

Synthesis and Characterization of ZnAl-LDH/Mn₃O₄ Composite for Degradation of Methylene Blue in Aqueous Solution



Tadesse Abebaw Mengistie

A thesis Submitted to the Department of Materials Science and Engineering,

School of Mechanical, Chemical, and Materials Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Materials
Science and Engineering

Office of Graduate Studies

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June, 2023

Adama, Ethiopia

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Mr. Tadesse Abebaw Mengistie

Main Advisor: Dinsefa Mensur (Asso.Prof.)

Co-Advisor: Osman Ahmed (Asso.Prof.)

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DECLARATION

I hereby declare that this Master Thesis entitled “Synthesis and Characterization of ZnAl-LDH/Mn₃O₄ Composite for Degradation of Methylene Blue in Aqueous Solution” is my own work and it has not been submitted for the award of any academic degree, diploma, or certificate in any other university. All sources of materials that are used for this thesis has been duly acknowledged through citation.

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LIST OF ACRONYMS

AOP	Advanced Oxidation Process
BET	Brunauer, Emmet, and Teller
CB	Conduction Band
DRS	Diffusive Reflectance Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FT-IR	Fourier Transformation Infrared Spectroscopy
H ₂ O ₂	Hydrogen Peroxide
LDH	Layer Double Hydroxide
MB	Methylene Blue
MMO	Mixed Metal Oxide
MO	Methyl orange
NPs	Nanoparticles
•OH	Oxygen Radicals
•O ⁻²	Oxygen Radicals
PL	Photoluminescence-Spectroscopy
ROS	Reactive oxygen species
RT	Room Temperature
SEM	Scanning Electron Microscopy
TM	Transition Metals
UV	Ultraviolet-Spectroscopy
VB	Valance Band
XRD	X-ray Powder Diffraction

ABSTRACT

Organic dyes are the major cause of water pollution, so that it is harmful for all living things. Photocatalysis is one of the most attractive and cost-effective approaches for removing such harmful pollutants in wastewater. Trimanganese tetra oxide nanoparticles are well-known catalyst for the removal of organic pollutants due to its natural abundance, low cost, low toxicity, and high catalytic activity. In this study, ZnAl-layered double hydroxide/ Mn_3O_4 nanocomposites were synthesized through in-situ growth of Mn_3O_4 nanoparticles on the layer double hydroxide sheet, in the ratio of (50:50, 60:40, 70:30) are done, and their names are assigned as ZM-5, ZM-6, and ZM-7 respectively. Various characterization techniques were used to characterize all synthesized nanocomposites. The degradation of methylene blue (MB) under visible light irradiation was employed to evaluate the photocatalytic performance of the prepared catalysts. The photocatalytic activities of bare- Mn_3O_4 , ZnAl-LDH, ZM-5, ZM-6, and ZM-7 catalysts were evaluated towards the degradation of methylene blue (MB), and 50.05 %, 48.6 %, 93.2 %, 94.96 %, and 97.16 % of methylene blue dye was degraded, respectively. Among the catalysts, ZM-6 catalysts had the highest performance and 97.16 % MB dye was degraded within 90 minutes under visible light irradiation. The increased degradation efficiencies could be attributed to the uniform distribution of Mn_3O_4 NPs on the LDH surface, which facilitates the generation of electron and hole pairs, lowers the recombination rate, improves charge transfer, improves visible light absorption, low agglomeration, and increases surface area. By providing enough space for NPs distribution, the LDH was able to induce the required photostability. The catalytic dosage and pH effect of ZM-6 catalysts were studied. Therefore, ZM-6 catalyst can be easily regenerated and reused up to five times without losing substantial catalytic activity.

Keywords: Photocatalyst, methylene blue, Trimanganese tetra oxide, Layer double hydroxide,

CHAPTER ONE

1. Introduction

1.1 Background

Water is one of the most essential resources for all living things, hence it's crucial to prevent pollution of water supplies (Q. Wang & Yang, 2016). Water pollution, which is linked to several diseases and kills two million people per year (such as salmonella, typhoid, skin infections, trachoma, cancer, cholera, and polio), has become a major problem on a global scale (B. Chen et al., 2019). When undesired things get into water, it becomes contaminated, which is bad for the environment and people's health (Haseena et al., 2017). Due to its severe and irreversible effects on ecosystems and human health, water pollution has recently gained significant attention. Typical wastes of concern include volatile organics, dioxins, dibenzofurans, pesticides, nitro-aromatic compounds, polychlorinated biphenyls, chlorophenols, asbestos, heavy metals, arsenic compounds, aviation fuel, solvent, degreasing agents and dyes (Patterson, 1985). Among them dyes must be the major worry when it comes to industrial effluent because of their high toxicity, non-biodegradability, and carcinogenic consequences (X. Zhang, Ma, Fan, Peng, & Komarneni, 2019). Its correct management has turned into a problem that has to be handled. Because the toxins present in the wastewater must be successfully eliminated in order to reuse the water properly, using conventional methods such as adsorption, coagulation, and membrane separation have hardly achieved a good effect and requires high cost (J. Li et al., 2017; Wiśniewski et al., 2019). Extremely strict requirements have driven researchers to create and advance novel methods in recent years in order to achieve higher mineralization rates with lower levels of detectable pollutants. Various physical, chemical, and biological treatment methods have been used to cure a wide range of municipal and industrial wastewaters, including those from the chemical, biological, food, and pharmaceutical industries. Effluents from pulp and paper, textile and dye manufacturing and landfill leachate various surface and ground waters are also being mineralized, removed, and oxidized via these methods (Mohajerani, Mehrvar, & Ein-Mozaffari, 2009).

Wastewater treatment approaches have included adsorption, catalytic oxidation, and photocatalytic degradation. Because it is simple to use and pollution-free, photocatalytic dye degradation has drawn a lot of attention among the several wastewater treatment methods. A wide range of metal oxide semiconductors may be used for photocatalysis, such as TiO_2 , ZnO , MgO , WO_3 , Fe_2O_3 , Mn_3O_4 , SnO_2 , and NbO_2 had been used for water treatment under UV and visible light irradiation (Mano, Nishimoto, Kameshima, & Miyake, 2015; Sukhdev et al., 2020). For the case of photocatalytic materials performance improvement, certain strategies have been executed such as doping (Razzaq et al., 2017), composite/hybrid/heterojunction formation, support materials such as LDH, coupling with noble metals or carbon-based materials (Ali et al., 2020; Ali, Razzaq, & In, 2019; Asif, Khan, & Asiri, 2015a).

Recently, LDH, also an interesting class of layered anionic clays, has captured the researchers' interest for their development and application in a variety of research areas such as adsorption and photocatalysis (Daud et al., 2019; Mohapatra & Parida, 2016). LDHs have been revealed very recently as extremely powerful functional materials employed in technologies to clean contaminated waters (Yihao Liu et al., 2020). LDHs have a high surface area and high anion exchange capacity due to the wide interlayer spaces and the substantial quantity of exchangeable ions, and they have the potential to be effective ion exchanger and adsorbents (Zhou et al., 2011). Combining LDH to metal oxide is the best technique to improve the degradation of different dyes (Takahashi et al., 2021). Due to their distinct chemical and physical characteristics, manganese oxides are a well-known transition metal oxide that has been the subject of much research. Ion and molecular sieves, catalysis, cathode materials for secondary rechargeable batteries and super capacitors are just a few of the potential uses for manganese oxides. Moreover, it is economical, non-toxic and has simple synthesis protocol (Asif et al., 2015a; Khan et al., 2021). However, pristine Mn_3O_4 tends to agglomerate, rapid recombination rate and exhibit a low specific surface area (Runqi Chen et al., 2022; Jarvin, Kumar, Vinodhkumar, Manikandan, & Inbanathan, 2021; Van Tran et al., 2022a), greatly influencing its catalytic efficiency. In this study, tri-manganese tetra-oxide supported with ZnAl-LDH composite catalyst for MB dye degradation under visible light conditions was reported for the first time. The synthesized catalysts were investigated and

ways to degrade MB when exposed to visible light. The catalytic efficiency of ZM-6 composite catalysts was enhanced by their low recombination, high adsorption effect, high visible light absorption, low agglomeration, and high surface area.

1.2 Statement of the problems

The application of Mn_3O_4 is limited to slow rate of reaction due to the narrow band gap and rapid rate of photogenerated charge carrier recombination, poor chemical and thermal stabilities of the material have led to aggregation of NPs and exhibit a low specific surface area (Lett et al., 2022; Yao, Xu, Yu, Zhang, Wang, et al., 2013; J. Zhao et al., 2017), greatly influencing its catalytic efficiency. Many studies have found that supporting Mn_3O_4 on an appropriate porous carrier, such as GO (Runqi Chen et al., 2022; Imboon, Khumphon, Yotkuna, Tang, & Thongmee, 2021) SiO_2 nanofibres (X. Wang, Dou, Yang, Yu, & Ding, 2017), LDHs (Takahashi et al., 2021), would enlarge its surface area and promote the catalytic process. Therefore, combining LDHs' high adsorptive capacity with Mn_3O_4 NPs' high catalytic activity for organic dye degradation should offer promising results.

1.3 Objectives

1.3.1 General Objectives

Synthesis and Characterization of ZnAl-LDH/ Mn_3O_4 Composite for Degradation of Methylene Blue in Aqueous Solution.

1.3.2 Specific Objective

- Synthesis of Mn_3O_4 nanoparticles using co-precipitation method.
- Synthesis of ZnAl-LDH using co-precipitation method.
- Synthesis of ZnAl-LDH/ Mn_3O_4 composites.
- Characterize Mn_3O_4 , ZnAl-LDH and ZnAl-LDH/ Mn_3O_4 composites.
- Evaluate the photocatalytic activity of the prepared catalyst on dye degradation.

1.4 The Scope of the Research

In this work, the synthesis of Mn_3O_4 and ZnAl-LDH was performed by a simple co-precipitation method. Furthermore, ZnAl-LDH/ Mn_3O_4 (ZM) composites (50:50, 60:40, and 70:30), labeled as ZM-5, ZM-6, and ZM-7, had been synthesized by the in-situ growth method, respectively. The synthesized samples had been characterized by different characterization

characterization techniques, and the degradation efficiency of the organic dye molecule had been evaluated. The pH effects, catalytic dosage, and reusability of the synthesized catalysts had been evaluated.

1.5 Significance of the study

This work primarily benefits industries such as textile, paper, cosmetic, and leather processing, which release effluent with high concentrations of organic dyes. The environmental pollution caused by these organic dyes will be reduced. The degradation of discharged organic contaminants reduces the potential for human exposure to them and the amount of oxygen that they could potentially absorb. From the perspective of human health, issues like cancer, mutation, and skin irritability brought on by organic dyes have also been minimized.

CHAPTER TWO

2. Literature Review

2.1 Wastewater

Inorganic and organic contaminants have caused water pollution, which has become a very sensitive issue worldwide. Urbanization, industrialization, the burning of fossil fuels, and other anthropogenic activities emit both inorganic and organic contaminants into aquatic environments. The dyes had eventually released into fresh and salt water after being employed in the plastic, leather, paper, pharmaceutical, food, and textile sectors. The dyes are water-soluble organic species; dyes and their metabolites are definitely harmful to humans and other living organisms (Kavithayeni, Geetha, & Akash Prabhu, 2019; Raghavendra, Sankarappa, Malge, Polymers, & Materials, 2020). They have high water solubility, making it particularly challenging to remove them from water and wastewater. Dyes were generally, used in the textile and food processing industries and released through their waste streams. In general, the waste stream of such industries contains bleaching agents, finishing chemicals, thickening agents, surface-active chemicals, metallic salts, and dyestuffs. Most dyes irritate the skin, harm the eyes, induce headaches, perspiration, nausea, skin discoloration, and other health issues (Anwer et al., 2019; Archana & Kiran, 2012; Lellis, Fávaro-Polonio, Pamphile, & Polonio, 2019; Singh, Arora, & technology, 2011; D. Zhu, Zhou, & Management, 2019; P. Zhu et al., 2020). Dyes can be natural or synthetic; naturally, occurring dyes are typically, obtained from plants, minerals, and insects. The synthetic dyes are water-soluble, water-insoluble, and in-situ color formation. According to chemical nature, the synthetic dyes are classified into sulfur, Anthraquinones, phthalocyanine, triarylmethane, and azo (Regmi, Joshi, Ray, Gyawali, & Pandey, 2018; J. Zhang, Tian, Wang, Xing, & Lei, 2018). Protecting water resources from pollution is crucial since water is one of all living things' most valuable resources and is also thought to be the only source of life (Becerra-Castro et al., 2015). Discharging of the untreated textile effluents into water is one of the major sources of water contamination. Both Organic and inorganic dyes decrease light transmission and prevent aquatic plants from photosynthesis. In addition, several of the dyes are said to be both extremely carcinogenic and poorly biodegradable (Atique Ullah et al., 2017). Currently, water is in

short supply in many cities across the globe. Nearly 40% of the world's food supply is produced, using irrigation systems, and variety of industrial operations rely on water. The quality of surface and groundwater, as well as its regional and seasonal availability, has a significant impact on the environment, economic growth, and development. Human activities have an impact on water quality, which is deteriorating, a result of causes such as population expansion, industrial production, urbanization, and climate change. The ensuing water contamination poses a major threat to both the planet's population and health (Halder, Islam, & human, 2015).

2.2 Methods of wastewater treatment

Many researchers try to find effective and efficient wastewater purification technological methods. Various treatments have been developed for the remediation of polluted water, such as adsorption(Cui et al., 2019), flocculation(Y. He et al., 2018), biological methods(Lakaniemi, Douglas, & Kaksonen, 2019), precipitation(Zeng et al., 2017) and advanced oxidation processes (AOPs) (Dong et al., 2018). These methods can be categorized, into two main groups based on the basic mechanism behind the removal of organic pollutants: Procedures for separation (physicochemical and physical) and methods for degradation (chemical and biological). Physicochemical methods usually exhibit low pollutant removal rates, owing to the pollutant's sludge formation, while the biodegradation techniques are interesting approaches from a sustainable point of view, but impeded by the recalcitrant nature of wastewaters containing antibiotic residues. Physical chemistry, electrochemistry, and biology are the primary areas of these technical approaches and advanced oxidation processes. The conventional processes such as adsorption, coagulation, and membrane separation have hardly achieved a good effect(Yang, Wang, Zhang, Yang, & Song, 2015). Therefore, it is necessary to develop effective methods to treat wastewater. Nowadays, more and more new technologies have been developed to decompose organic pollutants, such as carbon-based catalysts,(Cheng et al., 2017) photocatalysts,(Yanbiao Liu et al., 2016) electrocatalysts (Yanbiao Liu et al., 2014; Yanbiao Liu et al., 2015) and advanced oxidation processes,(Yi Li & Zhang, 2010) which offer attractive alternatives to traditional methods for treating wastewaters containing organic compounds. Among the different advanced oxidation processes, the Layered Double Hydroxides (LDHs) based Photocatalyst have been found to be very

effective in complete mining of organic pollutants (Chaudhury, Mishra, & Shah, 2019; Lakaniemi et al., 2019; C. Li, Wei, Evans, & Duan, 2015; Nichela, Berkovic, Costante, Juliarena, & Einschlag, 2013).

2.2.1 Advanced Oxidation Processes

Advanced oxidation processes (AOP) were first proposed in the 1980 (Glaze, Kang, & Chapin, 1987) with the aim to utilize reactive radicals, specifically hydroxyl radicals ($\text{HO}\cdot$), to oxidize a recalcitrant contaminants in water. Since, $\text{HO}\cdot$ radicals have high redox potential (2.8 eV) and are non-selective. With most substrates hydroxyl radicals have high reaction rate constants in the order of 10^8 - $10^{10} \text{ M}^{-1}\text{s}^{-1}$ along with very short lifetime in water ($10^{-6} - 10^{-9}\text{s}$) (Murcia Mesa et al., 2021). Most organic molecules and hydroxyl radicals interact through four fundamental mechanisms; electron transfer, hydrogen abstraction, radical addition and radical combination. These reactions at double bonds and aromatic systems will start a chain of events that degrades the molecules (Challis, Hanson, Friesen, Wong, & Impacts, 2014). Numerous studies on the use of AOPs in different aqueous matrices to remediate organic contaminants have been undertaken over the past few decades (Guo et al., 2019; Pignatello, Oliveros, MacKay, & technology, 2006; M. Zhang et al., 2019). AOPs techniques include a variety of ozonation-related technologies that have been employed successfully for wastewater treatment during the past few years. Fenton, Sulfate radical oxidations, photocatalysis, electrochemical oxidation, and ultrasound irradiation (Nidheesh, Zhou, & Oturan, 2018). They can be broadly characterized as oxidation techniques based on extremely reactive oxygen species such hydrogen peroxide (H_2O_2), hydroxyl radicals ($\cdot\text{OH}$), and sulfate radicals ($\text{SO}_4\cdot^-$), which offer pathways of the target compounds' breakdown into safe mineralized salts, CO_2 , and H_2O . Since the AOPs have the advantages of fast reaction rates and non-selective oxidation, they can degrade multiple contaminants at the same time (Kanakaraju, Glass, & Oelgemöller, 2018).

