

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**MODIFICATION OF LAYERED DOUBLE HYDROXIDES FOR
CATALYTIC DEGRADATION OF REFRACTORY ORGANIC
POLLUTANTS USING ADVANCED OXIDATION PROCESSES**

SULTAN AKDAĞ TÜRKAY

**A THESIS SUBMITTED FOR THE DEGREE OF
MASTER OF SCIENCES
ENVIRONMENTAL ENGINEERING DEPARTMENT**

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SUMMARY

In this thesis, the degradation of refractory organic pollutants by sonocatalytic and photocatalytic processes was investigated by enhancing the catalytic properties of layered double hydroxide (LDHs) through various modifications. The catalytic performance of ZnFe LDH was enhanced through lanthanum (La) doping. Following that, the synthesized La-ZnFe LDH was immobilized onto the polydimethylsiloxane (PDMS) sponge to increase the reusability of the catalyst. The morphological, structural, and optical properties of the LaZnFe LDH and immobilized catalyst were determined via XRD, FTIR, SEM, EDX, TEM, XPS, BET, and DRS analyses. Firstly, LaZnFe LDH was used for the peroxydisulfate-assisted sonocatalytic degradation of the metribuzin. By optimizing LaZnFe LDH dosage, metribuzin concentration, PDS concentration, pH, and ultrasonic power, 90.1% of the metribuzin was degraded. Secondly, LaZnFe LDH-embedded PDMS sponge was used for the peroxymonosulfate-assisted photocatalytic degradation of rifampicin. The effect of rifampicin concentration, PDMS sponge number, PMS dosage, pH, and light intensity on the rifampicin photodegradation process was investigated. Under optimal conditions, the rifampicin degradation efficiency of the process reached 92.8%. LaZnFe LDH and the immobilized catalyst were found to have good reusability and stability after four and seven consecutive cycles, respectively. By-products generated during the degradation of metribuzin, and rifampicin were detected by GC-MS analysis and these by-products were found to be less toxic or non-toxic in comparison to the target pollutants. According to the results, the application of modified LDHs for the sonocatalytic and photocatalytic processes for the degradation of refractory organic pollutants is quite effective.

Key Words: Refractory organic pollutant, Layered double hydroxide, Sonocatalytic degradation, Photocatalytic degradation, Nanomaterials.

ÖZET

Bu tezde, dirençli organik kirleticilerin sonokatalitik ve fotokatalitik yöntemlerle bozunması, çeşitli modifikasyonlar yoluyla katmanlı çift hidroksitin (LDH'ler) katalitik özelliklerini artırarak incelenmiştir. ZnFe LDH'nin katalitik performansı, lantanyum (La) katkılama yoluyla geliştirilmiştir. Bunu takiben, katalizörün yeniden kullanılabilirliğini arttırmak için sentezlenen La-ZnFe LDH, polidimetilsiloksan (PDMS) süngerine immobilize edilmiştir. LaZnFe LDH' nin ve hareketsizleştirilmiş katalizörün morfolojik, yapısal ve optik özellikleri XRD, FTIR, SEM, EDX, TEM, XPS, BET ve DRS analizleri ile belirlenmiştir. İlk olarak, metribuzinin peroksidisülfat destekli sonokatalitik degradasyonu için La-katkılı ZnFe LDH kullanılmıştır. LaZnFe LDH dozajı, metribuzin konsantrasyonu, PDS konsantrasyonu, pH ve ultrasonik güç optimize edilerek, metribuzinin %90,1'i bozulmuştur. İkinci olarak, rifampisinin peroksimonosülfat destekli fotokatalitik bozunması için LaZnFe LDH gömülü PDMS sünger kullanılmıştır. Rifampisin konsantrasyonunun, PDMS sünger sayısının, PMS dozajının, pH'ın ve ışık yoğunluğunun rifampisin fotodegradasyon süreci üzerindeki etkisi araştırılmıştır. Optimum koşullar altında, prosesin rifampisin bozunma verimliliği %92,8'e ulaşmıştır. LaZnFe LDH ve hareketsizleştirilmiş katalizörün, sırasıyla dört ve yedi ardışık döngüden sonra iyi bir yeniden kullanılabilirlik ve kararlılığa sahip olduğu bulunmuştur. Metribuzin ve rifampisin bozunması sırasında oluşan yan ürünler GC-MS analizi ile tespit edilmiş ve bu yan ürünlerin hedef kirleticilere göre daha az toksik olduğu veya toksik olmadığı bulunmuştur. Bu çalışmanın bulgularına göre, kalıcı organik kirleticilerin sonokatalitik ve fotokatalitik gideriminde modifiye LDH'lerin kullanımı oldukça etkilidir.

Anahtar Kelimeler: Dirençli organik kirleticiler, Çift katmanlı hidroksitler, Sonokatalitik bozunma, Fotokatalitik bozunma, Nanomateriyaller.

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LIST OF ABBREVIATIONS AND ACRONYMS

<u>Abbreviations</u>	<u>Explanations</u>
<u>and Acronyms</u>	
$\lambda_{\max}$	: Maximum absorbance wavelengths
)))	: Ultrasonic irradiation
e^-	: Electron
E_g	: Band gap energy
eV	: Oxidation potential
Fe	: Iron
h^+	: Hole
k_{app}	: Reaction rate constant
La	: Lanthanum
$O_2^{\bullet-}$	: Superoxide anion radical
$\bullet OH$	: Hydroxyl radical
pH_{pzc}	: pH at the point of zero charge
$SO_4^{\bullet-}$	: Sulfate radical
Zn	: Zinc
AOP	: Advanced Oxidation Process
BET	: Brunauer – Emmett – Teller
CB	: Conduction Band
DRS	: Diffuse Reflection Spectra
EDX	: Energy-Dispersive X-Ray Spectroscopy
FTIR	: Fourier Transform Infrared
GC-MS	: Gas Chromatography- Mass Spectrometry
LDH	: Layered Double Hydroxide
PDMS	: Polydimethylsiloxane
PDS	: Peroxydisulfate
PMS	: Peroxymonosulfate
ROS	: Reactive Oxygen Species
SEM	: Scanning Electron Microscopy
TEM	: Transmission Electron Microscope

