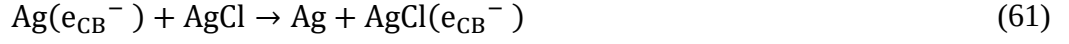
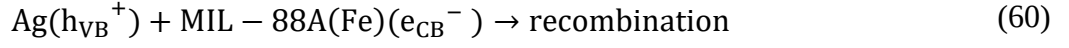
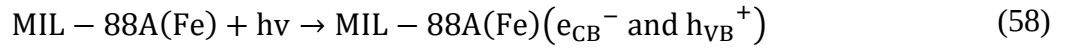
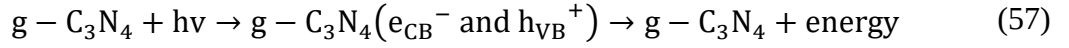
Due to their low band gap energies, both MIL-88A (1.95 eV) and g-C₃N₄ (2.7 eV) can be excited and produced electron-hole pairs when MIL-88A/g-C₃N₄ composite is exposed in visible light irradiation. For MIL-88A/g-C₃N₄ composite, since conduction band electron (e_{CB}^-) levels of g-C₃N₄ are more negative than MIL-88A, e_{CB}^- are migrated from g-C₃N₄ to MIL-88A. Since the energy levels of the valence band of MIL-88A are more positive than that of g-C₃N₄, the valence band gaps ($h\nu_{VB}^+$) are transferred from the MIL-88A valence band to the g-C₃N₄ valence band (Type 2 heterojunction), see Figure 5.38a. Thus, $h\nu_{VB}^+ - e_{CB}^-$ is successfully separated. Since the $h\nu_{VB}^+$ energy of g-C₃N₄ (1.75 eV) is smaller than OH⁻/OH• (Eq. 54) and H₂O/OH• (Eq. 55) oxidation potentials, $h\nu_{VB}^+$ cannot react with OH⁻ and H₂O to produce OH•. In this case, OH• radicals are not formed and $h\nu_{VB}^+$ of g-C₃N₄ directly oxidizes Diuron. The conduction band energy level of MIL-88A was calculated 0.25 eV, which is more positive than the redox potential of O₂/O₂•⁻ (-0.046 eV) (Eq. 56). Therefore, conduction band electrons of MIL-88A cannot react with O₂ adsorbed on the surface thus O₂•⁻ radicals are not formed (Li et al., 2015; Huang et al., 2017; Zhang et al., 2017; Shao et al., 2019; Gholizadeh Khasevani and Gholami 2019; Huang et al., 2022). In summary, it can be said that only valance

band holes of g-C₃N₄ contributes to DRN degradation in binary composite of MIL-88A/g-C₃N₄.



In the triple composite photocatalyst of Ag/AgCl@MIL-88A/g-C₃N₄, the radical generation mechanism is different (Figure 5.38b). Metallic Ag (Ag⁰) rapidly forms electron-hole pairs under visible light due to its surface plasmonic property, but the same is not the case for AgCl. Since AgCl has a band gap energy of 3.4 eV (Yentür and Dükkancı, 2020a), it cannot be activated by visible light to produce electron – hole pairs. However, due to the accumulation of electrons in the lowest vacant orbital of Ag, the Fermi level of Ag increases (0.4 eV) (Yang et al., 2014). Thus, the excess electrons are transferred to the conduction band of AgCl until the Fermi level of Ag reaches equilibrium again. In other words, Ag⁰ tends to maintain the equilibrium of the Fermi level (Yentür and Dükkancı, 2020a). In addition to Ag NPs, g-C₃N₄ also provide electrons to AgCl. As the conduction band level of AgCl (-0.16 eV) is more negative than that of reduction potential of O₂/O₂^{•-} (-0.046 eV), the conduction band electrons of AgCl react with O₂ to form O₂^{•-} radicals. However, the conduction band energy levels of MIL-88A could not react with O₂ to form O₂^{•-}, as the CB potential of MIL-88A (0.25 eV) is more positive than the reduction potential of O₂/O₂^{•-}. In this case, the role of Ag⁰ is not only to improve the utilization of visible light and provide electrons for AgCl, but also to serve as the recombination center of CB electrons of MIL-88A and the valence band holes on its surface. On the other hand, the g-C₃N₄ valence band holes contribute to Diuron oxidation, while MIL-88A valence band gaps react with OH⁻ to form OH[•] radicals. Besides that, since the h_{VB}⁺ energy of MIL-88A (2.2 eV) is more negative than H₂O/OH[•] (2.37 eV) oxidation potentials, h_{VB}⁺ cannot react H₂O to form OH[•] radicals.

The photocatalytic reaction mechanism was summarized using Eqs. 57-65 (Gholizadeh Khasevani and Gholami, 2019; Huang et al., 2018; Viswanathan et al., 2021; Wu et al., 2019). It is clear that in the triple composite photocatalyst of Ag/AgCl@MIL-88A/g-C₃N₄, all OH[•], O₂^{•-} and h⁺ contribute the degradation of DRN.