2.2.2 Photocatalyst

Photocatalysis is a reaction which accelerated by light energy in the presence of semiconductor materials. Induced light causes the semiconductor to produce electrons and holes for the oxidation and reduction reactions, respectively (Antonopoulou, Kosma,

Albanis, & Konstantinou, 2021). The photo-induced electrons and holes reacted with oxygen (O_2), water (H_2O), and hydroxyl groups to generate reactive oxygen species (ROS) such as hydroxyl radicals ($HO\bullet$) and superoxide radical anions ($O_2^{\bullet-}$) with strong oxidation abilities. These ROS are mostly accountable for the breakdown of persistent organic contaminants in wastewater (Isari, Payan, Fattahi, Jorfi, & Kakavandi, 2018). Depending on their energy band gap, these synthesized semiconductor NPs are activated by light of various wavelengths, such as UV, visible, and near-infrared light (Dreaden, Alkilany, Huang, Murphy, & El-Sayed, 2012). The semiconductor based photocatalysis is a promising technique for the abatement of environmental pollutants, especially for the waste water treatment. Due to its advantages over traditional methods, particularly for the quick oxidation of pollutants without the creation of polycyclic products, it has attracted a lot of interest (Pudukudy & Yaakob, 2016)

2.2.3 Working principle of photocatalysis for water purification

Photocatalysis have similar mechanism with the principles of the photochemical reaction that takes place in semiconductor but with some complexity (Paulos, 2020). The primary role of a photocatalyst is to accelerate particular oxidation and reduction reactions when incident visible light is present. Typically, a photocatalytic reaction takes three steps. Separation of electron-hole pair when the light strikes the catalyst, Charge carrier dispersion on photocatalyst surface and on the catalytic surface-active sites photocatalytic oxidation and reduction takes place. In order to cause the excited electron to jump to the conduction band after being stimulated, the incident light must have greater energy than the catalyst's band gap energy. When photocatalytic materials are exposed to light, they produce holes (h^+) at the VB and electrons (e^-) at the CB. The photogenerated h^+ and e^- can move around on the photocatalyst's surface, triggering the photooxidation and reduction processes. Furthermore, on the surface of the catalysts, the charge carriers react with O_2 and H_2O to spread $O_2^{\bullet-}$ And $HO\bullet$. The increased oxidation and reduction potentials of these radicals cause dye molecules to photo degrade (Dashairya, Sharma, Basu, Saha, & Compounds, 2019). Advanced oxidation process based on photocatalytic production of hydroxyl radical, which acts as strong oxidizing agents, have emerged as a promising technology for the degradation of organic pollutants (Ibhadon & Fitzpatrick, 2013; Namini, Delbari, Mousavi, & Ghasemi, 2021). This process provides an interesting

route for the removal of toxic pollutants, from complete mineralization alternatives to well-established oxidation technologies, including ozonolysis or oxidation with H_2O_2 under ultraviolet(UV) light irradiation. The photocatalyst absorbs light energy and produces photogenerated electrons which in term reduce adsorbed oxygen (O_2) to form superoxide radicals and photo generated holes react with H_2O to form hydroxyl radicals. The superoxide radicals can also generate hydroxyl radicals by reacting with hydrogen peroxide. The generated hydroxyl radicals subsequently oxidize the pollutants resulting in mineralization and complete degradation; these pollutants are broken down into smaller molecules such as CO_2 , H_2O and mineral acids, which are not particularly toxic. Electrons in the metal particles absorbing light with energies exceeding the band bending potential can transit to CB of n-type semiconductor. After electrons in the metal particle flow to CB of the semiconductor particle, the metal particle is oxidized from M^0 to M^+ . The n-type semiconductors can indirectly respond to visible light from the surface Plasmon resonance of the metal. As shown in Figure 1 the photo generated electrons are allowed to transfer to the metal particles to produce reduction processes, while more holes can transfer to n-type semiconductor surface to produce oxidation processes.

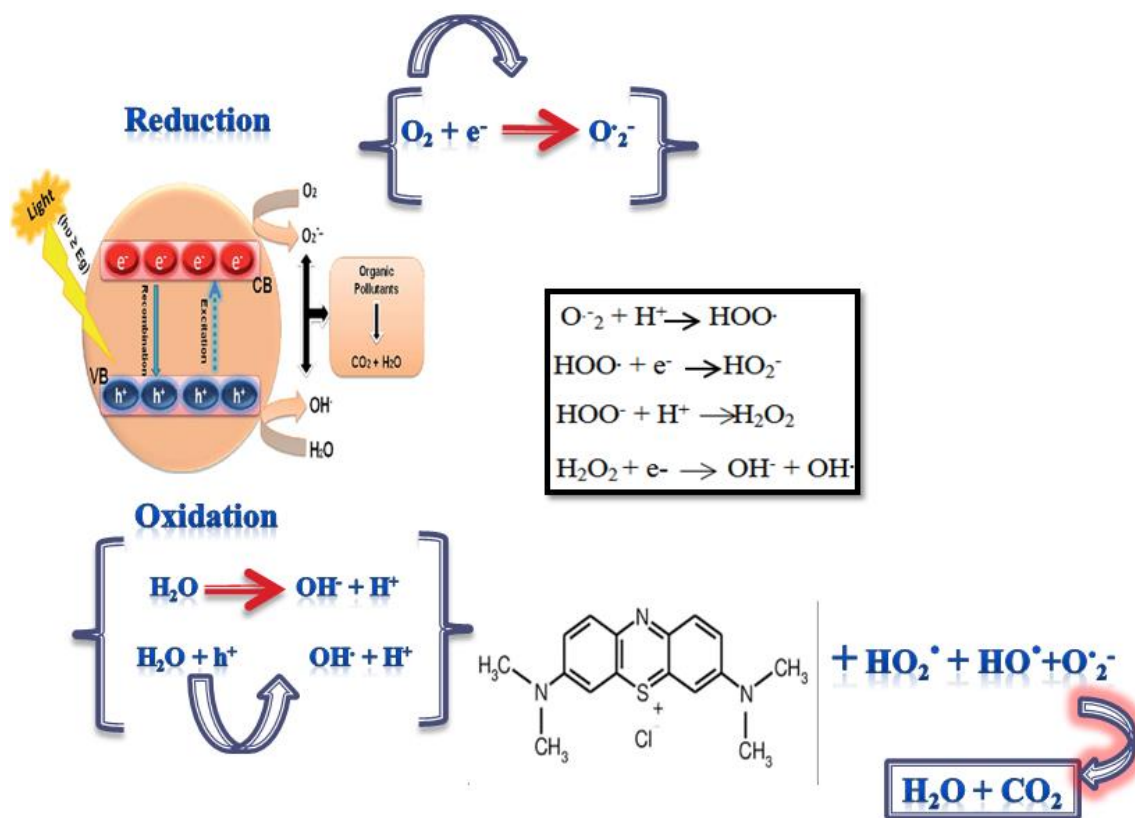


Figure 1. Photocatalyst working principle of metal oxide semiconductor (Ibhadon & Fitzpatrick, 2013).

2.3 Metal Oxides Nanoparticles (MOs)

Metal oxide semiconductor-based catalysts are an effective means of enhancing dispersion and efficiency (J. Pandey et al., 2017; Petitjean, Gagne, Beach, Xiao, & Anastas, 2016). For example, TiO₂ nanomaterials have been created as photocatalysts; additional nanomaterials utilized in photocatalytic processes include ZnO, Co₃O₄, SnO₂, WO₃, Fe₂O₃, and Mn₃O₄ (Hou et al., 2016; Ren et al., 2016; Rizal, Saleh, Prakoso, Taufik, & Yin, 2021; Tian et al., 2014; Tian et al., 2017; W. Wu, Jiang, & Roy, 2015). A wide range of metal oxide semiconductors may be used for photocatalysis, such as TiO₂, ZnO, MgO, WO₃, MnO₂, Fe₂O₃, SnO₂, Mn₃O₄ and NbO₂ had been used for water treatment under UV and visible light irradiation (Mano et al., 2015; Ren et al., 2016). Numerous aspects that affect the optical, electrical, chemical, and catalytic properties of metal oxides include their crystal structure, morphology, composition, intrinsic defects, doping, and other elements. In order to purify water, several chemical processes have developed, including chemical

oxidation, solvent extraction, catalytic degradation, etc. These, meanwhile, limit their practical utility because they take a lot of time and money. Nanotechnology is one possible method for providing a comprehensive remediation, focusing on the special properties of materials that emerge from nanoscale dimensions and guarantee the cleaning of water sources. This is made feasible by photocatalysis, a property of semiconducting oxides, or more specifically, transition metal oxides (TMO), which absorb photons to perform redox processes and break complex organic molecules into smaller species (Ullah & Dutta, 2008). When charged carriers (e/h^+) diffuse from the bulk to the surface with nanoparticles, their rate of migration is greatly accelerated, increasing the photoactivity. TMOs have been widely researched in photocatalytic applications for water remediation, including titanium dioxide (TiO_2), zinc oxide (ZnO), iron oxide (Fe_2O_3), and magnesium oxide (MgO) (Danish et al., 2021; Gautam et al., 2020). TiO_2 is the most frequently used of them all because to its photochemical stability, chemical inertness, and ecologically friendly properties (Junren Zhu & Jiang, 2021). Additionally, ZnO , a competitor, has superior electron mobility. The wide band gap prevents them from being used in photocatalytic degradation (UV light driven), despite the fact that they exhibit good characteristics. Therefore, band gap modification is necessary to increase photo degradation efficiency; this topic will be covered in more detail in the section (Sukri, Shameli, Isa, & Ismail, 2021). Now a day, Manganese dioxides have attracted intensive interest because of their low cost, environmental compatibility and abundant availability (Gong, Yu, Su, Xiong, & Mao, 2007; Z. Liu, Xing, Chen, Zhao, & Suib, 2008). Due to the existing unique layers or tunnels in lattices and high specific surface areas, manganese oxides have been widely investigated and extensively used in adsorption processes (Ruixue Chen, Yu, & Xiao, 2013). In addition, the modification of other adsorbents with Mn_3O_4 would actually improve their adsorption properties. Currently, Photocatalytic dye degradation is used in nanotechnology-based water purification; with a primary focus on three key aspects for effective operations are visible light-driven photocatalyst, high adsorption capacity, and large electron/hole recombination lifetimes. It has taken a lot of work to redshift the band gaps of transition metal oxides toward visible light-driven photocatalysis because of their wideband gaps. The rapid electron/hole pair recombination caused by the greater band gap further hinders the photocatalytic activity.

This might occur because of the present adsorbent's limited capacity for adsorption, creating a substantial bottleneck for dye mineralization. (S. Ahmed et al., 2011; Thiruvengkatachari, Vigneswaran, & Moon, 2008). In order to achieve the above-mentioned goals, two approaches are typically employed which are the doping of existing transition metal oxides with foreign transition metal ion to tune the band gap and hence, altering the optical absorption of the resulting nanocomposite. Introduction of foreign transition metal ions results in formation of spinel or mixed bimetallic transition metal oxides. Furthermore, co-adsorbents serve the purpose to enhance the adsorption capacity with larger electron/hole recombination lifetime. High adsorption capacity is achieved by the co-adsorbent, which will facilitate the charge transfer processes resulting in higher efficiency. In addition to the extensive body of literature compiled by the researchers, here we provide a succinct overview of the study on effective photo dye degradation using composites based on transition metal oxides, as well as the most recent trend towards photocatalytic studies. The ideal photocatalyst should process the following properties (i) photoactivity, (ii) biological and chemical inertness, (iii) stability toward photocorrosion, (v) suitability towards visible or near UV light, (vi) low cost, and (vi) lack of toxicity (Bhatkhande, Pangarkar, Beenackers, *Biotechnology: International Research in Process, & Technology*, 2002). According to studies, metal oxide nanoparticles mineralize poisonous inorganic substrates into less dangerous carbon dioxide and water as well as toxic organic contaminants into easily degradable molecules (Cao, Gong, Shu, Zhu, & Liang, 2019). Semiconducting metal oxides are the most commonly used photocatalyst but the application of mono-metal oxide is limited in practice because of their limitations such as wide and non-tunable band gap, low surface area, fast recombination rate of electron-hole pair, low charge transfer ability, and agglomeration. Mixed metal oxide (MMO) is a family of semiconducting metal oxides that combine advantages of individual constituents with enhanced photocatalytic property (Jian Yao Zhu et al., 2016). MMO prepared from LDHs have received significant attention because of their potential for photocatalysis (S. Xia, Shao, Zhou, Pan, & Ni, 2015; Yuan, Li, Zhang, & Wang, 2009).

2.4 Manganese Oxides (Mn_3O_4)

Mn is more eco-friendly and abundant on Earth than other transition metals (Safdar, Minh, Kinnunen, Jänis, & interfaces, 2016). Yet, due to Mn's various oxidation states, the required

electron transfer can be facilitated (Saputra et al., 2013). Trimanganese tetra oxide (Mn_3O_4) is a Mn oxide mixture that contains both divalent and trivalent Mn (Reddy & DeLaune, 2008). When compared to bulk materials, the qualities of micro- and nano-scale transition metal oxides often depend on their size, structure, and morphology and have a variety of unique physical and chemical functional properties (Yong Li & Shen, 2014). The Hausmannite crystal structure of Mn_3O_4 nanostructure has attracted the interest of researchers because to its low cost, optical, electrical, and magnetic capabilities (J. Gao, Lowe, & Abruna, 2011). It's also commonly utilized in catalysis, electrochemical reactions, soft magnetic materials, and battery applications. Hausmannite-phase Mn_3O_4 nanoparticles have been used in wastewater treatment (Govindan et al., 2017; Ma et al., 2019; Yosefi & Haghighi, 2019) and are thought to be a stable oxide (Duan et al., 2016; Xu, Le Xu, Li, Wang, & Yan, 2006). As one of the most stable manganese oxides, Mn_3O_4 possesses tetragonal hausmannite phase with octahedral and tetrahedral sites of its spinel structure. Mn_3O_4 exhibits a variety of applications in the catalytic decomposition of carcinogenic form, energy storage (Kumar et al., 2020), hydrogen storage (Kumar et al., 2015), supercapacitor, and oxy-dehydrogenation of alcohols (Yesuraj et al., 2022). Mn_3O_4 is a promising semiconductor material for photocatalytic uses, such as the photodegradation of organic contaminants. The formation of Mn_3O_4 compound in the alkaline aqueous solution may be formulated by the following reactions:



Manganese ions are firstly reduced in alkaline media to $\text{Mn}(\text{OH})_2$ and then decomposed into MnO (see 2) and (3). Finally, MnO is oxidized to Mn_3O_4 by the atmospheric oxygen (Dhaouadi, Ghodbane, Hosni, & Touati, 2012). The utilization of Mn_3O_4 nanoparticles for this purpose is not without its downsides, though. The poor stability of Mn_3O_4 nanoparticles under visible light irradiation is a significant disadvantage. According to several studies, visible light exposure causes Mn_3O_4 particles to change structurally and form MnOOH , which reduces the photocatalytic activity (Liew, Shi, & Li, 2011). Another

drawback is Mn_3O_4 's comparatively poor photocatalytic activity when exposed to visible light compared to other widely used photocatalysts like TiO_2 and ZnO (S. Wang et al., 2017). Additionally, it might be difficult and requires reaction condition optimization to create Mn_3O_4 nanoparticles using conventional techniques like sol-gel and hydrothermal synthesis.