US : Ultrasound
UV : Ultraviolet
VB : Valence Band
XRD : X-Ray Powder Diffraction



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1. INTRODUCTION

1.1. Aim of the Thesis

In the present study, the sonocatalytic and photocatalytic processes are used as the advanced oxidation processes that synergize in degrading refractory organic pollutants in the aqueous environment. The LaZnFe LDH was utilized to activate peroxydisulfate (PDS) under ultrasonic irradiation to degrade metribuzin. At the same time, the photocatalytic degradation of rifampicin via peroxymonosulfate activation was achieved by using LaZnFe LDH embedded PDMS sponge. Different analyses such as X-ray diffraction (XRD), Brunauer – Emmett – Teller (BET), SEM (Scanning electron microscopy), Fourier transform infrared (FT-IR), Energy dispersive x-ray analysis (EDX), and so forth are used to characterize the synthesized LDHs. The effect of various effective parameters on processes, including ultrasonic power, catalyst dosage, and pH is evaluated. Moreover, the degradation products of processes detected employing GC–MS analysis. Eventually, the generated ROSs and the degradation mechanism are introduced. It is expected that this study can help to know better the efficiency of LDHs and their modification with advanced oxidation processes to degrade refractory organic pollutants.

2. LITERATURE REVIEW

2.1. Refractory Organic Pollutant

In recent years, the release of organic pollutants into the aquatic media has become a global concern because of population growth and industrialization. Refractory organic pollutants refer to the class of organic compounds resistant to degradation because of their stable chemical structure [1]. A wide range of compounds, including pesticides, polychlorinated biphenyls (PCBs), antibiotics, dioxins, polycyclic aromatic hydrocarbons (PAHs), and certain dyes have been identified as refractory organic pollutants [2]. These pollutants are highly stable, have a long half-life, can be transported over long distances, and have a significant potential for bioaccumulation [3], [4]. Even in trace quantities, refractory organic pollutants pose a significant threat to the ecological environment as they are highly carcinogenic, teratogenic, and mutagenic in aquatic environments [5], [6]. Since pesticides and antibiotics are both refractory organic pollutants in the scope of the thesis, these two pollutants are also discussed in more detail and comprehensively.

2.1.1. Pesticides

Pesticides are chemicals used to prevent, eliminate, or control insects, fungi, weeds, and molds. Pesticides are categorized according to their target species, formulations, mechanism of action, and utilization patterns [7]. They are typically classified into insecticides, fungicides, herbicides, rodenticides, nematocides, virucides, and avicides based on their target species. Also, they can be categorized based on their chemical composition, such as organochlorines, carbamates, organophosphates, pyrethroids, and triazine [8]. Due to their persistence and toxicity, organochlorine pesticides are the most hazardous to the environment among pesticides [9]. Carbamates are chemical ester compounds derived from carbamic acids developed as a substitute for organochlorine pesticides. In comparison to organochlorine compounds, its simplified structure, easier degradability, and lower bioaccumulation make it widely preferred for use in applications [10]. Organophosphate pesticides were initially developed to control pests and currently account for 45% of the total pesticides

utilized globally [11], [12]. Despite being less persistent in the environment than organochlorines and carbamates, many organophosphate pesticides have a high level of toxicity [13]. Another insecticide class, pyrethroids, are made from pyrethrins extracted from *Chrysanthemum Cinerariaefolium* pyrethrum flowers [14]. Although it is less dangerous than other pesticide classes, its widespread usage endangers the aquatic ecosystem [15]. Triazines comprise a six-membered cyclic structure containing three nitrogen atoms and one Azina [16]. These pesticides, which are used for the control of weeds, have a long half-life, and may disrupt endocrine systems; as a result, they pose a risk to both human and environmental health [17]. Pesticide contamination typically originates from agricultural and industrial activities, and they can enter aquatic ecosystems via surface run-off, accidental leakage, spray drift, evaporation, and soil erosion [18]. Due to their toxicity, resistance to biodegradation, and persistence even in trace amounts, pesticides can significantly impact the ecosystem and human health [7]. In addition, because they have both acute and chronic impacts on non-target species, it is important to develop methods to efficiently remove these pollutants from the environment.

2.1.2. Antibiotics

Antibiotics, which treat a range of bacterial diseases in humans and livestock are one of the most prevalent types of pollutants detected in water bodies [19]. They can be categorized according to their chemical structure and mechanism of action [20]. In addition, they can be divided into narrow-spectrum and broad-spectrum antibiotics based on the types of bacteria they target [21]. Based on their chemical structure, antibiotics include tetracyclines, aminoglycosides, β -lactams, macrolides, sulfonamides, amphenicol, lincosamides, ansamycin, glycopeptides, quinolones, and others [22]. Generally, hospitals, pharmaceutical industries, livestock, and aquaculture are the major sources of antibiotics in raw and treated wastewater [23]. The uncontrolled increase in the release of antibiotics to the environment and the inability of conventional wastewater treatment processes to degrade antibiotics may cause negative effects on the ecosystem [24]. When antibiotics are released into the environment, they are not readily biodegradable, persisting in the environment for a long time.

As a result, antimicrobial resistance genes and bacteria develop [25], [26]. Furthermore, the World Health Organization (WHO) identifies antibiotic resistance as a global health crisis, so it is crucial to develop techniques to eliminate antibiotic residues [27].

2.1.3. Treatment of Refractory Organic Pollutants

Refractory organic pollutants such as pesticides, and antibiotics have the characteristics of strong chemical stability, high toxicity, and low biodegradability [28], [29]. Many biological, physical, chemical, and combined processes have been developed to degrade refractory organic pollutants from aquatic environments [30]–[32]. Due to their low cost and eco-friendliness, biological treatment methods are extensively employed in wastewater remediation. However, it is not successful in eliminating pollutants with low biodegradability, high stability, and high toxicity, and it takes time for microorganisms to decompose the pollutants [33], [34]. Physical methods include coagulation, adsorption, air stripping, and membrane technologies. Nevertheless, these methods are more expensive than biological methods and require post-treatment due to secondary pollution [33], [35]. Therefore, it is essential to find effective methods for the removal of refractory organic pollutants. AOPs, which have been developed as an alternative to conventional treatment methods, have recently attracted considerable interest due to their rapid degradation rates and ability to mineralize pollutants [36].