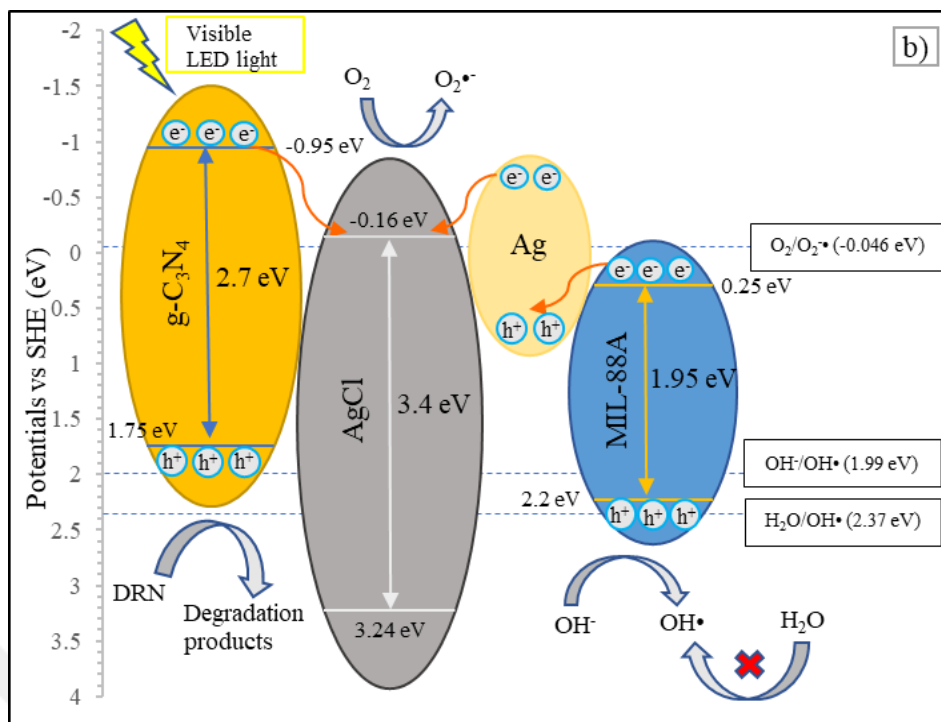


Figure 5.38 Schematic diagram of charge transfer mechanism of MIL-88A/g-C₃N₄ (a) and Ag/AgCl@MIL-88A/g-C₃N₄ (b) under visible light irradiation.

To investigate the dynamic behaviors of photoinduced charge carriers, the samples of g-C₃N₄, Ag/AgCl@MIL-88A, MIL-88A/g-C₃N₄ and ACM-gC-2 were characterized by photoluminescence spectra. The photoluminescence (PL) emission centered at around 490 nm, indicating that this peak is due to recombination of e_{CB}^-/h_{VB}^+ . From Figure 5.39a, it is clear PL spectrum of Ag/AgCl@MIL-88A exhibited stronger PL intensity than that of ACM-gC-2 sample, suggesting its high photo-generated electron-hole recombination tendency. ACM-gC-2 photocatalyst had the weakest PL intensity indicating the inhibition of charge recombination. As displayed in Figure 5.39b, the as-prepared MIL-88A/g-C₃N₄ nanocomposite had smaller semicircle compared with pure g-C₃N₄, which further demonstrated that the addition of MIL-88A was good for enhancing of the charge separation (Huang et al., 2018; Zhang et al., 2019; Xue et al., 2019; Yalçın and Dükkancı, 2022; Ye et al., 2018).

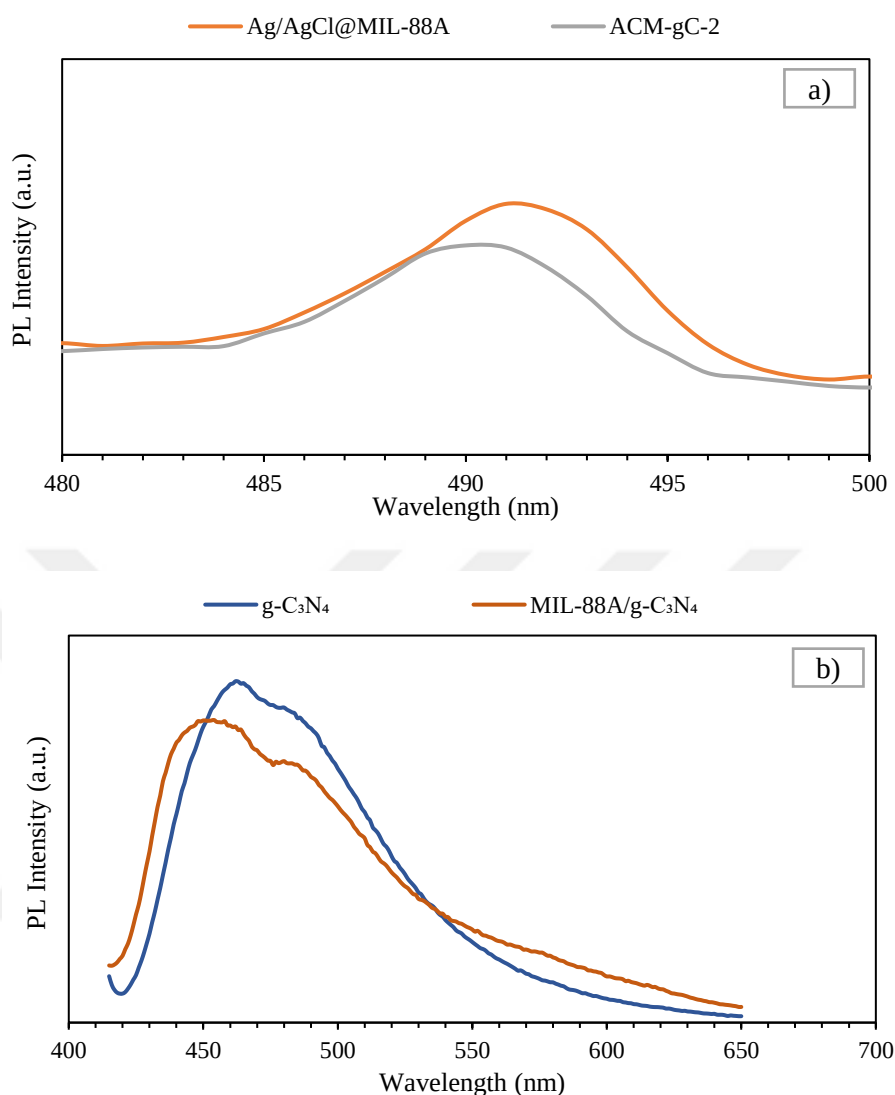


Figure 5.39 PL spectrum of Ag/AgCl@MIL-88A, and ACM-gC-2 (a), g-C₃N₄ and MIL-88A/g-C₃N₄ (b) samples.

5.3 Parametric Study on Photodegradation of Diuron over ACM-gC-7 photocatalyst

In order to assess the overall performance of a photocatalytic system, it is crucial to model and optimize the impact of many variables. The experimental design method was used to determine the best conditions for DRN photodegradation while minimizing the number of reactions. Response surface methodology (RSM) is an effective tool for designing experiments, as it allows for the investigation of the independent and interacting effects of multiple factors. The most common type of RSM is central composite design (CCD), which can analyze

and optimize the independent and interacting impacts of multiple factors in a catalytic system (Mazhari et al., 2018; Chaker et al., 2021; Taghipour et al., 2021).

The effects of initial DRN concentration, pH, and photocatalyst amount were examined using CCD, with the percentage of DRN degradation was entered as a response. The experimental design and optimization were carried out using Minitab 21 software. The CCD requires 20 experiments, containing 8 terms of cubic points, 6 terms of axial points, and 6 central point replications. Table 5.4 displays the three independent variables' range and five levels ($-\alpha$, -1, 0, +1 and $+\alpha$).