2.4.1 Synthesis Method of Manganese oxide Nanoparticles

In general, there are two basic categories of nanoparticle synthesis methods. These are “top-down” and “bottom up” methods. The bottom-up approach is one where smaller components of atomic or molecular dimensions self-assemble together, according to a natural physical principle or an externally applied driving force, to give rise to larger and more organized systems, Whereas the top-down approach is a process starts from a large piece and subsequently uses finer and finer tools for creating correspondingly smaller structures(Arole & Munde, 2014). Researchers used multiple techniques to synthesized Mn_3O_4 NPs in varied shapes. Numerous techniques, including hydrothermal, co-precipitation, solid state reaction, sol-gel process, thermal breakdown, two-phase hydrolysis approach, and others, have recently been developed to create Mn_3O_4 nanostructures. Co-precipitation method also the best method to synthesize different metal oxide nanoparticles, due to several advantages than the other methods, such low cost, easily control the morphology, easy of synthesis and easily control the parameters. The general synthesis methods of nanoparticles are shown in Figure 2.

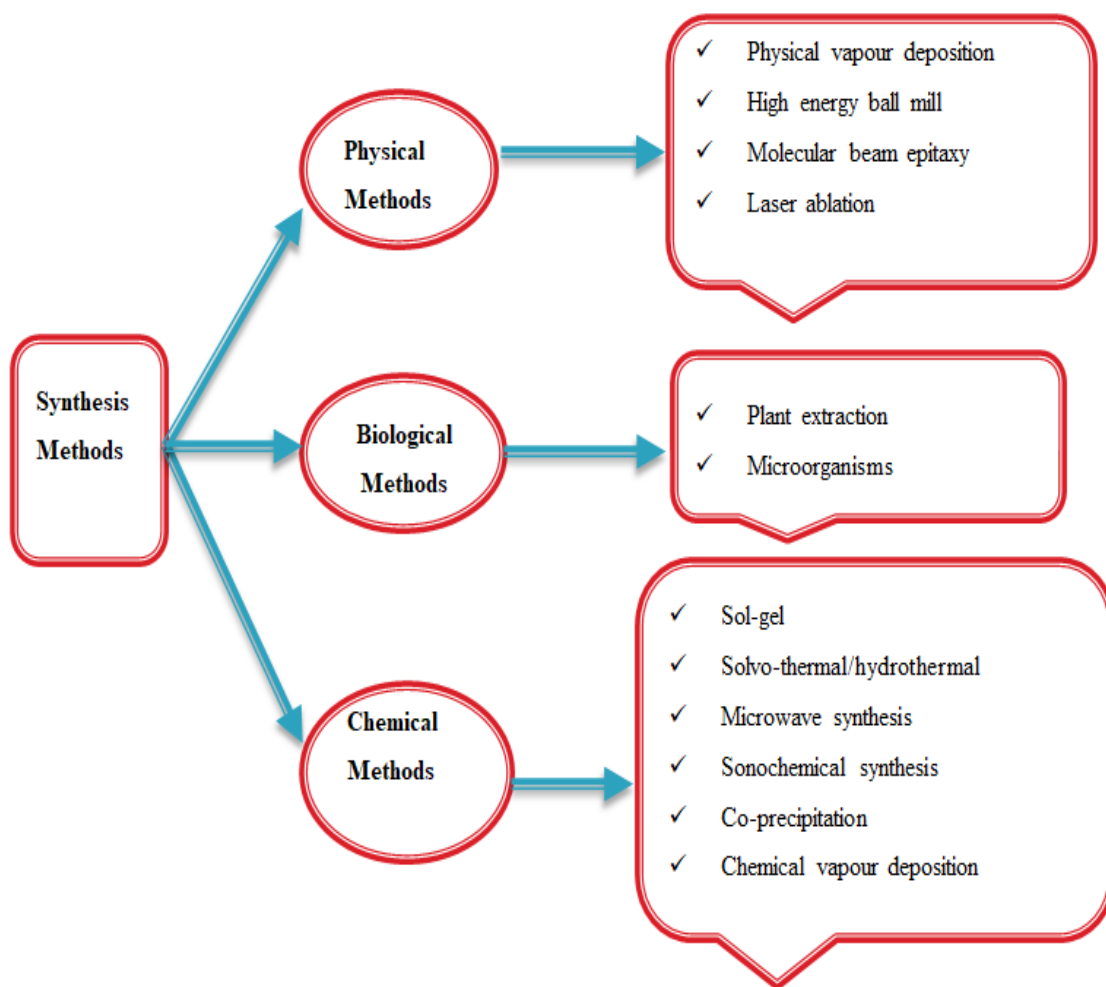


Figure 2. Methods for synthesizing nanoparticles (A. K. Pandey, Kumar, Maurya, & Singh, 2015).

2.4.2 Improvement of Photocatalyst Efficiency of Mn_3O_4 Nanoparticle

Photocatalysis has become promising technology since it applying abundant solar light for the aim of environment protection (degradation of organic pollutants) and energy production (production, reduction)(Haitosa et al., 2022). Numerous studies, in particular, have demonstrated Mn_3O_4 NPs efficiency as a photocatalyst for the breakdown of organic contaminants. Manganese oxide (Mn_3O_4) is a promising photocatalyst material with various applications in the field of water treatment, energy conversion, and environmental remediation. Here are some methods to improve the photocatalytic activity of Mn_3O_4 nanoparticles: Doping: To increase the photocatalytic activity of Mn_3O_4 nanoparticles, other elements such as thallium (Sheikhshoaie, Ramezanpour, & Khatamian, 2017), Cobalt

(Yoshinaga et al., 2018), and vanadium (S. Ramezanpour, I. Sheikhshoae, & M. Khatamian, 2017) can be doped into them. Doping can alter the electrical characteristics of nanoparticles, improve light absorption, and lower electron-hole pair recombination. Surface alterations: Graphene, silica, and titanium dioxide can all be used to coat Mn_3O_4 nanoparticles to change their surface properties (Yao, Xu, Yu, Zhang, & Wang, 2013). This could increase their photocatalytic activity, stabilize them better, and stop them from aggregating. The size of Mn nanoparticles has a significant impact on their capacity for photocatalysis. Smaller nanoparticles can absorb more light and produce more reactive species because they have a bigger surface area. Therefore, regulating the nanoparticles' size can enhance their photocatalytic activity. For instance, *Chen et al.'s (2017)* research discovered that Mn_3O_4 nanoparticles have strong photocatalytic activity toward the breakdown of organic dyes when exposed to visible light. According to a different study by *Zhang et al. (2019)*, Mn_3O_4 increases the photocatalytic degradation of tetracycline by lowering electron-hole recombination and enhancing the separation of photo-induced electron-hole pairs. Mn_3O_4 has also been researched for use in producing hydrogen and splitting water, among other things. Mn_3O_4 has been suggested as a viable photocatalyst because of its special qualities and encouraging outcomes observed in numerous investigations for various applications. Moreover, it has been noted that Mn_3O_4 nanoparticles' oxidation activity is greatly increased when mixed with noble metal nanoparticles, such as Ag and Pd (Ma et al., 2019; S. Ramezanpour, I. Sheikhshoae, & M. J. o. M. L. Khatamian, 2017), as noble metals can reduce the rate at which photogenerated electrons and holes recombine.

2.5 Removal of Organic Dyes by Supported Mn_3O_4 NPs

Mn_3O_4 NPs have vast range of applications are constrained by its facile aggregation and poor specific surface area throughout the preparation process. Various strategies need to be devised to increase the surface-active sites of the catalysts in order to improve their catalytic activity, such as decreasing particle size or creating mesoporous structures (Runqi Chen et al., 2022). Controlling the crystallinity of manganese oxide on supports is thus becoming more and more necessary now a day. Such as graphene, zeolites, can be considered effective and appropriate supports for the aforementioned purposes. Mn_3O_4 -based composites made of graphene oxide, zeolite, and a three-component composite of

Mn₃O₄/GO/Clin were successfully prepared with the aim of enhancing the photocatalytic activity of Mn nanoparticles were described by *Osgouesi, Khatamain and Kakili*. The hydrothermal method was used to prepared Mn₃O₄/GO nanocomposites (NC's) with different ratios of Mn₃O₄ nanoparticles (NP's) on the surface of graphene oxide (GO) sheet was described by *T. Imboon, J. Khumphon, K. Yotkuna, I.-M. Tang, and S. Thongmee*(Imboon et al., 2021). When Mn₃O₄ NPs were decorated with GO sheets, their photo-catalytic activity was increased, and the Mn₃O₄/GO NCs had the highest photo-catalytic activity as shown in Figure 3.

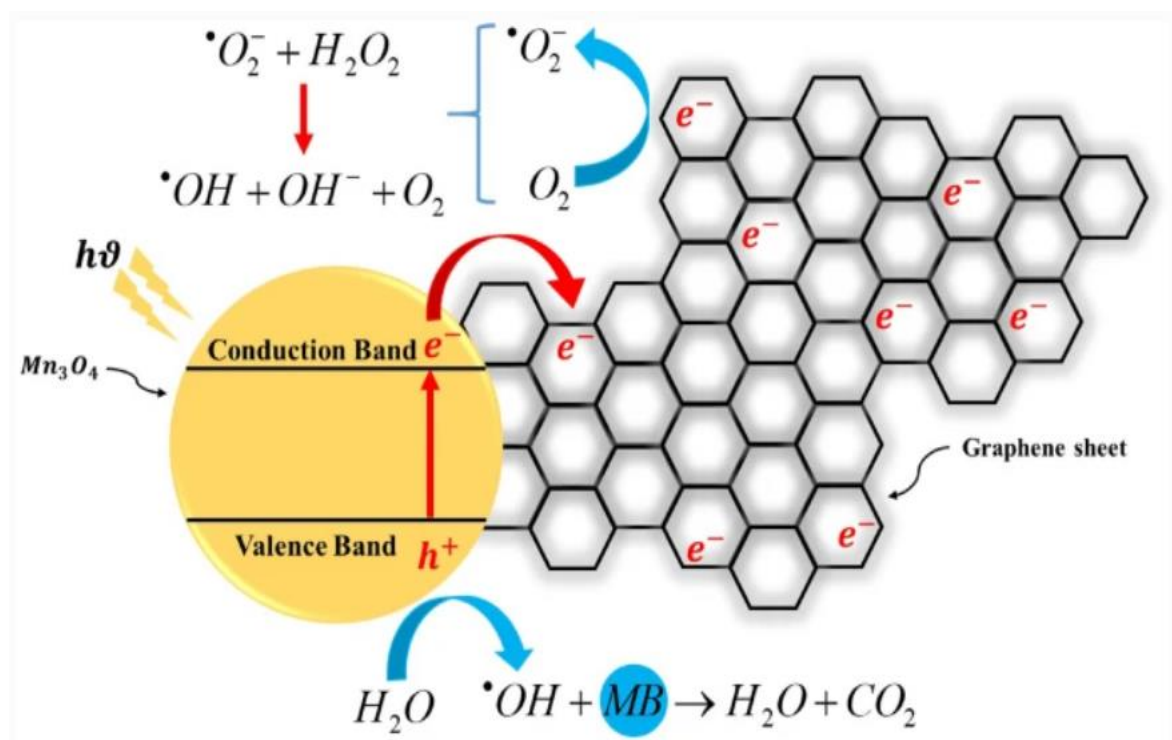


Figure 3. Schematic representation of Mn₃O₄/GO nanocomposite for photocatalyst activity (Imboon et al., 2021).

Table 1 Review on the performance of supported Mn₃O₄ NPs.

Catalyst	Dye	Time (min)	Efficiency	Application	Reference
Mn ₃ O ₄ /ZIF-8	Rhodamine B	120	78	catalytic	Hu, Deng, Lu, Lu, & Zhang, 2017)
Mn ₃ O ₄ @CNNS	4-CP	120	80	Catalytic	C. Chen et al., 2020)
Mn ₃ O ₄ /ZnO/ Eu ₂ O ₃	MO	150	71	Photocatalyst	(Shubha et al., 2021)
Mn ₃ O ₄ /GO	MO	240	95	Photocatalyst	(Osgouei, Khatamian, Kakili, & Physics, 2020)
Mn ₃ O ₄ @GO	MB	120	60	Photocatalyst	Imboon et al., 2021)
PMS@Mn ₃ O ₄ / MnO ₂	ciprofloxacin	120	96.7	Catalytic	Stegarescu et al., 2020)
MgAl ₂ O ₄ /CeO ₂ / Mn ₃ O ₄	MB	180	94.6	Photocatalyst	(J. Li et al., 2021)
BiOCl/Mn ₃ O ₄	Acid orange	120	52	Photodegradation	L. Yosefi, M. Haghighi, Mater. Res. Bull. 113, 51 (2019)

2.6 Layered Double Hydroxides (LDHs)

Several techniques for removing toxic colorants from wastewater have been widely reported in the literature, including adsorption, chemical oxidation, membrane technology, coagulation, photocatalytic degradation, and aerobic and anaerobic microbial degradation (Hague, Petroczi, Andrews, Barker, & Naughton, 2008). Among these processes, photocatalytic degradation is considered to be the most effective technique for the removal of dyes, because of their simple design, high efficiency, easy handling, and low cost (F. Liu, Chung, Oh, Seo, & interfaces, 2012; Long, Yu, Jiao, & Yang, 2016). Although various natural and synthetic materials, such as activated carbon, graphene, carbon nanotubes, zeolites, polymers, and LDHs used as adsorbents for dyes removal.

Among these, LDHs are favored due to their low cost, high stability, flexible interlayer space, large surface area, low toxicity, memory effect, reusability, and facile synthesis (Aragaw et al., 2022b). Inorganic layered materials at the nanoscale have garnered significant interest in the applications of new nanocomposites in recent years, (Crepaldi, Pavan, & Valim, 2000; Itaya, Chang, & Uchida, 1987; N. Li et al., 2017) ion exchangers, (Millange, Walton, Lei, & O'Hare, 2000; Zubair, Daud, McKay, Shehzad, & Al-Harthi, 2017) photochemistry, (Q. He, Yin, Sato, & Solids, 2004) and catalysis (Bizeto, Shiguihara, & Constantino, 2009; C. Zhang et al., 2016). LDHs known as anionic clays, are one of the most thoroughly studied layered materials (Cavani, Trifiro, & Vaccari, 1991). Positively charged metallic layers and interlayer anions and water comprise LDHs. The general formula of LDHs is $[M^{2+}_{1-x} M^{3+}_x (OH)_2]^{x+} [A^{q-}_{x/p}]_x \cdot mH_2O$ (Figure 4), also called hydrotalcite clay since they are derived from the natural available mineral, $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$. Where M^{2+} and M^{3+} are metallic bivalent cation and metallic trivalent cation, respectively, and A^{q-} is interlayer anion like CO_3^{2-} , NO_3^- , and Cl^- which are charge balancing anions (L. Zhang, Xiong, & Zhao, 2015). $X = M^{3+} / (M^{2+} + M^{3+})$ is molar fraction determined by the ratio of the two metal cations, which is subject to change for various applications. The values of x vary between 0.22 and 0.33 (Sajid, Jillani, Baig, & Alhooshani, 2022; Yu, Wang, O'Hare, & Sun, 2017). LDHs itself can perform as catalyst, as precursor for other catalysts and as catalyst support for various applications. It shows a layered arrangement containing anions on its interior part as shown in Figure 4. The layered structure is preserved by an existed water and hydroxyl anions on the inter layer. LDHs can be used as photocatalysts for the oxidation of organic pollutants because, when exposed to ideal wavelength range light, their valence electrons are stimulated into the conductive band and produce electron-hole pairs. LDHs could be an effective carrier for other high-performance catalysts because of the structure's abundance of water molecules and hydroxyl ions, which are necessary to produce $\bullet OH$ radicals during photocatalytic oxidation (Fu, Zheng, Zhou, Ni, & Xia, 2019).

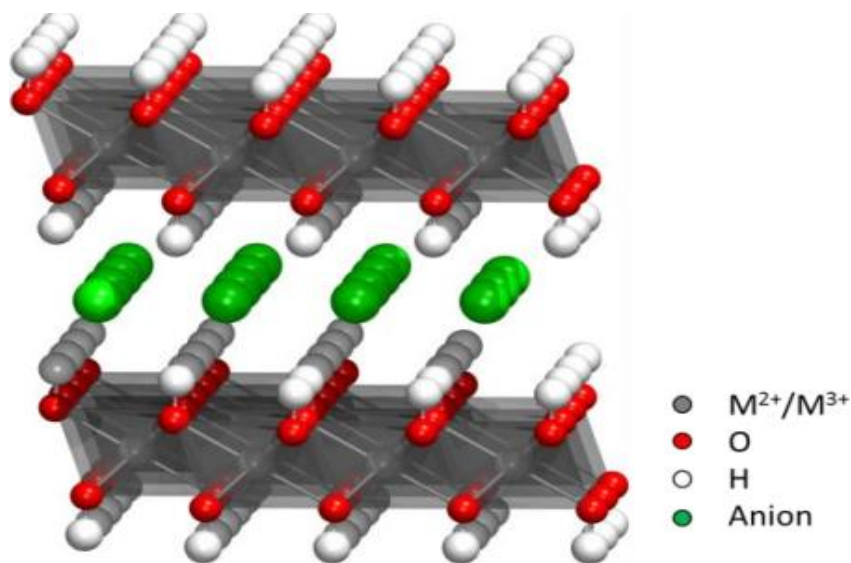


Figure 4. Structure of layered double hydroxide(LDHs) (Yu et al., 2017).