2.2. Advanced Oxidation Processes

Advanced oxidation processes (AOPs) are promising methods for degrading organic pollutants. These methods rely on the in-situ formation of reactive oxygen species (ROS) such as hydroxyl radicals ($\cdot\text{OH}$), sulfate radicals ($\text{SO}_4^{\cdot-}$), superoxide anion radicals ($\text{O}_2^{\cdot-}$), and hydroperoxyl radicals ($\text{HO}_2^{\cdot}$) which have high oxidation potential for pollutant removal [36]. Produced ROSs destroy and mineralize pollutants into CO_2 , H_2O , or harmless compounds [37]. Table 2.1 shows the oxidation potential of some oxidative species. According to Table 2.1, the $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ have a greater oxidizing capacity than the others; therefore, they are the most frequently used oxidant

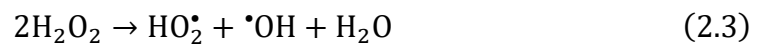
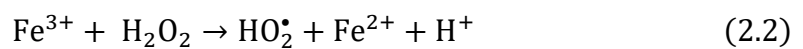
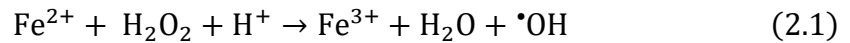
types in AOPs [38], [39]. The numerous AOPs utilized for pollutant removal are briefly described.

Table 2.1: Oxidation potential of oxidizing species.

Oxidizing Species	Oxidation potential (eV)
Hydroxyl radical ($\cdot\text{OH}$)	2.80
Oxygen (O_2)	1.23
Ozone (O_3)	2.10
Hydroperoxyl radical ($\text{HO}_2\cdot$)	1.65
Sulfate ($\text{SO}_4^{\cdot-}$)	2.60
Peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$)	2.01
Peroxymonosulfate (HSO_5^-)	1.80
Chlorine (Cl_2)	1.36

2.2.1. Fenton and Photo-Fenton

Fenton, one of the oldest AOP processes, relies on the production of $\cdot\text{OH}$ radicals due to the reaction of Fe (II) with H_2O_2 in an acidic environment. The process starts when ferrous ion decomposes H_2O_2 (Equation 2.1). The ferric ion can react with another H_2O_2 to be converted back to the iron ion, resulting in the formation of the $\text{HO}_2\cdot$ and the regeneration of the ferrous ion (Equations 2.2 and 2.3) [40].



2.2.2. Ozone-based Oxidation

Ozone, a powerful oxidant (2.07 eV), is very effective at mineralizing refractory organic pollutants. Ozone can eliminate pollutants via two different mechanisms: direct oxidation of the ozone molecule and oxidation by the $\cdot\text{OH}$ radical generated during ozone decomposition [41]. Despite the high redox potential of ozone, direct oxidation of the organic pollutant by ozone is slow, resulting in a low degradation efficiency because the organic pollutant is not completely oxidized [42]. Combining

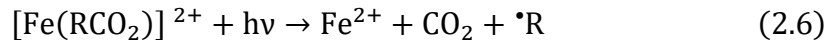
ozonation with other processes has been suggested to solve this problem. These methods, also known as ozone-based processes, consist of O₃/H₂O₂, catalytic ozonation, photocatalytic ozonation, sonolytic ozonation, and O₃/Fenton [43], [44].

2.2.3. Electrochemical Oxidation Processes

Electrochemical AOPs have emerged as an effective method for destroying pollutants in recent years [45]. It has the advantages of requiring no or very few additional chemicals or catalysts during the process, not causing secondary pollution, and having a high pollutant removal efficiency [46]. It comprises, electro-Fenton (EF), anodic oxidation, photoelectro-Fenton, and solar electro-Fenton processes [47]. In the EF process, H₂O₂ is generated in-situ at the cathode and then reacts with Fe²⁺ to generate the hydroxyl radical (•OH) via Equations 2.4 and 2.1 [48], [49].



In the photoelectron-Fenton process, the pollutant is exposed to UV or visible light irradiation under electro-Fenton conditions. By reducing Fe (OH)²⁺, Fe²⁺ is regenerated, and an additional •OH radical is produced. Fe (III) can also form photoactive complexes with R(CO₂), and photolysis of these Fe (III) complexes usually makes carboxylic acids that are hard for the •OH to destroy (Equations 2.5 and 2.6) [50].



In addition, the solar-based electro-Fenton processes have been developed because of the cost of UV lamps. In this procedure, solar radiation, a renewable energy resource, is employed as a replacement for ultraviolet radiation [51].

The oldest and simplest process, anodic oxidation, happens in two ways: direct and indirect oxidation. In direct oxidation, the pollutant is directly oxidized via electron transfer on the anode surface. In indirect oxidation, the pollutant is oxidized via electrogenerated oxidants on the anode [52].

2.2.4. Wet Air Oxidation

The wet air oxidation process relies on the oxidation of organic pollutants at high temperatures (100 °C-300 °C) and pressure (0.5 MPa- 20 MPa) in the presence of an oxidant [53]. In this procedure, by utilizing air or oxygen as the oxidizing agent, organic pollutants can be effectively converted into CO₂ and H₂O or less toxic intermediates [54].

2.2.5. Sonolysis and Sonocatalysis

The use of ultrasound irradiation to degrade organic pollutants has attracted considerable interest. Ultrasound is sound waves with a certain frequency exceeding the human ear's audible range (20–1,000 kHz) [55]. Ultrasound waves comprise cycles of compression and expansion. When ultrasonic waves pass through an aqueous medium, acoustic cavitation occurs. Figure 2.1 shows the cavitation phenomenon [56].