Table 5.4 The ranges and levels of the independent variables.

Variable	Original factors	Coded levels				
		-0.5	-1	0	+1	+0.5
X_1	[DRN] ₀ (ppm)	7.5	5	10	15	12.5
X_2	pH	5	3	7	11	9
X_3	Catalyst amount (g/L)	0.75	0.5	1	1.5	1.25

Three independent variables' effects on the response and their interactions were examined using the second-order polynomial equation shown below (Eq. 66):

$$Y = a_0 + \sum_{i=1}^k a_i X_i + \sum_{i=1}^k a_{ii} X_i^2 + \sum_{i=1}^k \sum_{j=1}^k a_{ij} X_i X_j \quad (66)$$

where Y represents the predicted response (degradation percentage of DRN after 45 min of reaction) and X_i and X_j represent independent variables. a_0 is the model's constant parameter, k is the number of variables, a_i , a_{ii} , and a_{ij} are the first-order constant, linear interaction, and quadratic coefficients, X_i^2 represents the square effects, and $X_i X_j$ is the interaction parameter (Mazhari et al., 2018; Parmar and Srivastava, 2022).

The results of the experimental CCD-RSM matrix at five levels of coded and experimental results are presented in Table 5.5. Y_{obs} values indicate percentages of

DRN degradation in the reaction time of 45 min. Y_{pre} is the predicted degradation percentages obtained from the model.



Table 5.5 DRN photodegradation efficiency utilizing CCD-RSM.

Runs	Factors						Responses	
	Coded variables' values			Real variables' values			Conversion (%)	
	X ₁	X ₂	X ₃	[DRN] ₀ (ppm)	pH	Catalyst amount (g/L)	Y _{obs}	Y _{pre}
1	0	0	0	10	7	1	99.12	97.94
2	-0.5	0	0	7.5	7	1	98.63	99.21
3	1	-1	1	15	3	1.5	93.85	93.48
4	0	0	0	10	7	1	99.03	97.94
5	0	0	0.5	10	7	1.25	98.27	98.93
6	-1	1	-1	5	11	0.5	95.59	95.94
7	0	0.5	0	10	9	1	98.05	98.44
8	-1	-1	1	5	3	1.5	99.81	100.09
9	1	1	-1	15	11	0.5	85.86	85.55
10	1	1	1	15	11	1.5	95.18	95.51
11	0	0	0	10	7	1	98.24	97.94
12	-1	1	1	5	11	1.5	99.09	98.56
13	0	0	-0.5	10	7	0.75	96.03	95.73
14	0	0	0	10	7	1	96.79	97.94
15	0	-0.5	0	10	5	1	98.29	98.25
16	0	0	0	10	7	1	97.68	97.94
17	0	0	0	10	7	1	97.73	97.94
18	-1	-1	-1	5	3	0.5	97.6	97.25
19	0.5	0	0	12.5	7	1	95.18	94.96
20	1	-1	-1	15	3	0.5	82.78	83.2

Analysis of variance (ANOVA) is a reliable tool for assessing the quality of fitted models. To determine the ideal operational circumstances for CCD, ANOVA analysis is used. This analysis helps to build mathematical equations that may be used to correlate signals to effective terms. Calculations were performed on the degrees of freedom (DF), mean squares (MS), and sum of squares (SS). Also, the P-value and F-value results from the ANOVA were used to determine the model significance. The terms evaluated were significant if their P-values were less than 0.05 and their F-values were high. Table 5.6 revealed that the two coefficients X_1 (initial DRN concentration) and X_3 (catalyst amount) were significant, while the X_2 coefficient (pH) was not. Also, the interaction of $X_1 * X_3$ is significant. The model predicts an F-value of 61.88 for DRN degradation by the ACM-gC-7 photocatalyst, as shown by Table 5.6 data. The F-value of 61.88 and P-value of <0.0001 in the quadratic model demonstrate that the model is statistically significant. The lack-of-fit (LOF) of the proposed model with the amount of 0.69 for DRN photodegradation by the ACM-gC-7 showed the insignificance. The predicted coefficient of designation value (R^2) was 0.9824. The high R^2 value demonstrated that the quadratic polynomial model equation fitted the experimental data well (Mazhari et al., 2018; Taghipour et al., 2021; Mousavi et al., 2021).

The following equation illustrates the obtained quadratic polynomial model (Eq. 67):

$$\begin{aligned}
 Y_{\text{obs}} = & 91.53 + 0.84X_1 - 1.80 X_2 + 18.8 X_3 - 0.1369 X_1^2 \\
 & + 0.102X_2^2 - 9.77 X_3^2 + 0.0446 X_1 * X_2 \\
 & + 0.734 X_1 * X_3 - 0.029 X_2 * X_3
 \end{aligned} \tag{67}$$

The response is significantly positively impacted by variables with positive coefficient values. While the response is negatively impacted by the variables with negative coefficients (Mousavi et al., 2021).

Table 5.6 ANOVA for DRN photodegradation performance using RSM model.

Source	DF	Sum of squares	Mean square	F-Value	P-Value
Model	9	355.463	39.496	61.88	1.39×10^{-7}
Linear	3	241.156	80.385	125.95	3.05×10^{-8}
X_1	1	153.701	153.701	240.82	2.52×10^{-8}
X_2	1	0.286	0.286	0.45	5.18×10^{-1}
X_3	1	87.168	87.168	136.57	3.75×10^{-7}
Square	3	80.97	26.99	42.29	5.46×10^{-6}
$X_1 \times X_1$	1	2.186	2.186	3.43	9.39×10^{-2}
$X_2 \times X_2$	1	0.5	0.5	0.78	3.97×10^{-1}
$X_3 \times X_3$	1	1.113	1.113	1.74	2.16×10^{-1}
2-Way Interaction	3	33.337	11.112	17.41	3.00×10^{-4}
$X_1 \times X_2$	1	6.372	6.372	9.98	1.02×10^{-2}
$X_1 \times X_3$	1	26.938	26.938	42.21	6.93×10^{-5}
$X_2 \times X_3$	1	0.026	0.026	0.04	8.43×10^{-1}
Error	10	6.382	0.638		
Lack-of-Fit	5	2.428	0.486	0.61	6.97×10^{-1}
Pure Error	5	3.954	0.791		
Total	19	361.845			
$R^2 = 0.9824$					

Figure 5.40 (a-c) depicts the effects of independent variables such as initial DRN concentration (X_1), pH (X_2), and catalyst amount (X_3) and their interactions using 3D response surface plots.