Numerous studies on LDH catalysts for various applications have been published (N. S. Ahmed et al., 2017; Aragaw et al., 2022c; Peng et al., 2018; F. Zhao et al., 2019). Here are several LDH-based works that has been reported for various applications. Synthesis of biodiesel using MgAl-LDHs was reported by Hsu *et al.* (Hsu, Wu, & Nguyen, 2019). Jia *et al.* (Jia et al., 2018) also summarized the amine functionalized MgAl-LDH nanosheets for Knoevenagel condensation. Another highly crystalline CuAl-LDH was reported by Li *et al.* for methyl orange degradation through Fenton reaction(J. Li et al., 2017). However, their findings indicated poorer reusability because of the hydrogen peroxide's inability to make contact with the active sites and the adsorption of pollutant intermediates to the surface. A mixed matrix membrane based on incorporating exfoliated Mg–Al–Fe LDH layers into polyethersulfone was synthesized by a phase inversion approach and utilized for the adsorptive removal of phosphate and fluoride ions from water by Jia *et al.* (H. Chen et al., 2018). Cu-Mg-Al May photocatalytically convert CO₂ to methanol with Cu²⁺ as an active site, which can considerably enhance CO₂ adsorption and photocatalytic conversion, according to Wang *et al.*

2.6.1 Synthesizing Methods of Layered Double Hydroxides (LDHs)

LDHs can be synthesized in different ways. Co-precipitation, microwave light technology, ion exchange procedure, and urea technique are a few examples of the preparation of LDHs (F. Wu, Liang, Peng, & Liu, 2014). Among them co-precipitation technique mostly used due to easy to synthesize, cost effective, and easy control the particle size.

2.6.2 Co-precipitation Method

The co-precipitation technique is the easiest and most regularly utilized of all techniques for the synthesis of LDHs. Co-precipitation method typically, a blended solution of two different metal salts in distilled water is added drop wise over hours to an aqueous solution contains organic particles with vigorous mixing. The pH can be adjusted by NaOH to accelerate co-precipitation reaction. Then precipitate, aged at room temperature for 24 hours, is centrifuged out, washed with distilled water completely and finally dried in oven as shown in Figure 5. Biomolecules LDH hybrids can be set up by ion exchanging interlayer anion of LDH with biomolecules(G. George & Saravanakumar, 2017). An aqueous mixed metal salt solution (anionic solution) and alkaline solution (cationic solution) are blended and aged to synthesis the Layered Double Hydroxide.

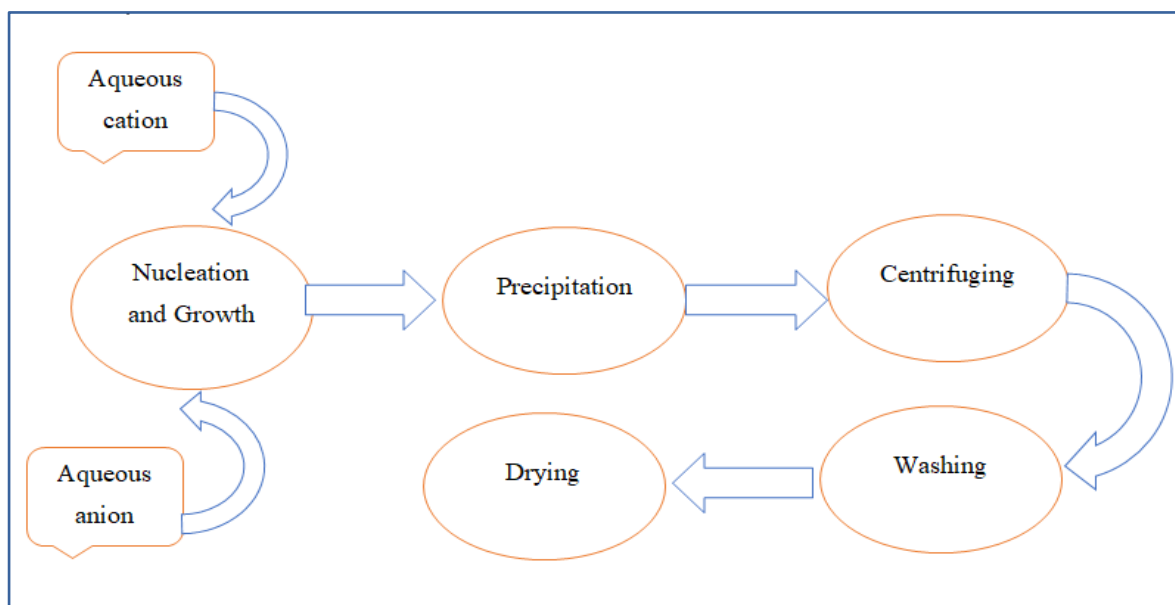


Figure 5. Flowchart of the Experimental Procedure of the Co-Precipitation Method(G. George & Saravanakumar, 2017).

2.6.3 Removal Efficiency of Layer Double Hydroxides (LDHs) as Support

LDH based material is known for the removal of pollutant from wastewater. However, LDH materials alone are insufficient for pollutant removal because to their considerably poorer charge transfer efficiency and higher photo-generated electron and hole-pair recombination rate (Z. Gao et al., 2021). As a result, combining LDH with other materials such as oxide, and sulfide semiconductors ((Ahamed, Akhtar, Alhadlaq, & Health, 2019; Pazoki, Shamsayei, Bagheri, Yazdani, & Heydari, 2020), metals (Lestari et al. 2021), and MOFs (Soltani, Pelalak, Pishnamazi, Marjani, & Shirazian, 2021) is crucial. For several applications, combining of LDH and metal oxides was employed. Primarily, such blending aids in the extension of the light absorption spectrum as well as the suppression of photogenerated carrier recombination. Recently, a new Ni-Fe LDH/ZnO composite for the degradation of Rhodamine B dye under light was created (J. Wu, Gong, Fu, & Pan, 2019). Mustafa et al. demonstrated Ni-Fe LDH/ZnO nanostructures for water splitting in addition to dye degradation (Mustafa et al., 2019). Xia et al. effectively synthesized $\text{SnO}_2/\text{ZnAl-LDH}$ and $\text{CeO}_2/\text{ZnAl-LDH}$ and their photocatalytic efficacy for 4-CP degradation from wastewater was evaluated (G. Xia et al., 2022). $\text{NiAl-LDH}/\text{MnO}_2$ and $\text{NiFe-LDH}/\text{MnO}_2$ composites were also created by Zheng et al. for high-performance asymmetric supercapacitors. It has been synthesized by loading of MnO_2 on LDH nanosheets with the aid of redox reaction. ZnAl-LDH with active phase/g- C_3N_4 high dispersion of the active phase in LDH with high energy conversion efficiency in the layered matrix, which might encourage the separation of photoinduced electrons and holes, was regarded as the cause of the enhancement in photocatalytic performance (X. Li et al., 2020). Similar to this, visible light area absorption has been extended using CeO_2 . Even if there are several types of CeO_2 employed for VI-active photocatalysis, CeO_2 still requires a support for greater stability and charge suppression recombination. Taking this concept into consideration, Nayak et al. demonstrated a visible light-induced $\text{CeO}_2/\text{MgAl-LDH}$ for the reduction of water, as shown schematically in Figure 6. It had been optimized by adjusting the $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ dosage. They discovered, namely, that 5 wt% CeO_2 displays more active photocatalysis. The smaller size of CeO_2 nanorods at 5 weight percent enables for uniformly distributed and produces a large surface area. CeO_2 also plays a role by reducing diffusion path for charge carriers and makes easy transfer of surface charge to the

surface of MgAl-LDH. Excessive CeO_2 may not bring enhanced activity due to shielding effect, agglomeration of CeO_2 nanorods and reduction of interfacial area. Consequently, active sites wrapped in response to excessive CeO_2 so that H_2 production level gets minimum.

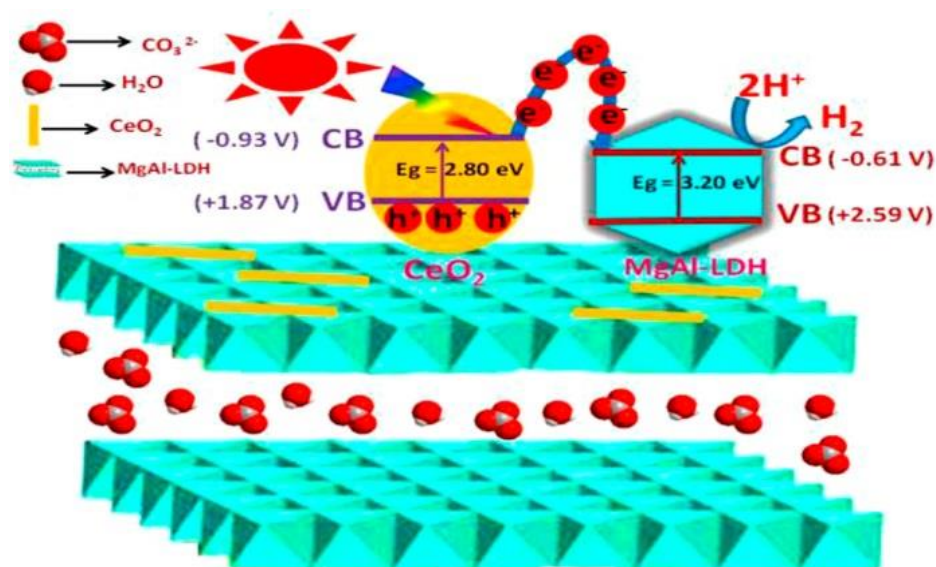


Figure 6 Graphical abstract of $\text{CeO}_2/\text{MgAl-LDH}$ composite (Nayak & Parida, 2016).

The tabulated works below are LDH-based reports for various activities that produced better results than the pristine material brought as reviewed in the table 2.

Table 2 LDH-supported nanoparticle applications.

LDHs	Working Mechanism	Pollutant	Activity	References
CeO ₂ /ZnAl-LDH	Photocatalytic degradation	4-CP	Degradation efficiency of 82.4%	(G. Xia et al., 2022)
Starch-NiFe-LDH	Adsorption	MO	Maximum removal of 90%	(Zubair et al., 2018)
Cu ₂ O/Mg-Al LDH	Photodegradation	MB	86.2 % of MB is degraded	(Y. Zhou, Hu, Yu, Jiao, & Catalysis, 2015)
Fe ₃ O ₄ /Zn-Cr LDH	Photodegradation	MB, MO	Adsorbed 528 mg/g of (MO) and decomposed ~95% of MB	(J. Q. Wang et al., 2012)
MgO ₂ /CuAl-LDH	Degradation, under dark condition	MO	69% of MO, was degraded within 100 min	(Aragaw et al., 2022b)
CeO ₂ -MgAl-LDH	Photodegradation	Phenol	Degrade~96% of 100ppm of 4-cp in 5hr	(Valente, Tzompantzi, & Prince, 2011)
Cu ₂ O/ZnAl-LDO	Photodegradation	MO	90.18% under visible light	(X. Wu et al., 2016)
Nb ₂ O ₅ -ZnAl-LDH	Photodegradation	CR	85% degrade under visible light	(Huang et al., 2016)
SnO ₂ /ZnAl-LDH	Photocatalytic degradation	4-CP	Degradation efficiency of 95.2%	(G. Xia et al., 2022)

These NPs' high surface area and catalytic activity can be held in place by the proper supports, which can stabilize them more successfully. Layered double hydroxide (LDH) is one of the most commonly used and has significance for gardening because of its intercalation capabilities. Support from LDHs would enable further size reduction of NPs, preventing NP aggregation (Arora, Mehta, Mishra, & Basu, 2018).

2.7 Research Gap

As a result of the literature review, various works and their limitations (such as fast recombination rates of photogenerated electron-hole pairs, lower specific surface area, charge density, and instability (Imboon et al., 2021) as well as agglomeration (Lett et al., 2023) (Gao et al., 2018) were discussed. However, no research has been conducted on (Mn₃O₄/ZnAl-LDH) nanocomposite for dye degradation. Furthermore, (Mn₃O₄/ZnAl-LDH) catalyst was synthesized by in-situ growth method. The synthesized sample was characterized by different techniques, and the degradation efficiency of the organic dye molecule was evaluated. Finally, the catalytic dosage, dye concentration, and reusability of the synthesized catalysts were evaluated.

CAPTER THREE

3. Materials and Methods

3.1 Chemicals and Materials

All of the chemical reagents were of analytic grade: Manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), (95 % purity) was purchased from LOBA CHEMIE PVT.LTD (India), Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Loba Chem 98 % purity, India), Aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) (98% purity) and Sodium carbonate (NaCO_3) (99.5% purity) were purchased from Alpha Chemika (India). Ethanol ($\text{C}_2\text{H}_5\text{OH}$) (98 % purity), Methylene blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$) (Carelabmed Chem, India), NaOH (97 %, Mumbai, India) and distilled water (DW) was used throughout the experiment.

3.2 Methods

3.3 Synthesis of Mn_3O_4 nanoparticle

Mn_3O_4 was prepared as the reported with little modification (Van Tran et al., 2022b). In the specific procedure, 100 ml of distilled water were used to dissolve 0.3 M (100 ml) of manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) for 30 minutes, and then 0.1M of NaOH was used to maintain the pH at 10 while being continuously stirred for two hours at 60 °C. The solution was aged for 10 hours and the precipitate repeatedly rinsed with distilled water, centrifuged for 10 minutes at 1200 rpm, and then dried in an oven at 100 °C. The powder was annealed for three hours at 500 °C in an open furnace. Figure 7 shows the schematics for the preparation of Mn_3O_4 nanoparticles.

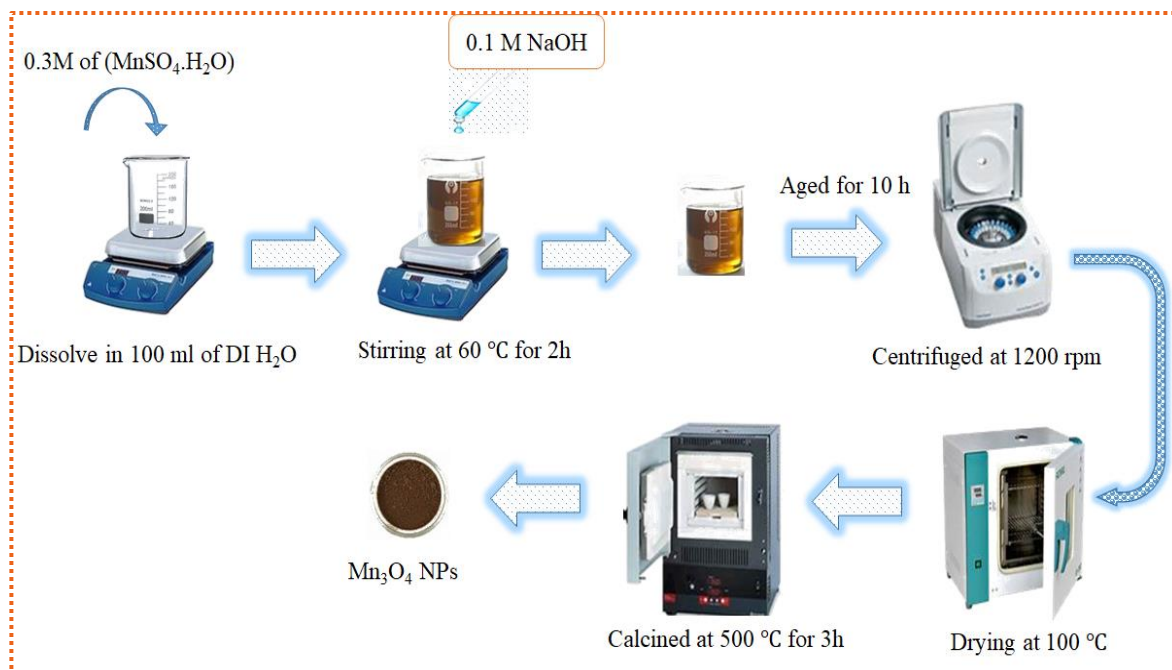


Figure 7. Schematics representation for preparation of Mn_3O_4 nanoparticles.