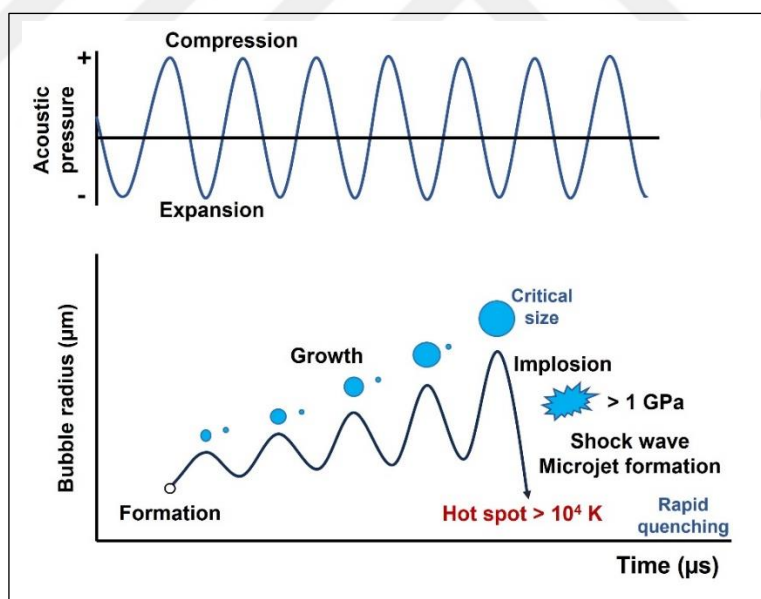
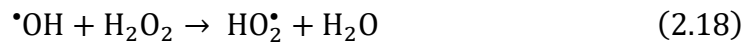


Figure 2.1: Schematic of cavitation phenomenon.

Microbubbles produced due to acoustic cavitation have a constant tendency to increase and decrease in size. When bubbles reach a size range of resonance, they achieve a maximum and collapse [57], [58]. The collapse of the bubble creates a local "hot spot" with high temperature (~5000K), and high pressure (~1000 atm) [55]. This high temperature and pressure combination causes water molecules to disassemble into

thermally highly reactive $\cdot\text{OH}$ and $\text{H}\cdot$ radicals (Equation 2.7) [59]. Additionally, some of the reactions occur according to (Equations 2.8-2.19). [60].



Compared to other methods, it has advantages such as being environmentally friendly, chemical-free, simple to operate, causing no secondary pollution, and generating oxidizing species in-situ [61]–[63]. However, sonolysis has limitations, such as high operating costs due to high energy consumption and the time necessary to completely mineralize pollutants. To overcome these limitations, ultrasonic processes can be combined with suitable catalysts to degrade pollutants [64], [65]. In

this method, known as sonocatalysis, the addition of a catalyst provides extra cavitation nuclei and increases the formation of reactive radical species, thereby enhancing the pollutants' removal performance [66]. Figure 2.2 shows the comparison of cavitation bubble formation in the sonolytic and sonocatalytic processes [67]. The mechanism of the sonocatalytic process consists of heterogeneous nucleation, sonoluminescence, and thermal catalytic mechanisms, respectively. In heterogeneous nucleation, the presence of the catalytic particle creates preferential sites on the solid surface or nucleation sites, thereby increasing the formation of cavitation bubbles and free radicals [68]. Sonoluminescence (SL) is a phenomenon that results from cavitation bubble collapsing. The light emitted during SL has a broad wavelength range (200-700 nm) and is composed of high-energy photons [69]. The energy from the produced light can exceed the band gap of the catalyst in the presence of the catalyst, leading electrons to move from the valence band (VB) to the conduction band (CB). This results in the hole generation in the valence band. Afterward, photogenerated electron-hole pairs react with accessible oxidants to produce reactive radicals [70], [71]. According to the hot spot theory, high temperatures can cause the thermal excitement of the catalyst and can also lead to the formation of electron-hole pairs [72].

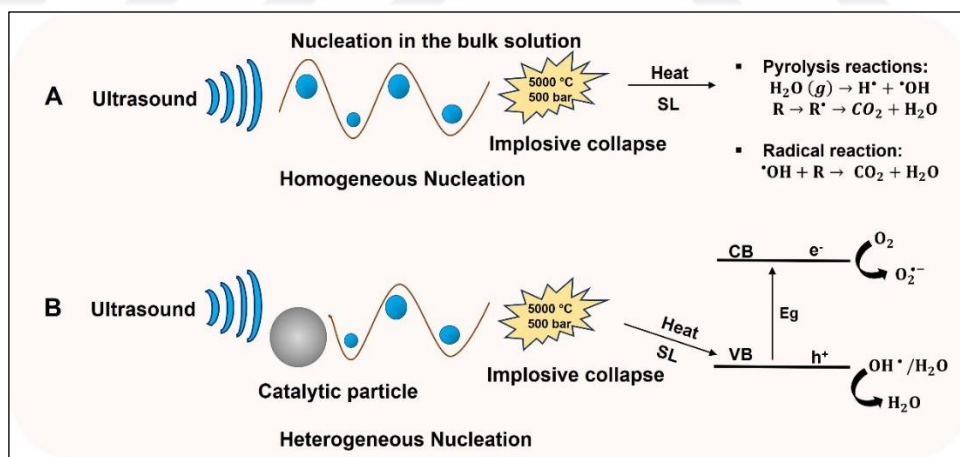


Figure 2.2: Cavitation bubble formation in sonolytic and sonocatalytic processes.

2.2.6. Photocatalysis

Among AOPs, photocatalysis garners a great deal of interest due to its cost-effectiveness, absence of secondary pollution, chemical stability of the utilized catalyst, and efficiency in pollutant removal [73].

The photocatalysis process can be categorized as homogeneous or heterogeneous. If the photocatalyst and the reaction medium are in the same phase, it is called homogeneous photocatalysis, whereas if they are not, it is referred to as heterogeneous photocatalysis [74]. The mechanism of the photocatalytic proses is shown in Figure 2.3 [75].