In the photocatalytic process, the initial concentration of DRN is one of the most influential factors. The impact of the initial DRN concentration (X_1) was studied using various DRN concentrations chosen between 5 and 15 ppm. As seen in Figure 5.40a and b, DRN degradation efficiency decreases substantially as the initial DRN concentration increases. Increasing the initial DRN concentration from 7.5 ppm to 10 ppm and later to 12.5 ppm, at pH 7 and a catalyst loading of 1 g/L caused the degradation of DRN to drop from 98.63% to 98.1% and subsequently to 95.18%, as shown in Table 5.5. It was observed that DRN degradation decreased from 97.6% to 82.78% when the initial DRN concentration was increased from 5 ppm to 15 ppm in the case of pH 3 and catalyst amount of 0.5 g/L. The degradation of DRN was also seen to decrease from 99.81% to 93.85% when the initial concentration of DRN was increased from 5 ppm to 15 ppm at a pH of 3 and a catalyst amount of 1.5 g/L. In other experiments where the DRN concentration was

increased from 5 ppm to 15 ppm, the pH was kept constant at 11 and the catalyst amount was kept constant at 0.5 g/L and 1.5 g/L values, a similar decrease in DRN degradation was observed. It was seen that the decrease of degradation with increasing initial concentration of DRN was more significant at low catalyst loading of 0.5 g/L. Decrease in DRN degradation while increasing DRN concentration may be due to insufficient radical production in the medium at high DRN concentration (Lopes and Salgado, 2021). Because high amount of DRN may prevent photon of light reaching the catalyst surface. Another reason of decline in photocatalytic degradation may be explained by the fact that more DRN molecules require more catalyst surface area and active centers.

Since the surface charge and properties of a catalyst are greatly influenced by the pH value, the pH value is a significant factor in the photocatalytic process. The effects of pH (X_2) were investigated at a range of pH values between 3 and 11, chosen in accordance with the DRN pK_a value (3.7) (Lopes and Salgado, 2021). When the pH was raised from 5 to 7, and 9, DRN degradation decreased slightly from 98.29% to 98.1% and 98.05% under the same conditions of initial DRN concentration was at 10 ppm and the catalyst amount was constant at 1 g/L. While the initial DRN concentration was 15 ppm and the amount of catalyst was 0.5 g/L, increasing the pH from 3 to 11 enhanced DRN degradation very slightly from 82.78% to 85.86%. Similarly, increasing the pH from 3 to 11 increased the DRN degradation from 93.85% to 95.18% in the case where the initial DRN concentration was 15 ppm, and the catalyst amount was 1.5 g/L. While the catalyst amount and initial DRN concentration were both held constant at 0.5 g/L and 5 ppm, respectively, the DRN degradation decreased from 97.6% to 95.59% when the pH was raised 3 to 11. Under the same conditions, when the amount of catalyst was 1.5 g/L, the percentage of DRN degradation changed little and decreased from 99.81% to 99.09%. As seen in Table 5.5 and Figure 5.40a and c, ambient pH has no significant effect on DRN degradation for the ACM-gC-7 catalyst (with P value of $0.52 > 0.5$, Table 5.6). In other words, throughout all applied pH ranges, the ACM-gC-7 catalyst exhibited good activity in DRN degradation. The pH can influence the surface charge of a catalyst, the formation of hydroxyl radicals, and positive holes. DRN is positively charged at pH is smaller than pK_a and negatively charged when the pH is greater than pK_a (Yeganeh et al., 2022). The presence of a greater

number of hydroxyl ions (OH^-) aids in the generation of photoactive hydroxyl radicals ($\text{OH}^\bullet$) with the reaction of positive holes (h^+), thus increases the photocatalytic degradation efficiency at alkaline pH. However, in basic media, ACM-gC-7 can carry a negative charge, causing in repulsion between hydroxyl anions and the photocatalyst surface. Depending on this situation, a reduction in the formation of hydroxyl radicals may be seen, resulting in a reduction in catalytic activity (Anirudhan et al., 2020). But on the other side, in an acidic media, the main oxidation species are positive holes (Anirudhan et al., 2018). The holes (h^+) have a significant effect on photocatalytic activity as mentioned in the section "5.2.12". In the present study, the highest photodegradation of 99.8% was achieved at an initial DRN concentration of 5 ppm, at a catalyst amount of 1.5 g/L, at pH=3 within in a reaction time of 45min.

The amount of catalyst had a significant effect on the activity in the photocatalysis process. From the economic point of view the amount of catalyst should be optimized. The amount of catalyst (X_3) was selected between 0.5 and 1.5 g/L to study the impact of catalyst amount on the photocatalytic degradation of DRN. According to Figure 5.40b and c, while the amount of catalyst increased, DRN degradation also increased. As can be shown in Table 5.5, the percentage of DRN degradation increased from 96.03% to 98.1 % to 98.27% when the catalyst amount was increased from 0.75 g/L to 1.0 g/L and then to 1.25 g/L, where the pH was 7 and the initial DRN concentration was 10 ppm. At the initial DRN concentration of 5 ppm, and the pH of 3, increasing the catalyst amount from 0.5 g/L to 1.5 g/L, resulting an increase in DRN degradation from 97.6% to 99.81%. Similarly, DRN degradation increased from 95.59% to 99.09% when the amount of catalyst was increased from 0.5 g/L to 1.5 g/L at a pH 11 with an initial DRN concentration of 5 ppm. When the initial DRN concentration was held constant at 15 ppm and the amount of catalyst was raised from 0.5 g/L to 1.5 g/L, it was observed that DRN degradation increased significantly from 82.78% to 93.85% in an acidic medium (pH=3) and from 85.86% to 95.18% in a basic medium (pH=11). It was clear that positive effect of catalyst amount was more significant at higher initial concentration of 15 ppm. Increasing the amount of catalyst increases the presence of active species on it and thus contributes positively to photodegradation of DRN. The increase in DRN degradation as the amount of catalyst increases can

be attributed to the increase in active sites and total surface area for photocatalysis (López-Ramón et al., 2019).