3.4 Synthesis of ZnAl-LDH

ZnAl-LDH was synthesized by a reported method with modifications (G. Xia et al., 2022). Solution A: an aqueous solution containing 0.018 M of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.006 M of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, with a molar ratio of Zn to Al of 3:1. Solution B: 0.2 M NaOH and 0.4 M Na_2CO_3 was added to 100 ml of deionized water and completely dissolved. Solutions A and B were dropped dropwise into 50 ml of deionized water while stirring, and the pH was kept at 9.5. The solution was stirred for another 30 minutes before being aged at 60 °C for 24 hours. The resulting product was centrifuged, neutralized, and dried at 80 °C until the powder was formed. The sample was then ground and labeled as ZnAl-LDH. Figure 8 shows the schematics for the preparation of ZnAl-LDH.

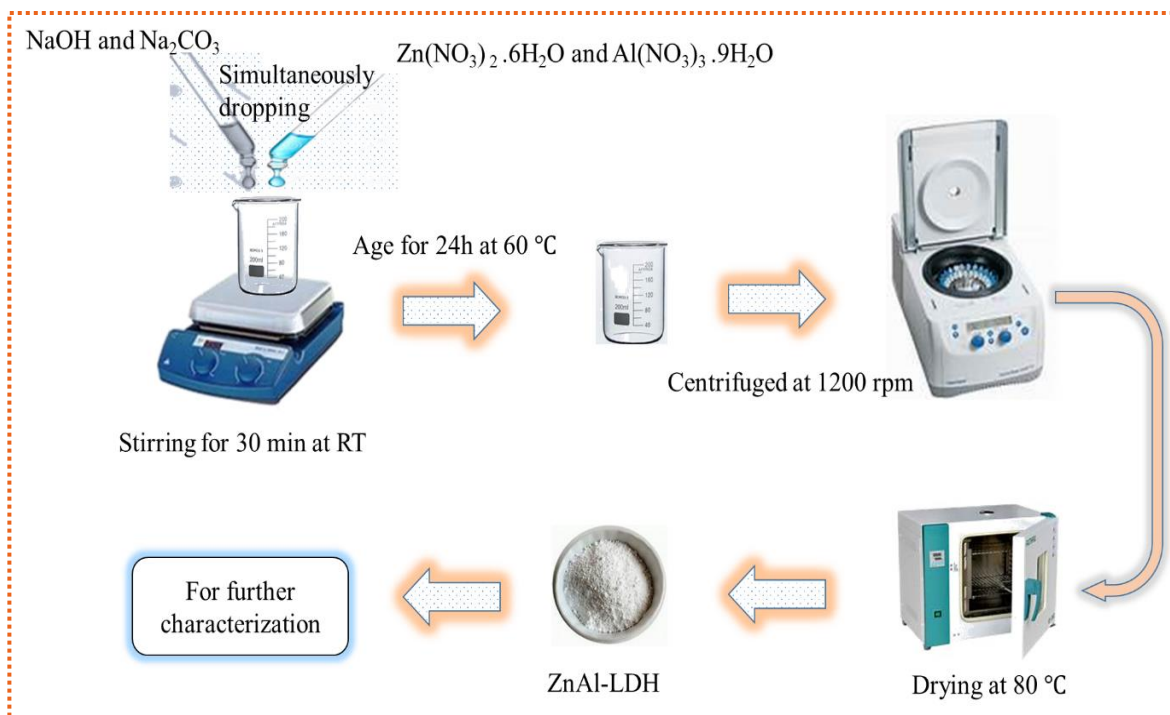


Figure 8. Schematics representation for preparation of ZnAl-LDH.

3.5 Synthesis of ZnAl-LDH/ Mn_3O_4 Composites

ZnAl-LDH/ Mn_3O_4 composite was prepared by a reported in-situ growth method with a little modifications (Aragaw et al., 2022a). 0.5 g, 0.6 g, and 0.7 g of ZnAl-LDH were added to three different beakers containing 100 ml of distilled water. The measured amounts were dispersed in an ultra-sonicator at room temperature for 1 hour to form a homogeneous suspension of 5, 6, and 7 mg/ml. Then, 1.33 g, 1.1 g, and 0.89g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were added into the above suspension, respectively. The suspensions were further stirred for 30 minutes at room temperature. The pH was adjusted to 10.5 using 0.2M of NaOH for each suspension. Keeping pH constant and further stirred for another 8 hours. The resulted mixtures were aged at room temperature (RT) for 12 hours for better crystallinity. The obtained precipitates were washed with water and ethanol. Finally, it was dried at 85 °C. Based on the mass concentration of ZnAl-LDH (5, 6, and 7 mg/ml), the composite was named as ZM-5 (ZnAl-LDH/ Mn_3O_4 -5), ZM-6 (ZnAl-LDH/ Mn_3O_4 -6), and ZM-7 (ZnAl-LDH/ Mn_3O_4 -7), respectively. Figure 9 shows the schematics for the preparation of ZnAl-LDH/ Mn_3O_4 nanoparticles, abbreviated as ZM.

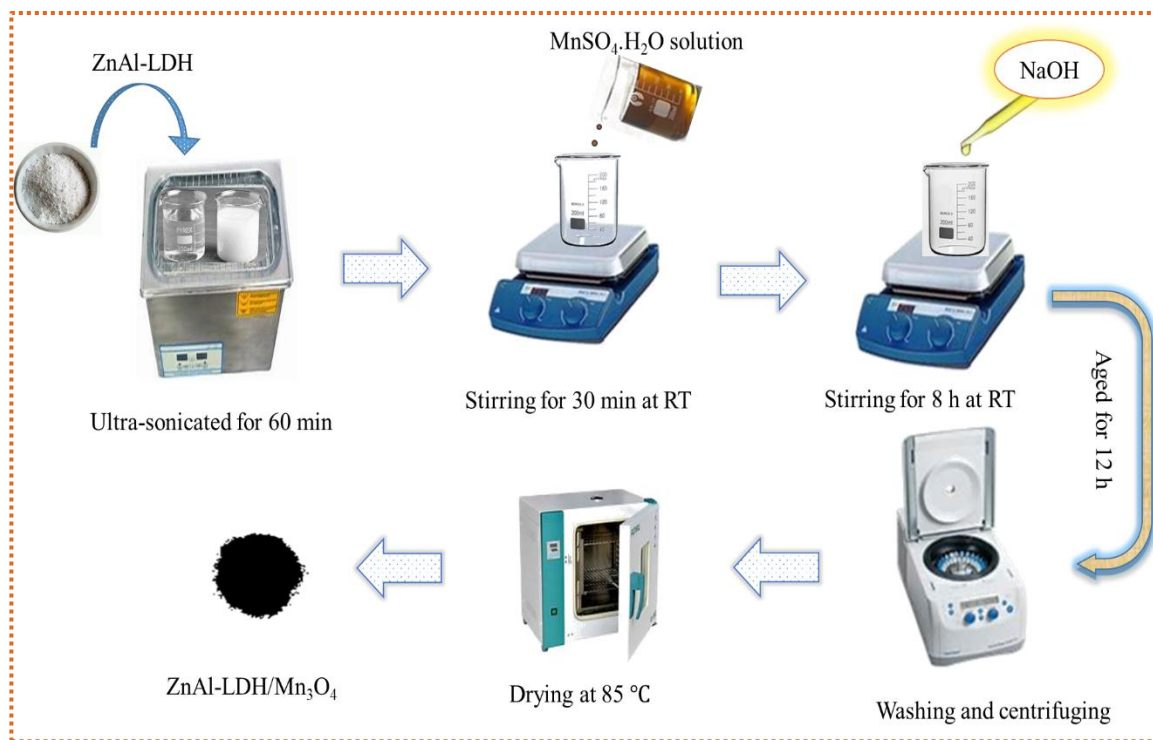


Figure 9. Schematics representation for preparation of ZM nanoparticles.

3.6 Characterization

X-Ray Powder Diffraction (XRD) (Shimadzu XRD-7000) characterized the crystallinity, crystalline size, and phase of the catalysts. Fourier Transform Infrared Spectroscopy (FT-IR) with Spectrum (NicoletTMiS50) FT-IR was performed using KBr pellets for the chemical functional group analysis. Absorption properties of nanoparticles were measured by Shimadzu-3600 Plus UV-vis spectrophotometer at room temperature. Photoluminescence (PL)-Spectroscopy of a JASCD FB-8500 was used to investigate the recombination at a certain excitation wave length. Electrochemical impedance spectroscopy (EIS) for study of charge transfer resistance was performed by Bio logic SP-300. Scanning Electron Microscopy (SEM) using JSM 6500F JEOL was used for morphology, analysis. Brunauer, Emmett, and Teller (BET) by Micromeritics ASAP 2020 were served for measuring surface area and pore size distribution directly. A Shimadzu-3600 Plus UV-vis spectrophotometer was used to assess the MB dye degradation.

3.7 Photocatalytic Activities

Photocatalytic activities of the as-synthesized samples were evaluated by the degradation of MB dye according to the method report with modification (Uddin et al., 2012). All of the tests were conducted in an open environment at ambient temperature. To verify the catalyst-pollutant adsorption-desorption equilibrium in each experiment, 100 ml of MB solution (10 mg/L) was mixed with 0.03 g of metal oxide catalyst for 30 minutes in dark condition. The mixture was consistently mixed during the tests. The light was turned on, and a 150 W halogen lamp was used as the visible light source, after 30 minutes of stirring in the dark. At predetermined irradiation intervals, 10 ml of the suspension was taken and separated by centrifugation (1500 rpm, 10 min). By measuring the absorption peak at $\lambda_{\text{max}} = 663.5$ nm with a UV-visible Spectrophotometer (Shimadzu, UV-1650 pc), the MB content was determined. By dispersing 0.125 g of the (ZnAl-LDH Mn_3O_4) catalyst in 500 mL of MB (10 mg/L) solution, the catalyst's reusability was also examined. The remaining solution was then separated from the catalyst using the same procedure, and the supernatant solution was then decanted away. The catalyst that was still in the beaker's bottom was used for the following photocatalytic reaction cycle five times using the same approach.

3.8 Electrochemical Studies

The electrochemical characteristics of the samples were studied using three-electrode quartz cells on an Electrochemical Potentiostat (Gamry Interface 1000) with 0.5 M Na_2SO_4 as electrolyte solution (Lam et al., 2021). The counter electrode was platinum wire, while the reference electrode was Ag/AgCl. The following process was used to make the working electrodes: The 10 mg of powdered sample was added to 1 ml of ethylene glycol and mixed well together by ultrasonography for 40 min. The 20 microliters of generated suspension were then spread out on fluorine-doped tin oxide (FTO) glass plate which have 2 mm thick and area of 2x2 cm, and dried at 80 degrees Celsius for three hours. The EIS was obtained with a 10 mV AC voltage amplitude in the frequency range of 100 kHz to 0.1 Hz.

CHAPTER FOUR

4. Results and Discussion

4.1 X-Ray Powder Diffraction (XRD) Analysis

XRD was used to determine the crystallinity of all synthesized nanomaterials. The diffraction peaks of Mn_3O_4 , ZnAl-LDH, ZM-5, ZM-6 and ZM-7 NPs were shown in the Figure 10. Bare- Mn_3O_4 Nps had shown in Figure 10a, the 2θ values were located at 18.1° , 29° , 31.2° , 32.4° , 36.2° , 38.2° , 44.5° , 50.9° , 54° , 56.1° , 58.7° , 60° , and 64.8° , corresponding to the crystal planes (101), (112), (200), (103), (211), (004), (220), (105), (312), (303), (321), (224), and (400) of Mn_3O_4 which is perfectly matched with card number (JCPDS card no. 24-0734). It has hausmannite tetragonal space group of I41/amd with unit cell parameters $a = b = 5.762 \text{ \AA}$, $c = 9.470 \text{ \AA}$. The absence of impurity peaks and fine sharp peaks confirmed that the prepared Mn_3O_4 particles are well crystallised, demonstrating the purity of Mn_3O_4 (Ghosh, 2020; Mahdy, Emam, Mussa, Abdel-All, Rashad, et al., 2023). As illustrated in Figure 10b, the ZnAl-LDH XRD patterns revealed the diffraction peaks at 11.8° , 23.5° , 34.8° , 39.3° , 46.8° , 60.3° and 61.6° can be ascribed to (003), (006), (009), (015), (018), (110), (113) lattice planes (JCPDS No. 38-0486). XRD patterns of the sample exhibited reflection at 11.8° , 23.5° and 39.3° , which were associated to the presence of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ compound which have been reported as the precursor phase for the ZnAl-LDH formation (Mendoza-Damián, Tzompantzi, Mantilla, Pérez-Hernández, & Hernandez-Gordillo, 2016). The absence of impurity peaks and the presence of sharp peaks revealed that the prepared ZnAl-LDH was efficiently crystallised, confirming purity. The XRD patterns of the composites (Figure 10 c-e) mainly showed the characteristics of Mn_3O_4 when the prepared Mn_3O_4 NPs were uniformly loaded on the ZnAl-LDH surface. Some diffraction peak signals of ZnAl-LDH were screened, which may be because of its small particles, high signals, and low crystallinity. The structure of Mn_3O_4 NPs was unaffected by ZnAl-LDH as a carrier, peaks of impurity were no longer observed. The ZnAl-LDH and tetrahedral phases' distinctive diffraction peaks are readily in the XRD patterns. The Scherrer equation was used to compute the crystallite sizes of the samples (Van Tran et al., 2022a)

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (4)$$

Where D is the size of the crystallite, λ is the wavelength of the X-ray source used ($\lambda=0.15406$ nm for Cu $K\alpha$ radiation), β is the width (in radians) of the peak at half its height (FWHM), θ is the Bragg angle, and k is the shape factor (0.9). The average crystallite size of Mn_3O_4 , ZnAl LDH, and ZM-5, ZM-6 and ZM-7 was determined to be around 25.9 nm, 19.23, 17.05 nm, 12.2 nm and 13.9 nm, respectively. The interaction between Mn_3O_4 and ZnAl-LDH can influence the size and dispersion of the Mn_3O_4 nanoparticles on the support surface. This could be due to a reduction in the agglomeration of the nanoparticles, which helps in achieving uniform dispersion of the Mn_3O_4 on the support surface. These changes may lead to an increase in the surface area of the Mn_3O_4 , reduction crystallite size, thereby enhancing the catalytic activity and stability of the material.

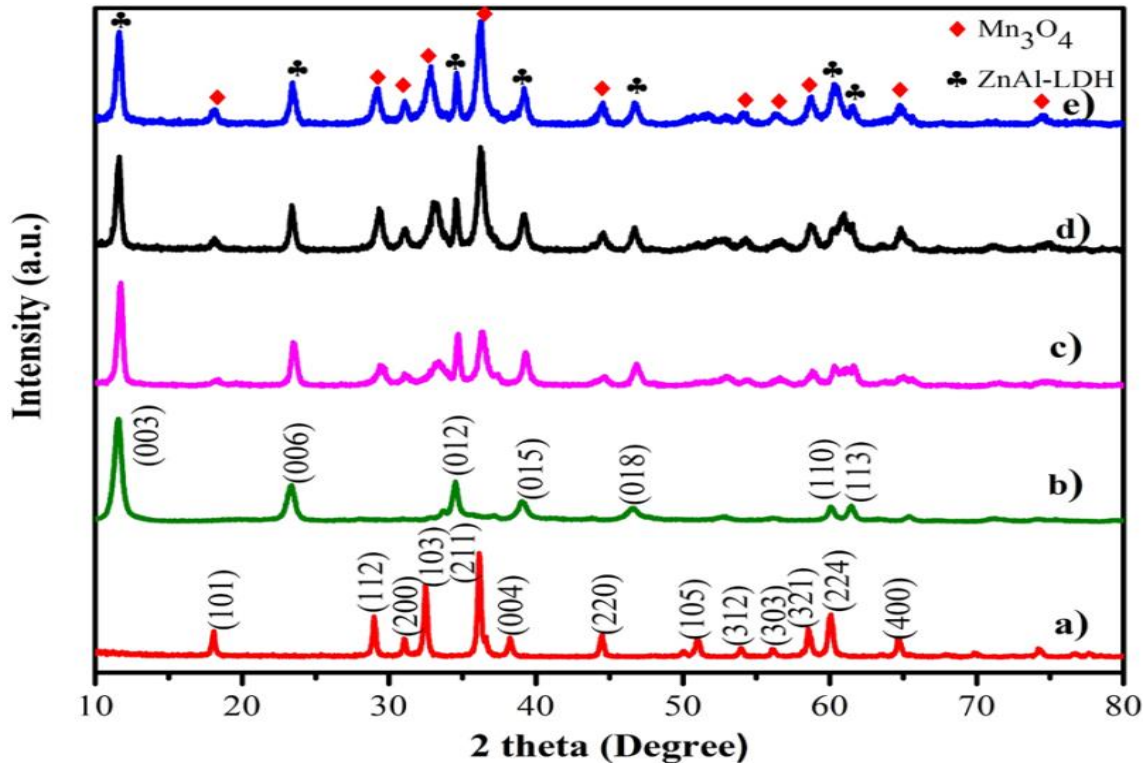


Figure 10. XRD patterns of (a) Mn_3O_4 NPs, (b) ZnAl-LDH, (c) ZM-7, d) ZM-6, and e) ZM-5.