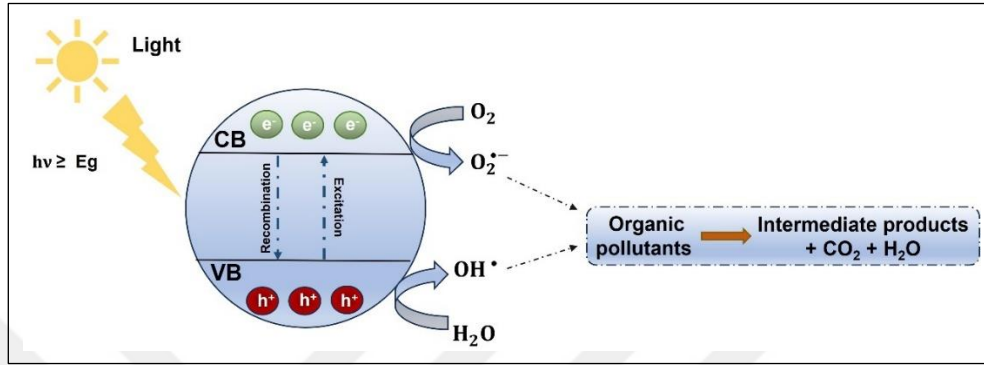
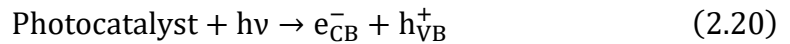


Figure 2.3: The mechanism of the photocatalytic process.

In the heterogeneous photocatalytic process, the semiconductor is initially illuminated with light. Photon absorption occurs when the excitation source's energy is equal to or greater than the bandgap energy of the semiconductor. An electron (e^-) in the valence band absorbs photon energy and is excited to the conduction band. Consequently, a hole (h^+) is formed in the valence band (Equation 2.20) [76].



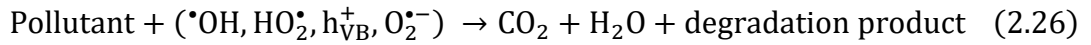
h_{VB}^+ reacts with water to produce hydroxyl radicals ($\cdot\text{OH}$) (Equations 2.21 and 2.22), and e_{CB}^- reacts with oxygen to produce $\text{O}_2^{\cdot-}$ radicals or $\text{HO}_2^{\cdot}$ radicals (Equations 2.23, 2.24, and 2.16).



After these reactions, the H_2O_2 is immediately separated by light into the $\cdot\text{OH}$ (Equation 2.25).



The radicals that are formed degrade the pollutant into CO_2 , H_2O , and intermediates via Equation 2.26 [77]–[80].

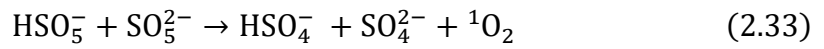
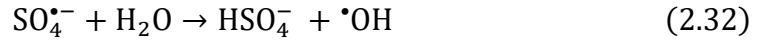
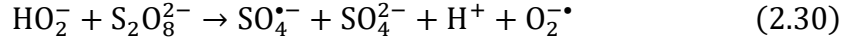
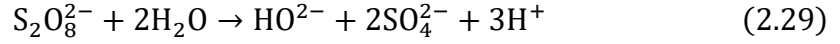
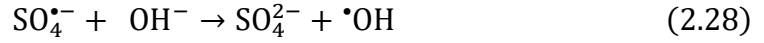


2.2.7. Persulfate-based Processes

Persulfate-based AOPs have been developed due to the properties of the $\text{SO}_4^{\cdot-}$ which include stronger oxidation potential, higher rate of radical generation, and fewer requirement reaction conditions than the $\cdot\text{OH}$ [81]. Persulfate (PS) includes peroxydisulfate (PDS) and peroxymonosulfate (PMS). Since the oxidative potential of the PS anion is less than that of the $\text{SO}_4^{\cdot-}$ radical, PS must be activated to accelerate degradation reactions and produce $\text{SO}_4^{\cdot-}$ radicals [82]. Therefore, various methods including light radiation, ultrasound irradiation, heat, transition metals, and catalysts are employed for persulfate activation [24]. The heat activation of PS is based only on the formation of $\text{SO}_4^{\cdot-}$ radicals by temperature control, with no requirement for any additives. The O-O bond of PS is absorbed and broken as the temperature of the reaction increases, resulting in $\text{SO}_4^{\cdot-}$ radical generation. Similarly, PS is activated by breaking the O-O bond in the presence of UV radiation [83].

The activation of PDS and PMS by ultrasound irradiation primarily involves the hydrolysis of water molecules (Equation 2.7). Because of the cavitation effect, PDS produces $\text{SO}_4^{\cdot-}$ (Equation 2.27). Then, $\text{SO}_4^{\cdot-}$ reacts with OH^- formed as a result of the hydrolysis of H_2O to form the $\cdot\text{OH}$ (Equation 2.28). As a result of certain reactions, various ROS can be produced (Equations 2.29 and 2.30). The PMS then generates $\text{SO}_4^{\cdot-}$ radicals under ultrasonic irradiation due to cavitation (Equation 2.31). The $\cdot\text{OH}$ radical is formed when $\text{SO}_4^{\cdot-}$ radicals react with water (Equation 2.32). In addition, the PMS reaction can generate singlet oxygen ($^1\text{O}_2$) (Equation 2.33) [84].





In addition, PS can be activated via homogenous or heterogenous catalysis. Due to the difficulty of recovering homogeneous catalysts and the metal ion leaching problem, activation with heterogeneous catalysts is preferred [85]. Radical and non-radical pathways are involved in the activation of PS by heterogeneous catalysts. Biochar, metal-doped material, and LDHs are examples of heterogeneous catalysts used in the activation of PS [86].

2.3. Layered Double Hydroxides

Layered double hydroxides (LDHs), also known as two-dimensional anionic clay or hydrotalcite-like compounds, have recently gained interest in various application fields [87]. They are represented by the general formula $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+} \cdot \text{A}^{n-}_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} is a divalent cation (Mg^{+2} , Mn^{+2} , Zn^{+2} , Ni^{+2} , etc.), M^{3+} is a trivalent cation (Fe^{+3} , Mn^{+3} , Al^{+3} , Cr^{+3} , etc.), A^{n-} is the interlayer anion, and x is molar ratio of $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$ [88], [89]. The x value is typically in the range of 0.2-0.33 i.e., the ratio $\text{M}^{2+}/\text{M}^{3+}$ is between 2:1 and 4:1 [90]. A^{n-} can be inorganic, organic, or complex biomolecule anions such as Cl^- , CO_3^{2-} , SO_4^{2-} , acetate, lactate, amino acids, etc. [91].