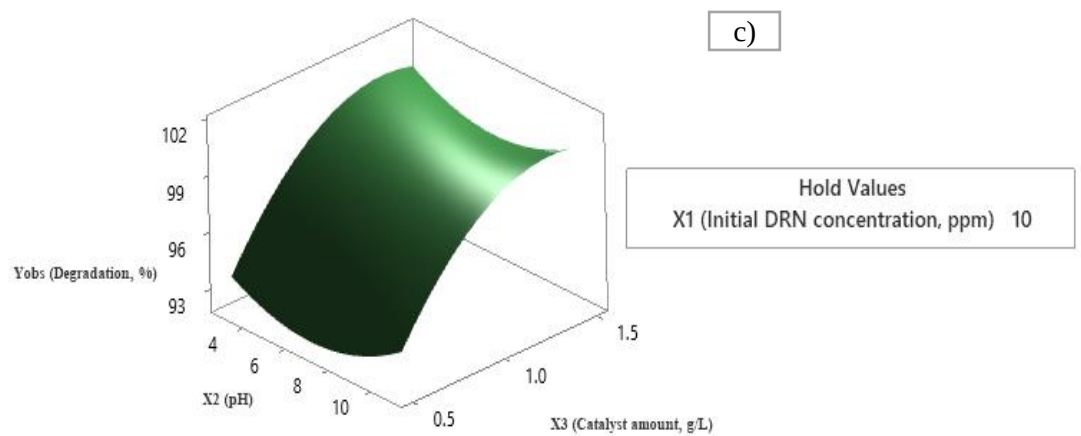
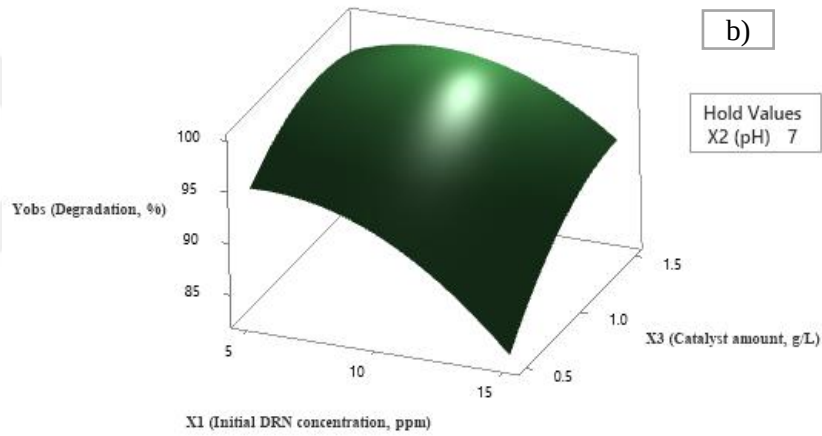
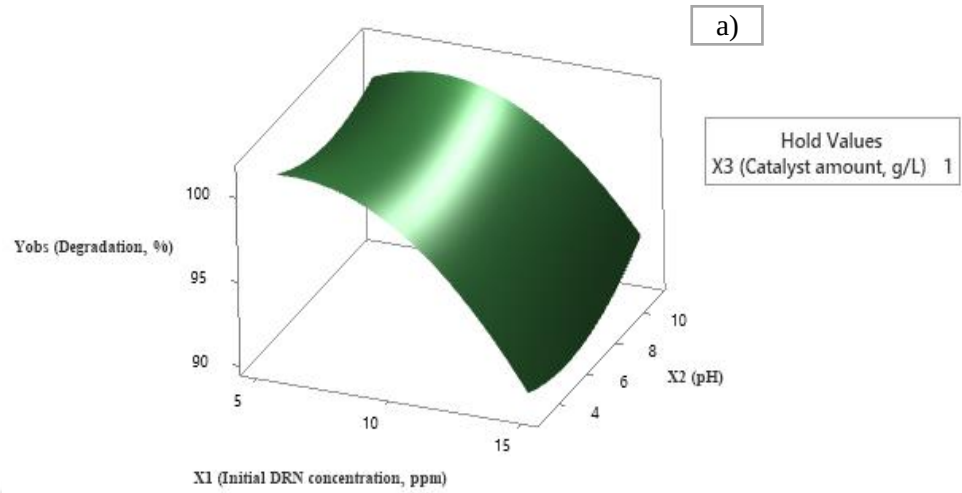


Figure 5.40 DRN degradation percentage surface plots in 3D as a function of (a) initial DRN concentration and pH, (b) initial DRN concentration and catalyst amount, and (c) pH and catalyst amount.

As a result, the pH of solution has no significant influence on DRN photodegradation and improving photocatalytic performance might be achieved by lowering the initial concentration of DRN or increasing the amount of the catalyst. According to the response optimization results (Figure 5.41), it was observed that the DRN degradation was 99.38% (in 45 min reaction time) at optimum conditions where the pH was 3, the DRN concentration was 6.82 ppm, and the catalyst amount was 1.22 g/L. In addition, 100% degradation was obtained after 1 h of reaction time under the specified optimum conditions.

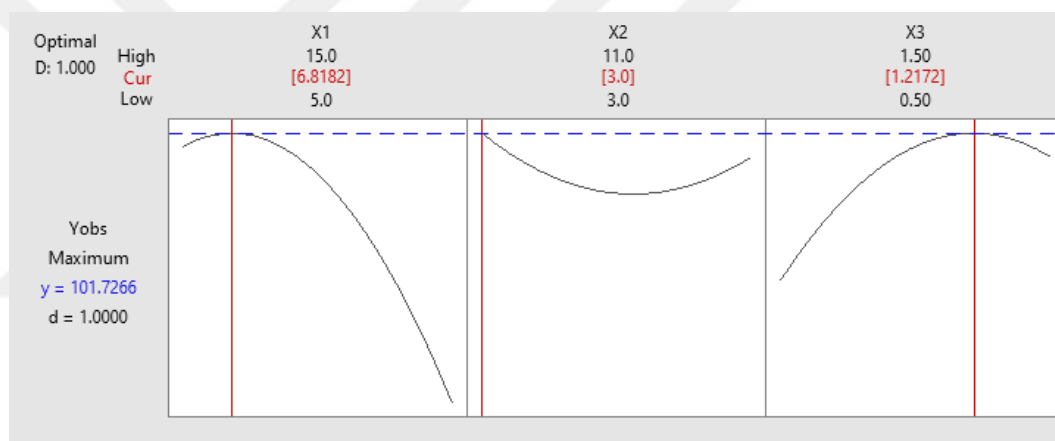


Figure 5.41 Response optimization results for DRN photodegradation.