4.2 Uv-Vis Diffuse Reflectance Spectroscopy (DRS) Analysis

A UV-Vis spectrometer was used to determine the absorption spectra and bandgap energies in order to describe the optical characteristics. The optical bandgap of the Mn_3O_4 and ZM-6 catalysts were estimated using Tauc's relation, Eq. (5) (Lett et al., 2023).

$$(\alpha h\nu)^n = k(h\nu - E_g) \quad (5)$$

E_g is the bandgap energy in eV, α is the absorption coefficient, k is absorption constant, $h\nu$ is the incident photon energy (eV), and n is nature of transition, $n=2$ for direct allowed transitions and while it is 0.5 for indirect allowed transitions. The bandgap energy is determined by plotting the $(\alpha h\nu)^2$ versus $h\nu$ as illustrated in Figure 11 by extrapolating the line drawn tangent to the resulting curve. As we can see that the value of the direct bandgap for the, ZM-6 and Mn_3O_4 nanoparticles are 2.41 and 1.89 eV (S. Raha, D. Mohanta, & M. Ahmaruzzaman, 2021). The numerous -OH groups in the anionic clays LDH may have helped to increase electron transfer, which is why composites use visible light more effectively than pristine Mn_3O_4 does. This is also attributed to the formation of nanocomposites. ZM-6 composite has a larger surface area, which allows more photons to be absorbed, resulting in a higher efficiency of light absorption and transfer. This property results due to the broader optical absorption range of the composite.

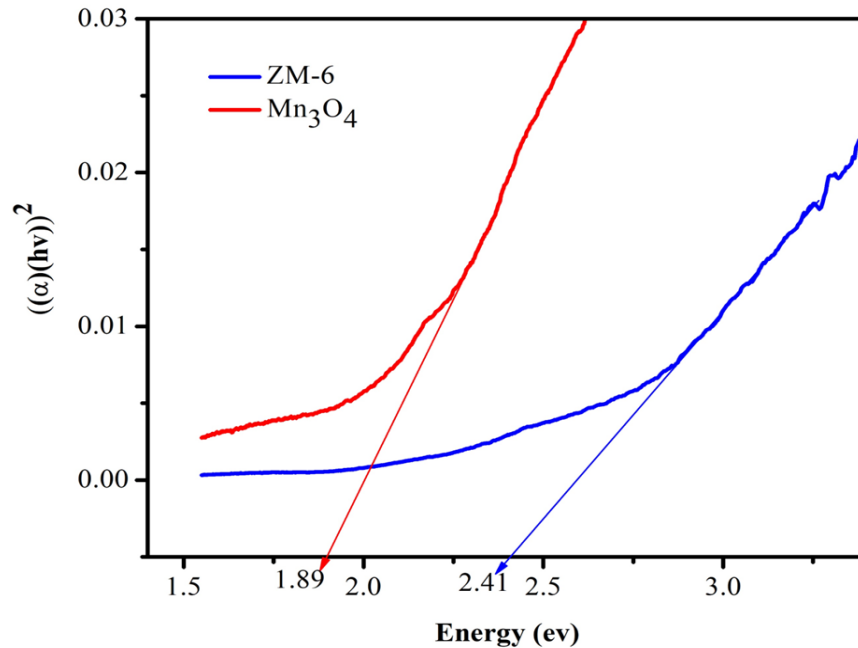


Figure 11. The energy band gap of Mn_3O_4 , and ZM-6 composite.

4.3 Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

Fourier transform infrared spectroscopy (FTIR) has been used to determine the presence of vibrational bands in the prepared samples. Fourier transformation infrared spectroscopy measurements were performed to further identify the chemical bonds and functional groups in the photocatalysts. FTIR spectra of Mn_3O_4 , ZnAl-LDH, and ZM-6 nanoparticles are shown in Figure 12. Three pronounced peaks were seen in the $400\text{--}650\text{ cm}^{-1}$ area of the Mn_3O_4 NPs FT-IR spectra (Figure.12a). The vibration of manganese species (Mn^{3+}) in the octahedral site of Mn_3O_4 is responsible for the vibrational peak at 418 cm^{-1} . The vibration frequency at 484 cm^{-1} is related to the distortion vibration of Mn-O in an octahedral site, and the third vibration frequency at 602 cm^{-1} is a characteristic of Mn-O stretching modes at tetrahedral sites. This outcome further demonstrated that the prepared sample was Mn_3O_4 NPs (Mahdy, Emam, Mussa, Abdel-All, & Rashad, 2023). The FTIR spectra of the LDH materials are shown in Figure 12 b). The stretching mode of the OH groups in the brucite-like layer and the absorption of water are responsible for the broad absorption bands seen in curve (b) at $3400\text{--}3500\text{ cm}^{-1}$. The bending vibration of H-O-H is identified as a band at 1631 cm^{-1} . At $1368\text{--}1392\text{ cm}^{-1}$, the CO_3^{2-} band may be seen. Additionally, the LDHs' Zn-O and Al-O vibration modes are confirmed by the absorption bands seen below 1000 cm^{-1} , and the bands at about 500 cm^{-1} are attributed to the vibrations of O-Zn-O and O-Al-O (G. Xia et al., 2022). All feature bands of Mn_3O_4 NPs and ZnAl-LDH were included in the ZM-6 spectra, as illustrated in Figure 12c. It was therefore possible for Mn_3O_4 to spread on the LDH's surface. The obtained composites were what was desired, according to the FT-IR results.

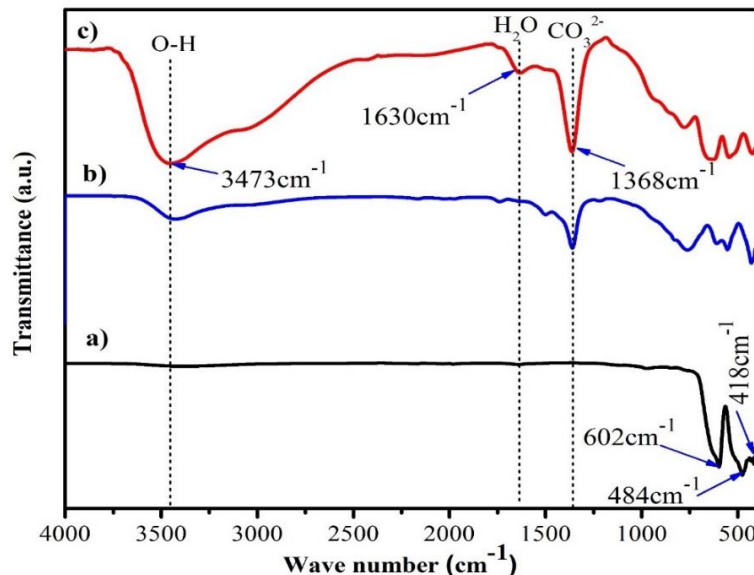


Figure 12. FTIR spectra of a) Mn_3O_4 b) ZnAl-LDH and c) ZM-6.

4.4 Scanning Electron Microscope (SEM) Analysis

To study the surface morphology, Scanning Electron Microscopy (SEM) was taken for pure- Mn_3O_4 , ZnAl-LDH and ZM-6 nanoparticles as shown in Figure 13a-c. SEM images are appropriate for demonstrating the nanoparticles' surface morphology, size and shape. Figure 13a, shows a rough agglomeration representation of the microscopic morphology of pure- Mn_3O_4 NPs (J. Li et al., 2021). Figure 13b, displays the prepared ZnAl-LDH, which has a typical flat, sheet-like structure. Figure 13c, displays the ZM-6 composite SEM microscopic morphology. It can be seen that Mn_3O_4 NPs were uniformly and densely loaded on the surface of LDH nanosheets.

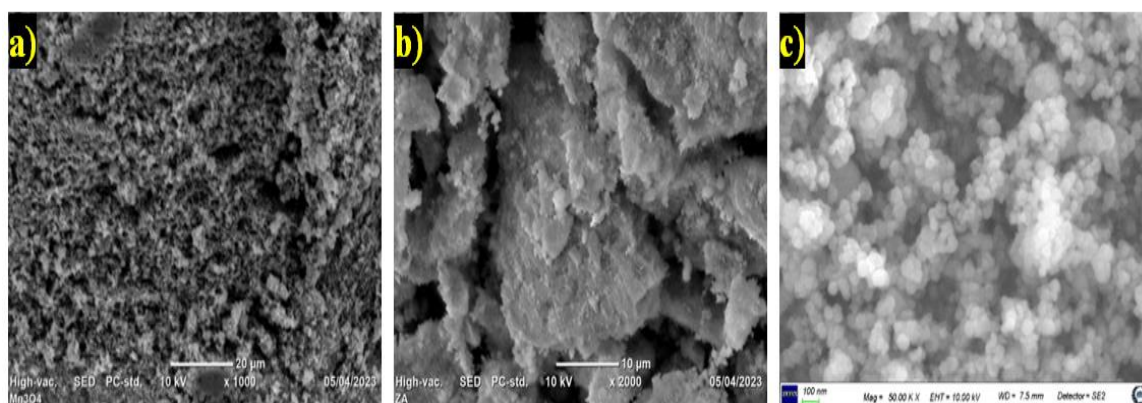


Figure 13. SEM image for nanoparticle of (a) pure- Mn_3O_4 (b) ZnAl-LDH, and c) ZM-6.

4.5 Brunauer, Emmett, and Teller (BET) Analysis

Brunauer, Emmett, and Teller (BET) analysis is a technique used to measure the surface area of materials. The specific surface area of the ZM-6 powder was 537.928 m²/g, compared to 479.796 m²/g for the bare Mn₃O₄. When Mn₃O₄ nanoparticles are spread on the surface of ZnAl-LDH, the surface area of the composite increases. ZnAl-LDH have high porosity and act as a dispersing agent, which decreases the formation of agglomeration between Mn₃O₄ nanoparticles as a result, the surface area of the ZM-6 composite increased (Mahdy, Emam, Mussa, Abdel-All, & Rashad, 2023). These designs allow the catalyst to degrade organic pollutants effectively and quickly, even if they can bind to its surface due to its increased surface area.

Table 3 The measured BET data of Bare-Mn₃O₄ and ZM -6 nanoparticles.

	Bare-Mn ₃ O ₄	ZM -6
Specific surface area (a _s)	479.796 m ² /g	537.928 m ² /g
Total pore volume	0.1072 m ³ /g	0.1741 m ³ /g
Pore size	1.448 (nm)	1.156 (nm)

4.6 Photoluminescence (PL) Analysis

Photoluminescence (PL) spectroscopy was used to examine electron transfer, electronic structure, and photoelectric activity. PL emission spectra of piristine-Mn₃O₄, ZnAl-LDH and ZM-6, catalysts were evaluated at room temperature at the excitation wavelength of 250 nm to examine the impact of ZnAl-LDH on the photoluminescence of Mn₃O₄ NPs. The PL spectra of these samples are shown in Figure 14. The peak around 428 nm should be attributed to radiative recombination of Fermi level electrons due to the defect formation. Whereas the peak at 520 nm may be the result of the d-d transition involving Mn³⁺ ions(Rizal, Saleh, Taufik, & Yin, 2021). This intense emission was noticed because of a band-band transition around 428 nm. The peak intensity of ZM-6 is lower than that of bare-Mn₃O₄. This is due to the uniform dispersion of Mn₃O₄ NPs on the ZnAl-LDH

surface, the peak intensity can also decrease, and the excited electrons are subsequently confined in the surface by means of typical defects. As a result, the photocatalytic activity of ZM-6 was increased by suppressing the electron-hole recombination(Jarvin et al., 2021)

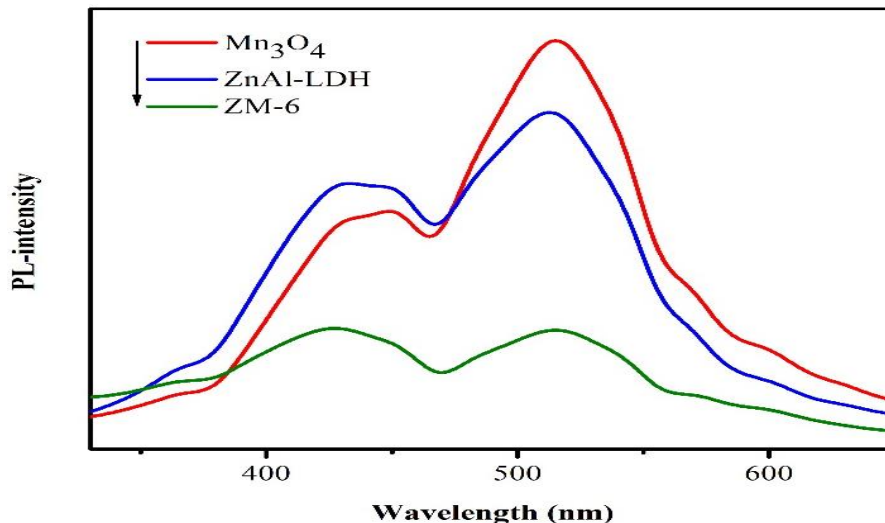


Figure 14. Room temperature PL spectra of a) pristine-Mn₃O₄, ZnAl-LDH and ZM-6 samples.

4.7 Electrochemical Impedance Spectroscopy (EIS) Analysis

Electrochemical Impedance Spectroscopy (EIS) was used to further explore the interfacial charge transfer dynamics in the photocatalyst. The photocatalysts' Electrochemical Impedance Spectroscopy (EIS) Nyquist plots of Mn₃O₄, ZnAl-LDH and ZM-5, ZM-6 and ZM-7, are displayed, in Figure 15. ZM-6 arc radius was smaller than that of the pristine-Mn₃O₄, which indicating that the ZM nanocomposites had a higher efficiency of charge separation and transfer across the interfaces of Mn₃O₄. The possible explanation could be that the combination of Mn₃O₄ and ZnAl-LDH alters the electrochemical properties of the system, which affects the charge transfer mechanism. The interaction between the two materials may change the surface area, charge distribution, and charge transfer, leading to variations in the impedance response. Furthermore, the presence of ZnAl-LDH may modify the adsorption and reaction of the electrolyte species at the Mn₃O₄ NPs surface, resulting in an overall decrease in the impedance intensity and improving the charge transfer of photogenerated charges. These facts support the findings of investigations into photoluminescence (PL) (S. Raha, D. Mohanta, & M. J. S. R. Ahmaruzzaman, 2021; J. Zhao et al., 2017).