2.3.1. The General Structure of LDHs

The general structure of LDHs is shown in Figure 2.4 [90]. The structure of LDHs is derived from the brucite mineral $\text{Mg}(\text{OH})_2$, in which Mg^{+2} ions are octahedrally coordinated with six OH^- groups at the vertices [92]. By sharing their edges, these octahedrons form flat layers of neutral charge that are held together by hydrogen bonds [93]. As trivalent metal cations replace divalent metal cations, a positive charge occurs on the layers that are subsequently stabilized by the presence of anions and water molecules in the interlayer space [94]. Due to the lack of restrictions on the choice of divalent and trivalent cations other than charge and size, and almost no restrictions on the choice of anions between layers, LDH exhibits flexibility in composition and structure [95].

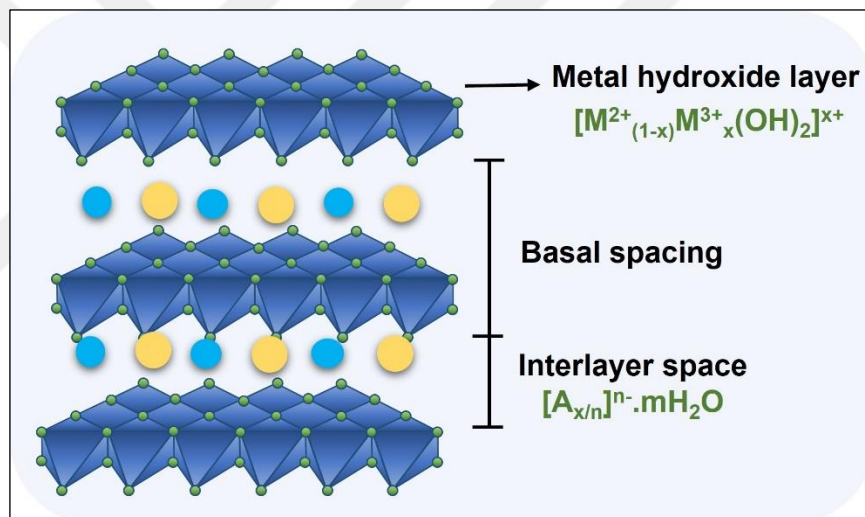


Figure 2.4: General structure of layered double hydroxides.

2.3.2. Characteristics of LDHs

The physicochemical characteristics of LDHs make them promising and practical nanomaterials that have applications in many fields. Compositional flexibility, adjustable bandgap high surface area, high anion exchange capacity, and high chemical stability are the essential characteristics of LDHs [96]. Because its structure contains covalent and electrostatic attraction and hydrogen bonding, LDH possesses high thermal stability [97]. Additionally, LDH has a "memory effect" characteristic. After the calcination process, LDHs are converted into mixed metallic

oxides. This indicates that calcined LDHs can reconstitute their original layered structure when put in a solution containing guest anions [98]. In addition, its simple synthesis, low cost, and excellent recyclability are significant properties [99,100]. Therefore, LDHs have been widely used in various applications including drug delivery systems [101], adsorption [89], [102], catalysis [103]–[105], CO₂ capture systems [106], electrochemical sensors [107], [108], supercapacitors [109] thanks to compositional variation in the layers and the interlayer anions.

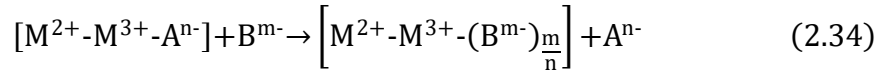
2.3.3. Synthesis Methods of LDHs

LDH and LDH-based nanocomposites can be synthesized using a variety of synthesis methods, according to the literature. The choice of synthesis technique can affect the properties of LDH and its application functionality [110]. In addition to the choice of synthesis method, other important variables in LDH synthesis include the pH of the solution, the presence of anions in its interlayers, the M^{+2}/M^{+3} ratio, drying and aging techniques, the speed at which the precursors are mixed, temperature, and pressure [111].

Co-precipitation is the most common and easy method for the preparation of LDH. This method can be performed under low or high supersaturation conditions. Co-precipitation at low supersaturation is based on slowly adding a solution containing the target anion to be intercalated into a vessel that already has a predetermined amount of divalent and trivalent cations present and then creating an alkaline environment by adding base or urea hydrolysis. Metal salts precipitate by increasing the pH and maintaining it at a specific value. A solution containing mixed metal salts is introduced dropwise to an alkaline solution containing the required interlayer anion in high supersaturation co-precipitation. Nevertheless, because the pH is continually changing in the high supersaturation co-precipitation process, less crystalline material is produced [91]. Following that, the precipitated solution undergoes a thermal treatment and aging process to improve the materials' crystallinity and purity.

In the ion exchange method, also known as the indirect method, LDH is first prepared by co-precipitation with host anions, and then it is changed with the preferred anions. When the divalent or trivalent metal cations or anions are unstable in an alkaline solution, this method can be preferred [112]. The following equation can be

used to understand the synthesis of a new phase of LDHs via an ion exchange method [91]:



where A^{n-} and B^{m-} are host anions and desired anions, respectively. The electrostatic interactions between the exchanged anions and the positively charged LDH layers determine the anion exchangeability [113].

One of the frequently used methods, the hydrothermal method, allows for the formation of LDHs with characteristics like high crystallinity, small particle size, and large surface area [114]. LDH's characteristics are improved, and its efficiency is increased by using the hydrothermal method in addition to other synthesis techniques [115].

The reconstruction method known as the memory effect method may also be used to synthesize LDH. This method is based on calcining LDHs at high temperatures (300-500 °C) to remove their anions, water molecules, and hydroxyl groups from their interlayers to obtain mixed metal oxides [116]. In addition, these calcined LDHs can regenerate when exposed to water and anions.

Due to its high-water solubility and weak Bronsted base characteristics, urea can be employed as a precipitating precursor in the synthesis of LDH [117]. The urea hydrolysis method is based on mixing the metal ion solution and the urea solution, followed by the decomposition of the urea by hydrothermal treatment. Due to the slow rate of urea hydrolysis, this method results in LDH production with high crystallinity and homogenous particle distribution [112]. However, using this method only for synthesizing LDH-containing carbonate interlayer reduces its applicability [114].