Figure 5.42 depicts a good correlation between the experimental data and the quadratic polynomial model based on the consistency between observed and predicted values.

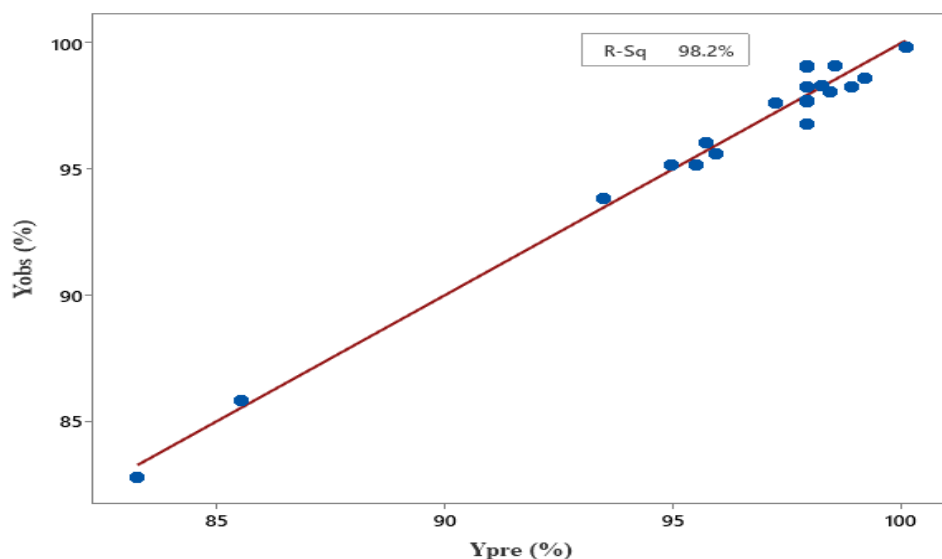


Figure 5.42 Plot of observed yields (Y_{obs}) vs predicted yields (Y_{pre}) for ACM-gC-7 catalyst in degradation efficiency of DRN.

5.4 Effect of Sonication on Photocatalytic Oxidation of DRN over ACM-gC-7 photocatalyst

Sonication involves ultrasound-induced sonochemical reactions. Ultrasound can be expressed as sound waves of a certain frequency above (20-1000 kHz) humans hearing. The mechanisms of sonolysis is based on acoustic cavitation. Acoustic cavitation involves the formation, growth and implosive collapse of tiny bubbles (called as micro-reactors) in a liquid at very small time intervals. The collapse of cavitation creates local hot temperatures (5200K) and high pressures (500 atm) that facilitate breaking chemical bonds of water, resulting formulation of free radicals via Eqs. 68-71:



In addition to radical formation that would oxidize organic pollutants in water, under the extreme conditions given above hydrophobic pollutants can be degraded thermally inside the cavity and/or cavitation-liquid interface. Whereas hydrophilic and non-volatile compounds can not degrade by cavitation directly.

The other effect occurs when sound waves applied a liquid is acoustic streaming (time- independent fluid flow, mechanical effect). The frequency of the sound is the very important parameter that should be investigated in sonication. Generally, the chemical effect (radical production) increases, and the mechanical effects decrease with an increase in frequency (Abdurahman et al., 2021; Yalçın and Dükkancı, 2022; Yentür and Dükkancı, 2021).

However, due to the formation of hydrophilic intermediates during the reaction, sonication alone is not effective in degrading organic pollutant containing wastewaters. In this regard, the presence of a solid catalyst in sonication process (sonocatalytic) could provide additional active sites for nucleation of bubbles which increases the number of cavitation bubbles formed. Sono-photocatalytic (visible or UV light, ultrasound and catalysis together) oxidation is the other hybrid process that will enhance the efficiency of sonication.

In the content of this study, probe type transducer at low frequency of 20 kHz and plate type transducer at high frequency of 850 kHz were utilized as sonication sources. Calorimetric method was used to determine actual power dissipated into the water. For this purpose, 150 mL (in the case of probe type transducer) or 200 mL (in the case of plate type transducer) of water was poured in a beaker and the temperature of water was recorded against time. The ultrasonic power actually reaching the system is obtained according to Eq. 72:

$$\text{Power (W)} = \left(\frac{dT}{dt} \right) C_p m \quad (72)$$

where (dT/dt) is the temperature rise per second, C_p is heat capacity of water ($4.187 \text{ kJ kg}^{-1} \text{ K}^{-1}$ at 20°C) and m is mass of water used in kg (Dükkancı, 2019). The actual powers were calculated as 30 W for probe type transducer and as 24 W for plate type transducer.

Experiments were conducted under the following conditions: initial DRN concentration of 10 ppm, catalyst loading of 1 gL^{-1} , at a temperature of 25°C and neutral pH under visible LED light irradiation within 60 min of irradiation. The most active photocatalyst of ACM-gC-7 was used in the runs.

As seen in Figure 5.43a and b, low frequency of sonication (20 kHz) gave the photocatalytic efficiency of 31.42% within the reaction time of 60 min. In the case of sonocatalytic oxidation, photodegradation of DRN increased slightly to 33.66%.

However, the degradation efficiency enhanced significantly to 96.56% in sono-photocatalytic oxidation within the same reaction duration. But this efficiency was under the photocatalytic efficiency alone.

Similar result was obtained in the case of high frequency (850 kHz) of sonication. Sonication alone achieved 56.83% degradation and it was increased to 63.65% in sonocatalytic oxidation. In sono-photocatalytic oxidation the observed degradation was 80.61% which is lower than that of photocatalytic oxidation alone.

It was clear that addition of catalyst in sonication system enhanced the degradation of DRN. Presence of catalyst powder provide additional nuclei for cavitation bubbles thus increases the formation of active radicals. Both at high frequency and low frequency of ultrasound, sono-photocatalytic oxidation enhanced the efficiency of sonication. However, the obtained degradation of DRN was higher in photocatalytic oxidation than that of sono-photocatalytic oxidation. It may be said that ACM-gC-7 is a good photocatalyst rather than a sonocatalyst.