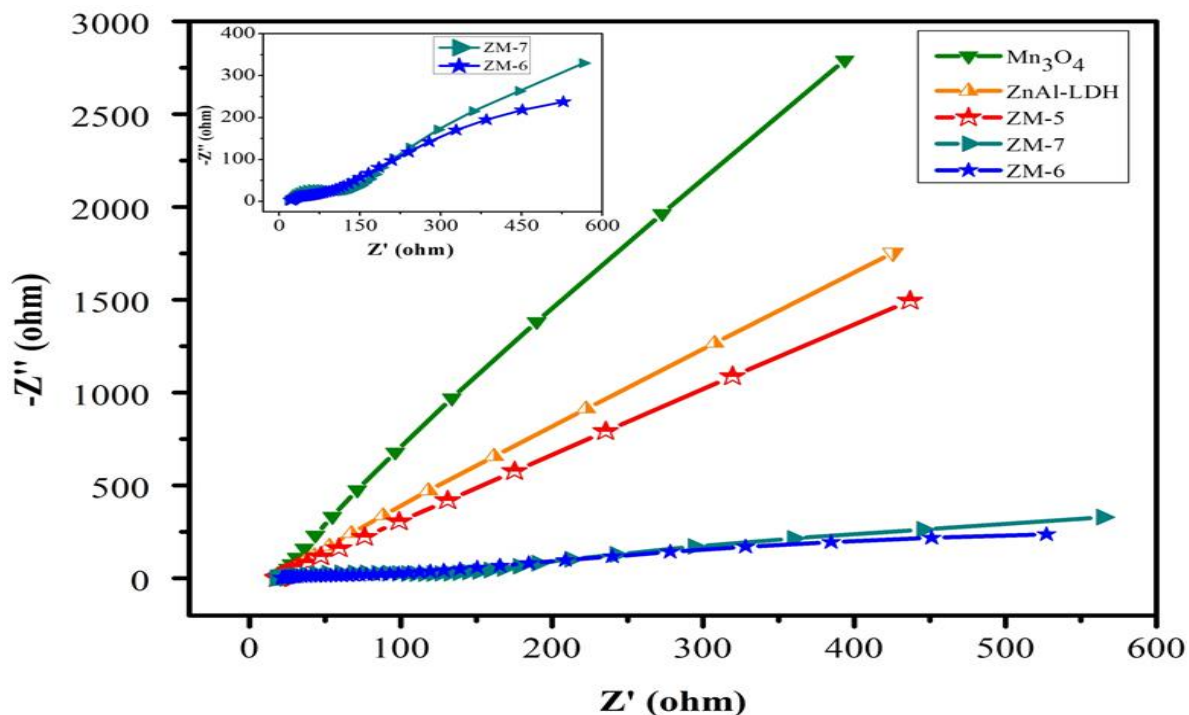
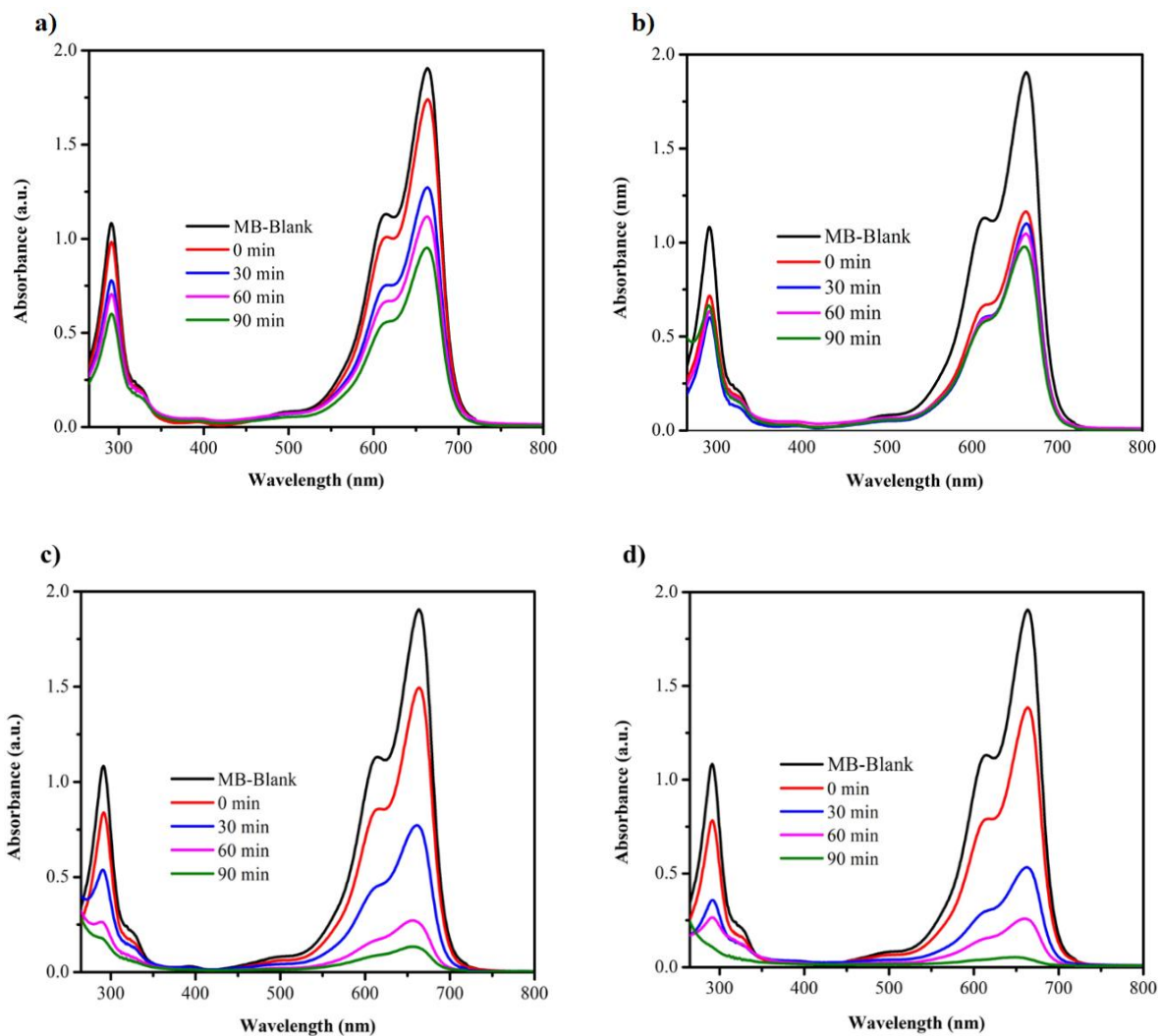


Figure 15. Nyquist plot EIS of pristin-Mn₃O₄, ZnAl-LDH, ZM-5, ZM-6, ZM and ZM-7 Nano particles.

4.8 Photocatalytic Activity Evaluation

Methylene blue (MB) dye, a prominent pollutant in water discharged by textile companies, which was used to test the photocatalytic degradation efficiencies of the as prepared samples. While conducting the experiment under visible light irradiation, create an organic pollutant model. Photocatalytic activity of Mn₃O₄, ZnAl-LDH, ZM-5, ZM-6, and ZM-7 are displayed as shown in Figure 16 (a-f), and all samples are compared to determine which catalyst has the highest photocatalytic activities due to diverse effects. The rate of degradation of a photocatalyst is often determined by its stability, surface area, charge transferring resistance, and crystalline structure. Furthermore, when Mn₃O₄ was supported with ZnAl-LDH, the degradation efficiency of the composite NPs, ZM-5, ZM-6, and ZM-7, were 93.02, 97.16%, and 94.96%, respectively. Among these, ZM-6 catalyst had higher degradation efficiency, which degrades 97.16% of MB dye in 90 minutes under visible light. ZnAl-LDH acts as a support structure for Mn₃O₄ nanoparticles, provides a larger surface area for the nanoparticles to disperse, inhibit the formation of agglomeration, increasing the contact area between the catalyst and the reactants. This enhances the

photocatalytic of ZM-6 nanoparticle is because of more active sites are available for reaction. As a result, the performance of composite nanoparticles (ZM-6) increased. As shown in Table 4, the photocatalytic degradation of the current work is higher than the previous work, even though degrading the MB dyes in a short period of time than the previous studies.



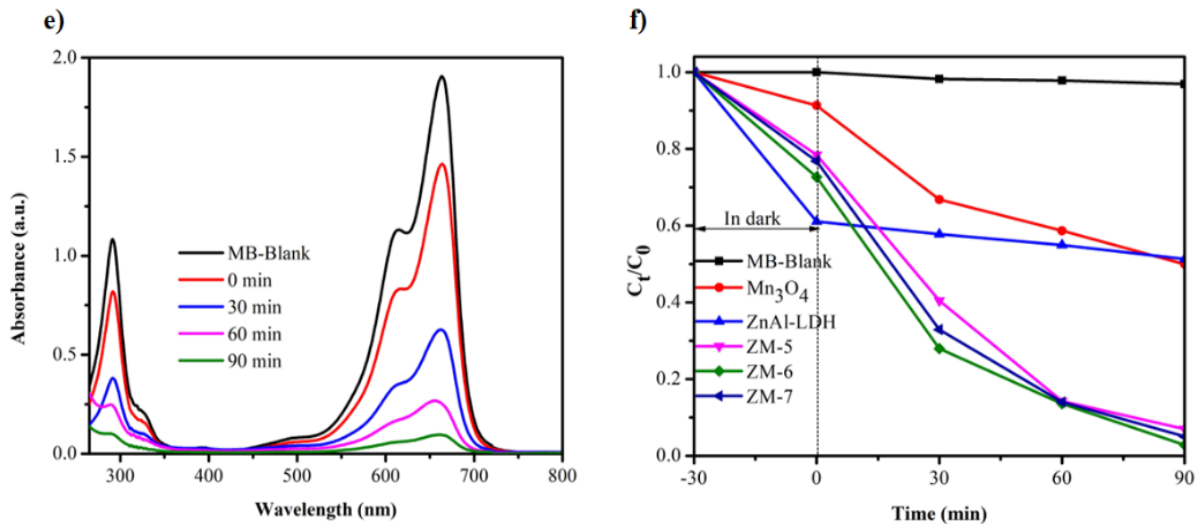


Figure 16. Photocatalytic Activity of a) Mn_3O_4 , b) ZnAl-LDH, c) ZM-5, d) ZM-6, e) ZM-7, and f), C_t/C_0 of the degradation each sample.

Table 4 Comparing the current photocatalytic degradation with previous works.

No.	Nanocatalyst	Pollutant	Degradation (%)	Time (min)	Reference
1	Mn_3O_4 flower	MB	72	180	(Y. Wang et al., 2015)
2	$\text{Li}_2\text{Mn}_{0.8}\text{Ni}_{0.2}\text{SiO}_4/\text{Mn}_3\text{O}_4$	Reactive Blue	79	120	(Mahdy, Emam, Mussa, Abdel-All, & Rashad, 2023)
3	$\text{Mn}_3\text{O}_4\text{-rGO}$	MB	60	120	(M. Jarvin, S. A. Kumar, G. Vinodhkumar, E. Manikandan, & S. J. M. L. Inbanathan, 2021b)
4	$\text{Mn}_3\text{O}_4\text{-rGO}$	MO	88	120	(Yao, Xu, Yu, Zhang, Wang, et al., 2013)
5	$\text{Ag}/\text{Mn}_3\text{O}_4$	CR	78	120	(Rizal, Saleh, Prakoso, et al., 2021)
6	$\text{Mn}_3\text{O}_4/\text{GO}/\text{Zeolite}$	MO	95.5	240	(Osgouei et al., 2020)
7	Mn_3O_4	MB	50	90	The present work
8	ZnAl-LDH/ Mn_3O_4	MB	97.16	90	The present work

4.8.1 Photodegradation Kinetics

Langmuir Hinshelwood kinetic equations were utilized to determine the kinetics of photodegradation.

$$\ln C = -kt + \ln C_0 \quad (6)$$

Rearranging Equation.6 gives

$$\ln \frac{C_0}{C} = -kt \quad (7)$$

Where C_0 and C are the initial dye concentration (mg L^{-1}) and the dye concentration (mg L^{-1}) at time t , and k is the pseudo-first-order reaction rate constant (min^{-1}) respectively. The initial concentration (C_0) and the ratio of dye concentration at time t (C) were plotted versus time. The slopes were used to determine the degradation rate constants. Figure 17 (a, b) displays the curve fitting of pristine- Mn_3O_4 , ZnAl-LDH, ZM-5, ZM-6 and ZM-7 degradation by the pseudo-kinetic equation and the rate constants (k) of those samples, and Table 5 shows the Percentage Degradation Efficiency (PDE) and kinetic rate constant (k) and correlation coefficients (R^2). Figure 17 (a-b) shows the kinetic study of pristine- Mn_3O_4 , ZnAl-LDH, ZM-5, ZM-6 and ZM-7 degradation using pseudo-first-order kinetic plot and the rate constants (k) of those samples, ZM-6 had the greatest degradation efficiency (97.16%), highest degradation rate constant ($29.35 \times 10^{-3} \text{ min}^{-1}$). This superiority of ZM-6 composite over other samples is due to the fact that ZnAl-LDH materials have a large surface area and can support Mn_3O_4 , increasing the composite photocatalyst's surface area and enhancing its photocatalytic activity. The layered structure of ZnAl-LDH materials can also allowing for the effective transfer of electrons to the surface. Which facilitates the separation of photo-excited electron-hole pairs and decreases the charge carrier recombination rate(Jarvin et al., 2021)

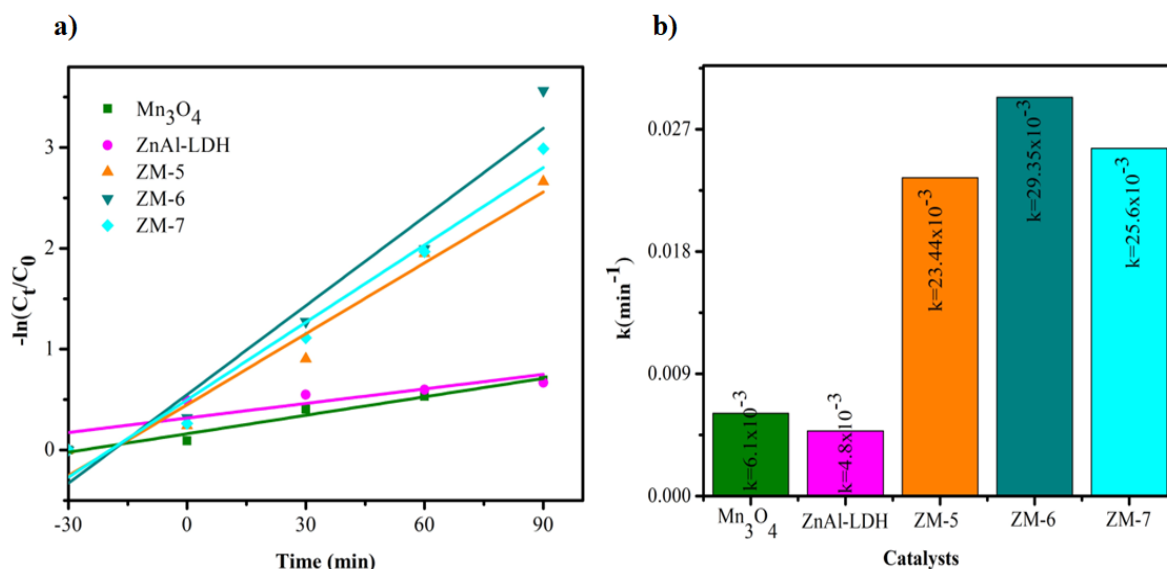


Figure 17. The kinetics study of a) Prestine- Mn_3O_4 , ZnAl-LDH, ZM-5, ZM-6 and ZM-7 degradation using pseudo-first-order kinetic plot b) The rate constants of those catalysts.

Table 5 Percentage degradation efficiency, kinetic rate constant, and correlation coefficients of ZnAl-LDH/ Mn_3O_4 samples.

	Mn_3O_4	ZnAl-LDH	ZM-5	ZM-6	ZM-7
PDE (%)	50.05	48.60	93.02	97.16	94.96
K (min ⁻¹)	6.1×10^{-3}	4.8×10^{-3}	23.44×10^{-3}	29.35×10^{-3}	25.6×10^{-3}
R ²	0.96433	0.64469	0.95117	0.93074	0.95817

4.8.2 The pH Effect

The pH of the dye solution plays a key role in photocatalytic degradation events. In the present investigation, the ZM-6 catalyst test solution was tested for both acidic and alkaline pH by adding suitable amounts of NaOH and HCl solutions. The MB degrading experiment was conducted out in acidic media with a pH of 3 and 5, in a neutral with pH of 7 and in basic media with a pH of 9 and 11. As the pH of MB dye solution is increase, the photocatalytic degrading efficiency of the catalyst increases gradually from acidic to basic as seen in Figure 18 a and b. The degradation efficiency of the ZM-6 composite catalyst is

higher in basic medium. However, in acidic environments, the MB degradation efficiency dropped, this is due to the same charge resulting in a columbic repulsive force between the catalyst and the dye molecules, and therefore the catalyst adsorption capacity is decreased (Asif, Khan, & Asiri, 2015b).