2.3.4. Modification of LDHs

LDHs are employed as an efficient catalyst for the decomposing of persistent organic pollutants. However, the catalytic performance of LDHs may be impacted by their low charge transfer efficiency and irregular aggregation [118]. Some strategies are developed to enhance the physic-chemical properties and catalytic activity of LDHs. Moreover, modification strategies enable the design and production of catalysts

based on new functional LDHs [100]. The application of some modified LDHs in AOP methods is given in Table 2.2. The primary techniques for modification include the adjustment of active metal ions, the adjustment of intercalated anions, and the modification of the active sites [119]. For instance, anion intercalation increases the structure's stability by balancing the positive charge of brucite layers. Various anions such as inorganic anions, metal complexes, phthalocyanine, and polyoxometalates, are utilized depending on the application [120].

Cation or anion doping is one of the most effective strategies for enhancing the catalytic performance of LDHs. In cationic doping, another cation is introduced into the main layer of LDHs to replace the divalent or trivalent cation, whereas, in anionic doping, anions with a high-resolution product constant are introduced into the host layer to partially replace the hydroxyl group in the octahedral units [119]. The charge density of the LDH laminates is modified and efficient separation of the photogenerated hole with the photo-excited electron is achieved by doping agents such as noble metal, transition metal, and rare earth elements to the basic octahedral structure of LDHs, thereby improving the catalytic performance of LDH [121], [122]. In metal element doping, rare earth elements with abundant reserves, high stability, and oxygen storage-release capacity are particularly interesting [118]. Rare earth elements can effectively capture photogenerated electrons, thereby impeding the recombination of photogenerated electrons and holes [123]. For instance, Wani et al. synthesized neodymium-ZnAl LDH (Nd-ZnAl LDH) by hydrothermal technique, and Nd-ZnAl LDH showed higher photocatalytic activity than ZnAl LDH because Nd reduced electron-hole pair recombination [124]. Furthermore, the introduction of Nd doping enhanced the specific surface area of ZnAl LDH, leading to an enhanced adsorption capacity for pollutant molecules on its surface. In another study, Ce doping was used to modify ZnAl LDH to enhance its phenol degradation efficiency [125]. Undoped LDH and Ce-doped LDH achieved the photocatalytic degradation of phenol is 63% and 90%, respectively. This increase in degradation efficiency can be attributed to increased electron-hole separation by Ce doping.

Another modification method is in combination with semiconductor, carbon-based, and magnetic materials [126]. Many metal oxides, including TiO_2 , Cu_2O , NiFe_2O_4 , CeO_2 , ZnTiO_3 , Fe_3O_4 , SnO_2 , ZnFe_2O_4 , and can be combined with LDH due to its high stability and absorption capabilities. This results in an increase in specific

surface area and efficient separation of photo-induced electrons (e^-) and holes (h^+), which improves the efficiency of LDHs [100], [127].

Due to their high specific surface area, electrical conductivity, chemical stability, and durability, carbon-based materials such as biochar (BC), graphitic carbon nitride ($g-C_3N_4$), carbon fibers, carbon quantum dots, graphene, carbon nanotubes (CNTs) and are combined with LDHs [100]. For example, Gholomi et al. [128] incorporated the BC material into the ZnCo LDH structure and used it to remove gemifloxacin under UV light irradiation. When ZnCoLDH was combined with BC, the removal efficiency of gemifloxacin increased by 32.3%, attributed to the reduction in LDH aggregation and decreased electron/hole recombination rate.



Table 2.2: Utilization of modified LDHs in various AOP applications.

Modification type	LDH type	Synthesis method	Pollutant	Degradation process	Ref.
Doping	V-ZnFe	Co-precipitation	Pymetrozine	Sonocatalytic degradation	[129]
Doping	Nd-ZnAl	Hydrothermal	Congo red, Rose Bengal, Fast green dye	Photocatalytic degradation	[124]
Doping	Ce-ZnAl	Co-precipitation	Phenol	Photocatalytic degradation	[125]
Doping	Mn-MgAl	Co-precipitation	Phenol	Persulfate activation	[130]
Doping	La- CoFe	Co-precipitation	Tetracycline	Persulfate activation	[131]
Heterostructure formation and doping	F and Cl-g-C ₃ N ₄ /ZnAl	Co-precipitation	Tetracycline	Photocatalytic degradation	[132]
Heterostructure formation	g-C ₃ N ₄ / Ce- MgAl	Solvothermal	Congo red organic dye	Photocatalytic degradation	[133]
Heterostructure formation	r-GO/NiFe	Hydrothermal	Moxifloxacin	Sonophotocatalytic degradation	[134]
Heterostructure formation and doping	S and Graphitic Carbon Nitride/NiFe	Co-precipitation	2,4-Dinitrophenol	Photocatalytic degradation	[135]
Heterostructure formation	CdS/ZnCr	Hydrothermal	Tetracycline	Photocatalytic degradation	[136]
Heterostructure formation	BC@ZnCo	Hydrothermal	Gemifloxacin	Photocatalytic degradation	[128]

2.3.5. Applications of LDHs on Sonocatalytic and Photocatalytic Processes

LDH and LDH-based nanocomposites are used in many AOP methods due to their excellent properties. LDHs are increasingly used as semiconductor material in the sonocatalytic and photocatalytic degradation of pollutants. Table 2.3 demonstrates the sonocatalytic degradation activity of several LDHs and LDH-based materials. For example, Gholami et al. [137] utilized FeCu LDH for the sonocatalytic decomposition of cefazolin sodium. While the sonolysis process had a degradation efficiency of 6.8% for cefazolin sodium, the efficiency was enhanced to 73.4% when FeCu LDH was used as a sonocatalyst. In another study, Sadeghi Rad et al. [138] synthesized rGO-CuCr LDH for sonocatalytic degradation of dimethyl phthalate. While the rGO-CuCr LDH alone had a 30% dimethyl phthalate degradation efficiency, the combination of ultrasonic irradiation and rGO-CuCr LDH increased the removal efficiency to 72%.

In addition, the photocatalytic degradation of different pollutants through LDH and LDH-based nanocomposites is shown in Table 2.4. For instance, Acatitla et al. [139] synthesized MgAl LDH for the photocatalytic degradation of oxytetracycline. Under UV-light, MgAl LDH dosage of 0.5 g/L was used to degrade 50 mg/L of oxytetracycline, achieving a 70% degradation within 300 min. Wang et al. [140] examined the performance of ZnFe-LDH for tetracycline photocatalytic degradation. In this study, 15 mg/L of tetracycline was degraded 66.9% in 120 min using 1 g/L ZnAl LDH under 500 W visible light.