As seen from Figures 5.43 and 5.44, high frequency sonication was more effective in removal of DRN, 31.42% and 56.83% DRN degradation was achieved at low frequency of 20 kHz and high frequency of 850 kHz, respectively. Degradation of 33.66% and 63.85% were achieved in sonocatalytic oxidation of DRN in probe type and plate type ultrasonic system, respectively. At high frequency, relative number of cavitation bubbles are higher than that of low frequency of sonication due to the fast cavitation events. In addition to this, comparatively smaller bubbles are formed that takes shorter time to collapse at high frequency of sonication. This two effect cause production of more hydroxyl radicals. Moreover, at high frequencies, the formed $\text{OH}\cdot$ radicals tended to approach the bulk phase rather than combination to produce H_2O_2 (Yentür and Dükkancı, 2021; Jun et al., 2019).

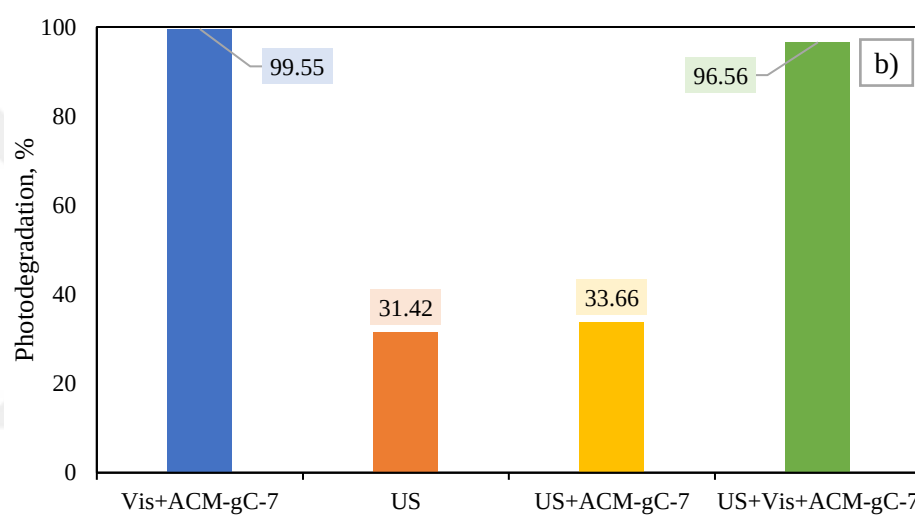
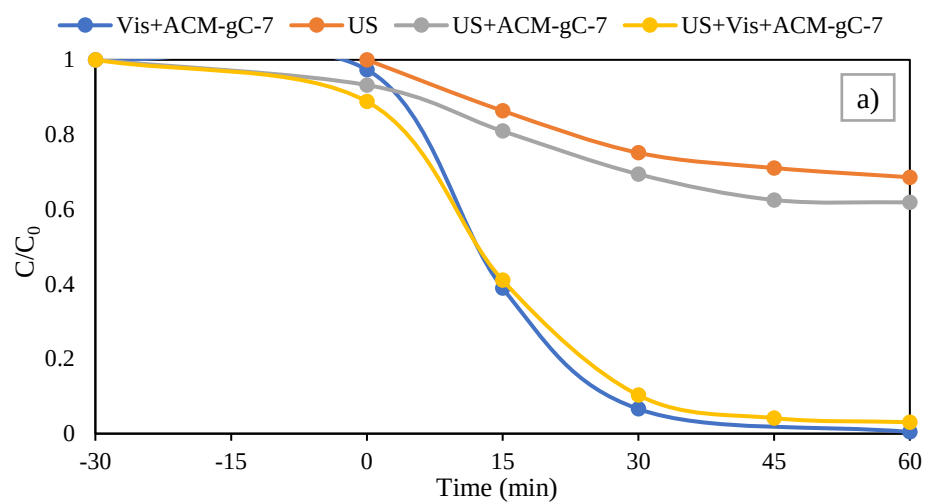


Figure 5.43 Effect of sonolysis on photodegradation of DRN a) change of DRN concentration with time, b) photodegradation% after 1 h of reaction ($[\text{DRN}]_0 = 10 \text{ ppm}$, catalyst loading = 1 g/L , $T = 298 \text{ K}$, LED light power = 93.4 W , ultrasonic frequency = 20 kHz).

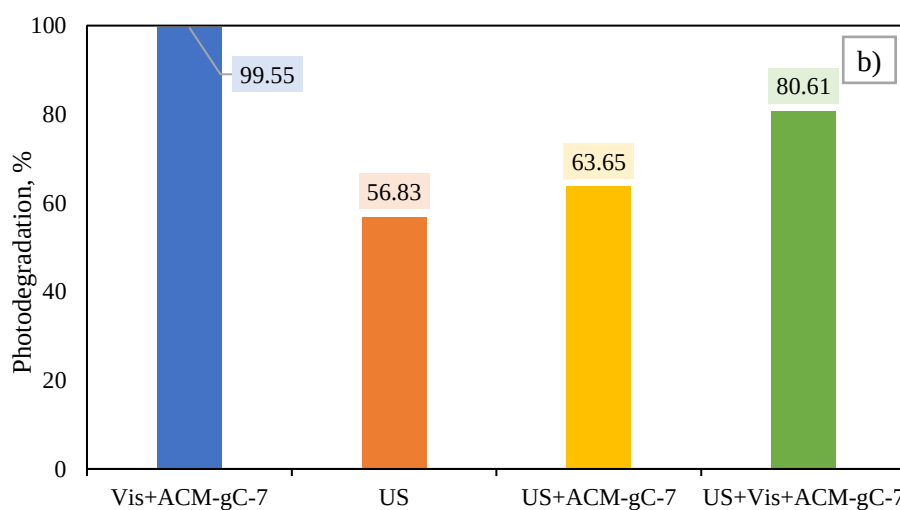
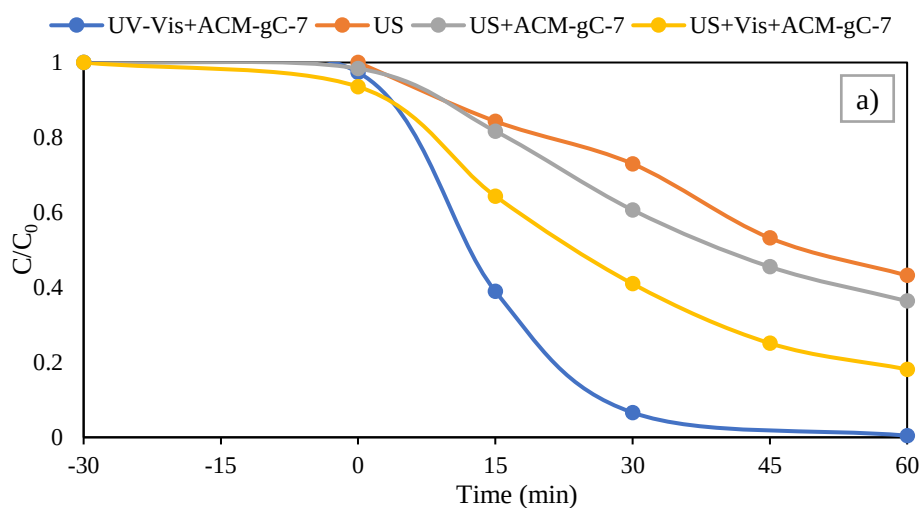


Figure 5.44 Effect of sonolysis on photodegradation of DRN a) change of DRN concentration with time, b) photodegradation% after 1 h of reaction ($[DRN]_0 = 10$ ppm, catalyst loading = 1g/L, $T = 298K$, LED light power = 93.4W, ultrasonic frequency = 850 kHz).