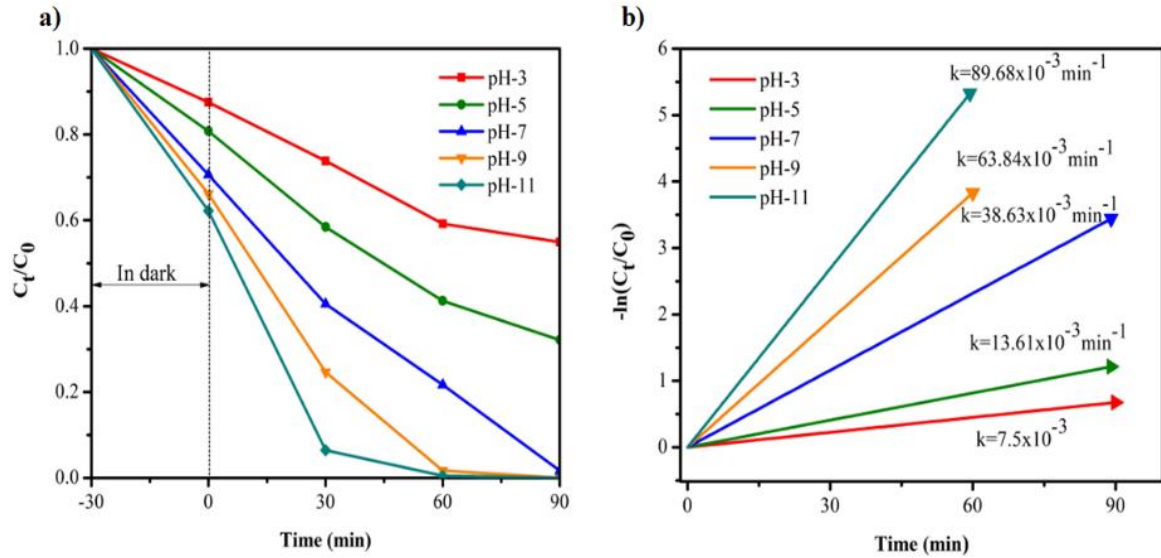


Figure 18. Effect of pH on degradation of Methylene blue at fixed 0.03 mg of ZM-6 catalyst and 10 ppm of MB solution.

4.8.3 Effect of Catalytic Dosage on Degradation of MB

To evaluate the effect of catalyst dosage on photodegradation of MB, we varied the catalyst dosage of ZM-6 from 0.1 to 0.5 g/L at a constant pH. Figure 19 depicts MB % degradation as a function of catalyst dosage, with degradation efficiency increasing from 0.1 to 0.4 g/L and subsequently decreasing as the catalytic dosage reaches 0.5 g/L. The rise in photo degradation of catalyst dosage from 0.1 to 0.4 g/L, as well as the highest degradation efficiency at 0.4 g/L, could be attributable to the availability of additional active sites and light penetration, which could ultimately enhance the photocatalytic activity. When compared to 0.4 g/L of catalyst, photocatalytic activity is lower at 0.5 g/L. As the nanocomposite dose increases, particles may accumulate and prevent light from reaching the photocatalyst surface. There might be fewer active sites that are exposed to light as a result, which might reduce the photodegradation efficiency (Shawky, Mohamed, Mkhallid, Awwad, & Ibrahim, 2020).

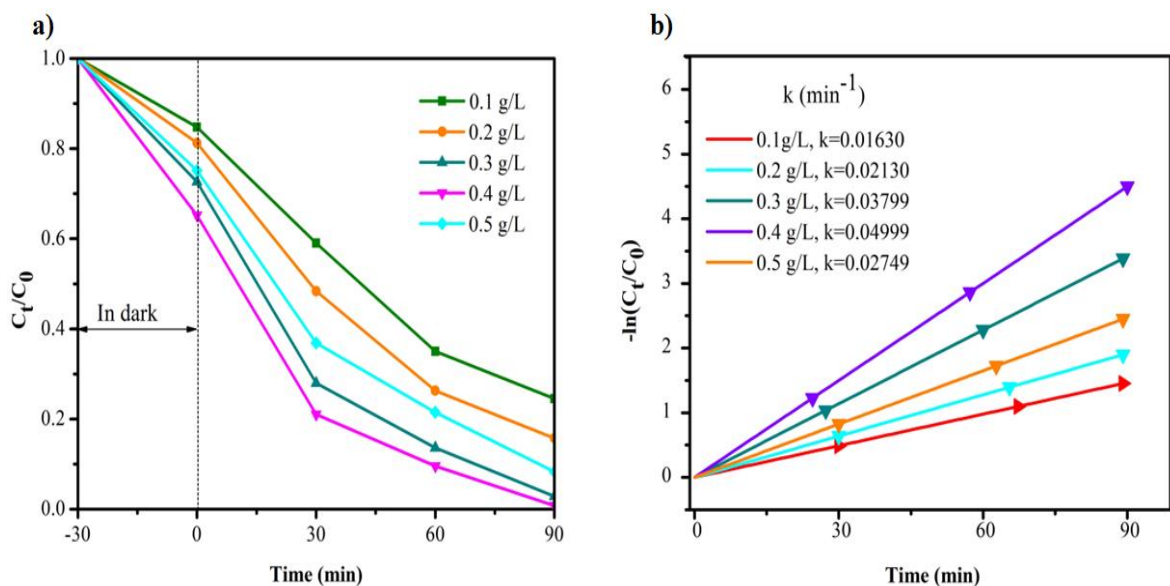


Figure 19. Effect of ZM-6 Catalytic dosages on degradation of Methylene blue 10 ppm of MB solution.

4.8.4 Reusability of the Catalyst

The stability of the catalyst is an important factor for practical application. In this study, the reusability of a prepared ZM-6 nanocomposite catalyst was evaluated for the degradation of MB dye under visible light illumination for five consecutive cycles, as shown in Figure 20. After each photocatalytic experiment, the catalyst was washed with distilled water and ethanol, collected, and dried in an oven at 100 °C until it dries completely (Ajmal, Majeed, Malik, Idriss, & Nadeem, 2014; Nekoeinia, Yousefinejad, Hasanpour, & Yousefian-Dezaki, 2020). The prepared catalyst was effective for up to 5 cycles of reuse, after which there was a slight decreasing in photocatalytic performance. This might be as a result of the catalyst being lost during the recovery process and a decrease in the active sites on the catalytic surface. These results suggest that the synthesized ZM-6 nanocatalyst for photocatalysis is highly stable and reusable. Additionally, the XRD pattern for the recycled photocatalyst demonstrated the stability of the distinctive crystallographic planes present in ZM-6 before and after reuse, which exhibit excellent photo stability even after five cycles, which confirms that ZnAl-LDH/Mn₃O₄ (ZM-6) nanocomposite, has excellent stability under light.

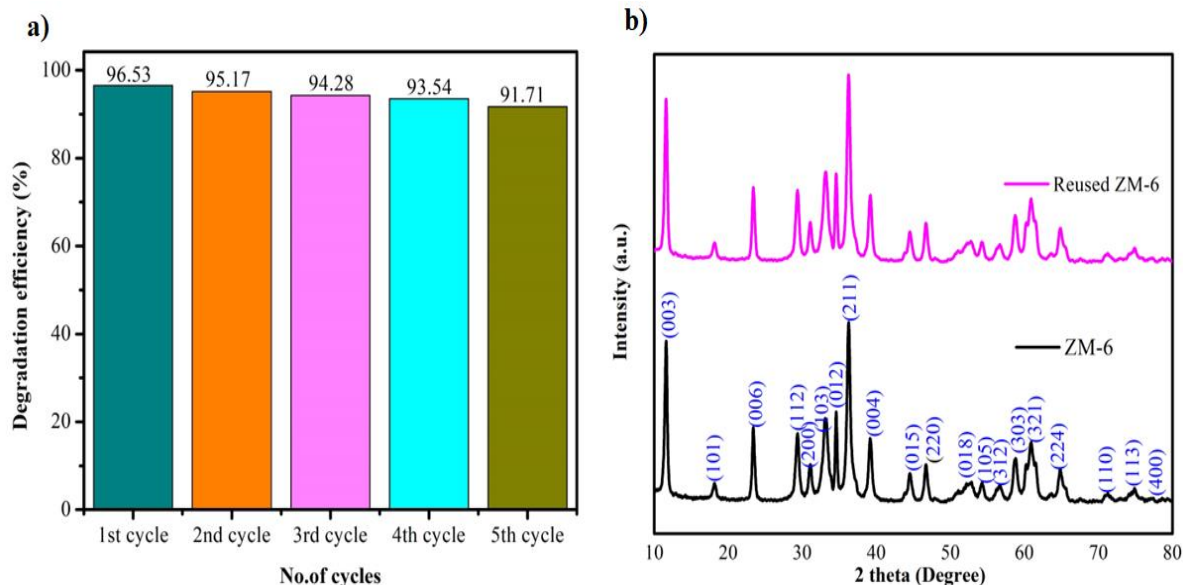


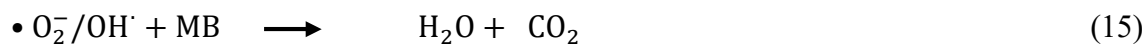
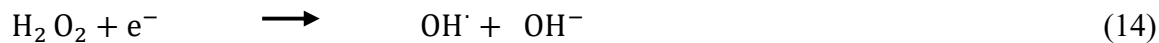
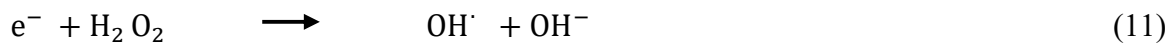
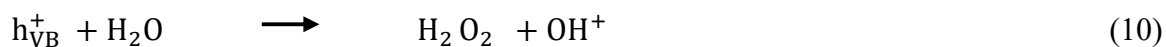
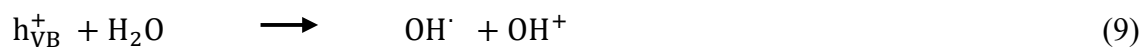
Figure 20. a) Reusability test ZM-6 catalyst for photocatalytic degradation of Methylene blue under Visible light irradiation (b) XRD pattern obtained for the recycled ZM-6 catalyst.

4.8.5 Mechanism of Photodegradation

The possible working mechanism of ZnAl-LDH/Mn₃O₄ (ZM-6) is proposed as follows in Figure 21. When a photon with energy equal to or greater than the band gap energy of the photocatalyst strikes the surface of the ZM-6 nanocomposites electrons will be excited to conduction band leaving holes behind in valence band of Mn₃O₄. In this way, electron-hole pair will be generated. The excited electrons to conduction will react to oxygen molecules which is absorbed on the surface of the photocatalyst to create super-oxide radical(O₂^{•-})(reduction). Meanwhile, the holes left behind in valence band of the photocatalyst react with water molecules and create [•]OH radicals(oxidation). Furthermore, OH⁻ ions on the surface of ZnAl LDH react with holes and create additional hydroxyl radicals ([•]OH)(A. George et al., 2022). The generated [•]O₂⁻ and [•]OH radicals which are highly reactive species react with organic contaminants and degrade them into less harmful substances and other byproducts like CO₂ and H₂O.

In ZM-6 composite, Mn₃O₄ NPs are dispersed over ZnAl LDH surface which gives them higher surface area by reducing particle size when compared with unsupported Mn₃O₄ nanoparticles which internally leads to having more active sites ready for surface reaction to

occur. This, together with their synergistic effects, the enhanced activity of ZM-6 nanocomposites is due to quick dye adsorption on LDH followed by rapid photodegradation Mn_3O_4 by supported NPs. Furthermore, the Mn_3O_4 particle size was reduced to expose more active sites and the area in contact with the target pollutants was increased, both of which increased photocatalytic efficiency. The ability of LDH to adsorb can bring organic pollutant molecules close to the catalyst surface, where hydroxyl and superoxide radicals are formed. This could explain why ZnAl-LDH/ Mn_3O_4 NPs have higher photocatalytic activity than bare Mn_3O_4 NPs. The following equations could best describe the reaction of photocatalytic abilities:



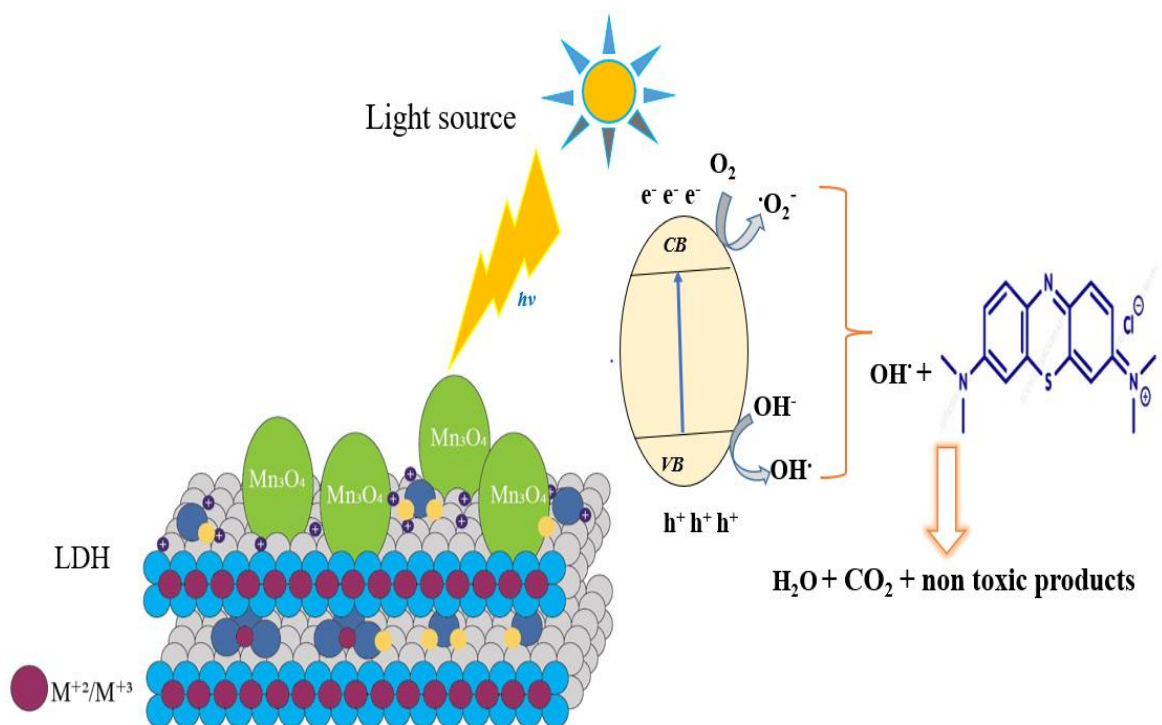


Figure 21. The proposed mechanism of photocatalytic degradation of methylene blue.

CHAPTER FIVE

5. Conclusion and Recommendations

5.1 Conclusions

This work, describes ZnAl-LDH/Mn₃O₄ composites which were synthesized by an in-situ growth method, and their names were assigned as ZM-5, ZM-6 and ZM-7. The composite catalysts were characterized by different techniques. XRD analysis approved the formation of hausmannite tetragonal structures of Mn₃O₄ NPs, and well-organized two-dimensional ZnAl-LDHs. SEM images shows Mn₃O₄ NPs was uniformly loaded on the surface of ZnAl-LDH. UV-Vis DRS showed that the synthesized samples had efficiency of absorption in visible region. ZM-6 composite has good photoluminescence properties by increasing the lifespan of photogenerated charge carriers, and they also displayed photocatalytic degradation efficiency of 97.16% in 90 minutes for MB when exposed to visible light. The increased photocatalytic activity was attributable to the synergistic effect of the homogenous dispersion of Mn₃O₄ NPs, MB adsorption on ZnAl-LDH, since the structure of ZnAl-hydroxyl-rich LDH, low agglomeration, and high surface area. The maximum photocatalytic activity at pH 11 implies an interatomic attraction force between the negatively charged ZM-6 catalyst and the positively charged MB that will be adsorbed to the catalyst's surface. The higher photodegradation efficiency of 0.4 g/L could be attributable to the availability of more active sites and the ease of light penetration. The reusability of the produced catalyst for up to five cycles demonstrates that the catalyst was stable and efficient.

5.2 Recommendations

To improve Mn_3O_4 's photocatalytic performance in real-world applications, a variety of actions might be advised. To finish the research project, implement the following suggestion:

- It is possible to use for other organic dyes degradation, like methylene orange, Congo red, Naphthol Yellow, etc.
- It is possible to use for various applications, including batteries, super capacitors, solar cells, piezoelectric devices, biosensors, transistors, textiles, rubber products, light-emitting diodes, laser diodes, and anti-bacterial agents.
- Free radical scavenging studies should also be carried out to identify the principal active chemical involved in the degradation process.

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