6. CONCLUSIONS

In this thesis, a series of g-C₃N₄ supported Ag/AgCl doped MIL-88A composites were fabricated and characterized by SEM, XRD, XPS, FT-IR, UV–vis DRS, N₂ adsorption studies and PL. Ag/AgCl@MIL-88A/g-C₃N₄ composites were prepared by changing the photodeposition time, Ag loading amount and type of sacrificial agent and light source. The activities of as-prepared composites were examined on the photodegradation of herbicide diuron (DRN) in aqueous solution under visible LED light irradiation. The effect of addition of oxidant on photocatalytic oxidation was investigated using H₂O₂ and PS. Also, the photocatalytic oxidation was performed in various water matrix. Experiments on trapping agents, toxicity assessment, and recycling (reusability) were conducted over the most active ACM-gC-7 triple composite. Experimental design (RSM-CCD) was used to optimize conditions for DRN photodegradation and the effects of initial DRN concentration, pH, and amount of photocatalyst were investigated. Finally, the effect of sonication on the photocatalytic oxidation of DRN over ACM-gC-7 photocatalyst at low (20 kHz) and high (850 kHz) frequencies was examined. The results of all these studies are presented below:

- The DRN photodegradation percentages over various catalysts after 120 min of irradiation was as follows: ACM-gC-2 (45.42%) > g-C₃N₄ (27.05%) > MIL-88A/g-C₃N₄ (26.87%) > Ag/AgCl@MIL-88A (19.11%) > MIL-88A (2.21%). Experiments were conducted under visible LED light irradiation with the initial DRN concentration of 10 ppm, catalyst loading of 1g/L, and at a temperature of 298K.
- As the photodeposition time in the catalyst preparation step increased from 30 min (ACM-gC-1) to 1 h (ACM-gC-2), the photocatalytic degradation of DRN increased from 35.26% to 45.42% after a reaction time of 2 h. However further increase in the photodeposition time from 1 h to 2 h (ACM-gC-3), the degradation of DRN increased slightly (from 45.42% to 46.9%).
- At the Fe:Ag mole ratios of 0.25:0.75, 0.5:0.5, and 0.75:0.25 (ACM-gC-4, ACM-gC-2, and ACM-gC-5, respectively), the obtained photodegradations were 94.4%, 45.42%, and 23.7%, respectively within the reaction time of 2 h.

- For photocatalysts prepared with different sacrificial agents as ACM-gC-6 (EtOH), ACM-gC-8 (glycerol), and ACM-gC-7 (just water), the complete degradation of DRN was obtained after 2 h of irradiation. However, ACM-gC-4 that was prepared with ammonium oxalate exhibited a somewhat lower rate of photodegradation of DRN (94.4%).

- The composite photocatalysts that were synthesized with different light sources, visible LED (ACM-gC-7) and high pressure Na Lamps (ACM-gC-9) gave similar photodegradation (>99%) of DRN after a reaction time of 2 h.

- ACM-gC-8 photocatalyst showed the highest TOF value (1.58 h^{-1}), suggesting the introduced Ag NPs favored oxidation ability of photodegradation reaction by the help of local surface resonance effect of them. It was followed by ACM-gC-7 photocatalyst with TOF value of 1.54 h^{-1} . TOF results were in good agreement with photodegradation.

- Based on the parameters of the synthesis, ACM-gC-7 (with a photo-reduction time of 1 h, Fe:Ag mole ratio of 0.25:0.75, and contained no sacrificial agent) exhibited the highest activity and achieved almost complete degradation within 60 min of irradiation.

- Addition of oxidants shortened the time for the complete degradation of DRN and leading to mineralization. In the presence of H_2O_2 or persulfate, complete degradation of DRN was achieved in 15 min and 30 min, respectively. In the absence of oxidants, there was no TOC reduction; however, in the presence of PS and H_2O_2 , TOC reductions of 30.69% and 34.85%, were achieved within 2 h of reaction, respectively.

- As actual water bodies contain different inorganic ions and natural organic matter, the effects induced by the water matrix species were investigated and no detrimental effect was observed.

- Trapping experiments revealed that superoxide radicals ($\text{O}_2^{\bullet-}$) and photo-generated holes (h^+) are the main reactive species in the photodegradation process.

- High stability and reusability of the composite ACM-gC-7 could be considered as one of the important result of the study which was confirmed by three consecutive cyclinc tests.

- In the toxicity tests, the treated DRN solution was 48.5% less toxic than the untreated DRN solution.

- Within the scope of the parametric study, the effects of pH (in the range of 3-11), photocatalyst amount (in the range of 0.5–1.5 g/L), and initial DRN concentration (in the range of 5–15 ppm) were evaluated on the photocatalytic oxidation of DRN over ACM-gC-7 photocatalyst. Based on the results, the pH of the solution has no significant effect on DRN photodegradation, and photocatalytic performance could be enhanced by decreasing the initial concentration of DRN or by increasing the amount of photocatalyst. In optimal conditions, where the pH was 3, the DRN concentration was 6.82 ppm, and the catalyst amount was 1.22 g/L, 99.38% of the DRN was degraded in 45 min, as determined by the response optimization results.

- Based on the sonication experiments, high frequency sonication was more effective in the removal DRN than low frequency sonication, 31.42% and 56.83% DRN sono-degradation were achieved at 20 kHz and 850 kHz, within 60 min, respectively. Similarly, in the sonocatalytic oxidation of DRN, 33.66% and 63.85% were achieved at 20 kHz and 850 kHz sonication, within 60 min, respectively.

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