Table 2.3: Applications of some LDHs and LDH-based materials on the sonocatalytic process.

LDH Type	Pollutant	Experimental Conditions	Degradation Efficiency (%)	Ref.
FeCu	Cefazolin sodium	[Catalyst]: 1 g/L, [Pollutant]: 0.1 mM, US power: 300 W, pH: 6.5, contact time:80 min.	73.4	[137]
ZnFe	Acid Red 17	[Catalyst]: 0.5 g/L, [Pollutant]: 20 mg/L, US power: 300 W, pH: 6, contact time: 120 min	92	[141]
rGO/NiFe	Moxifloxacin	[Catalyst]: 1 g/L, [Pollutant]: 20 mg/L, US power: 150 W, pH: 8, contact time: 60 min	72.4	[134]
rGO/ZnCr	Rifampicin	[Catalyst]: 1.5 g/L, [Pollutant]: 15 mg /L, US power:150 W, pH: 8, contact time: 60 min	64.3	[142]
rGO/CuCr	Dimethyl phthalate	[Catalyst]: 0.75 g /L, [Pollutant]: 15 mg /L, US power: 150 W, pH: 8, contact time: 30 min	72	[138]
CuZnTi	Methylene blue	[Pollutant]: 10 mg/L, [Catalyst]: 0.5 g/L, pH: natural pH , contact time: 90 min	71	[103]

Table 2.4: Applications of some LDHs and LDH-based materials on the photocatalytic process.

LDH type	Pollutant	Light source	Experimental conditions	Degradation Efficiency (%)	Ref.
ZnCo	Gemifloxacin	UV- light	[Pollutant]: 15 mg/L, [Catalyst]: 0.75 g/L, pH: 5.5, Light intensity: 10 W (UV-B) Contact time:130 min	60.4	[128]
MgAl	Oxytetracycline	UV- light	[Pollutant]: 50 mg/L, [Catalyst]: 0.5 g/L Light intensity: 2.16 W pH: natural pH, Contact time: 300 min	70	[139]
ZnAlTi	Methylene blue	Solar light	[Pollutant]: 10 mg/L, [Catalyst]: 1 g/L, pH: natural pH, Contact time:120 min	99	[143]
Ag/ZnO/ZnAl	Bisphenol A	Visible light	[Pollutant]: 10 mg/L [Catalyst]: 0.5 g/L, pH:7, Light intensity: 120 W, Contact time:360 min	80	[144]
SnO ₂ /ZnAl	4-chlorophenol	Xenon lamp	[Pollutant]: 10 mg/L, [Catalyst]: 0.4 g/L, Light intensity:500 W	95.2	[145]
ZnFe	Tetracycline	Visible light	[Pollutant]: 15 mg/L, [Catalyst]: 1 g/L, Light intensity: 500 W Contact time: 120 min	66.9	[140]

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. Test Compounds

In this study, two separate refractory organic pollutants from the herbicide and antibiotic classes were chosen as the model pollutants. These pollutants are metribuzin and rifampicin, respectively.

Metribuzin, a herbicide of the triazine class, is employed to control of weeds [146]. This herbicide, which is extensively used due to its low cost and effectiveness, can contaminate surface and groundwater through runoff and leaching due to its physicochemical properties [147]. Due to its half-life of 5-50 days, high solubility, resistance to hydrolysis, and toxicity, it poses a threat to aquatic life [148,149]. Metribuzin exhibits high toxicity towards aquatic organisms, as evidenced by its 96-h LC50 values for rainbow trout ranging from 42 to 76 mg/L, 96-h LC50 value of 175.1 mg/L for carp, and 48-h LC50 value of 150 mg/L for copepods [150]–[152]. In addition, exposure to metribuzin causes toxic symptoms in mammals on the activities of the central nervous system and organs such as the liver and kidneys [153]. The characteristics of this pollutant are described in Table 3.1 [154], [155].

Table 3.1: Physicochemical properties of metribuzin.

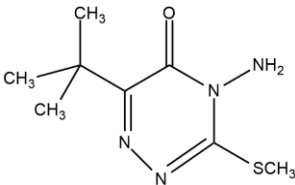
Name	Metribuzin
IUPAC name	4-amino-6-tert-butyl-3-methylsulfanyl-1,2,4-triazin-5-one
CAS Number	21087-64-9
Molecular 2-D Structure	
Molecular formula	C ₈ H ₁₄ N ₄ OS

Table 3.1: Continued.

Molecular weight	214.29 g/mol
Acid dissociation constant (pKa)	1.0
Octanol-water partitioning coefficient (log Kow)	1.7
$\lambda_{\max}$ (nm)	294

Rifampicin a semi-synthetic broad-spectrum antibiotic, is widely utilized in tuberculosis treatment. This antibiotic inhibits DNA-dependent RNA synthesis, thereby inhibiting bacterial growth [156]. It is of concern because of its low biological stability and high water solubility, as well as the emergence of antibiotic-resistant bacteria if released into the aquatic environment [157]. Moreover, its toxicity to both humans and animals is quite considerable. The LC50 value for *Artemia salina* was determined to be 312.94 $\mu\text{g/mL}$, while the LD50 values for rats and mice were 550 and 640 mg/kg, respectively [158], [159]. The characteristics of rifampicin are described in Table 3.2 [160].

Table 3.2: Physicochemical properties of rifampicin.

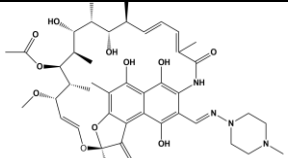
Name	Rifampicin
IUPAC name	5,6,9,17,19,21-hexahydroxy-23-methoxy-2,4,12,16,18,20,22-heptamethyl-8-[N-(4-methyl-1-piperazinyl)formimidoyl]-2,7-(epoxypentadeca[1,11,13]trienimino)-naphtho[2,1-b]furan-1,11(2H)-dione 21-acetate
CAS Number	13292-46-1
Molecular 2-D Structure	
Molecular formula	$\text{C}_{43}\text{H}_{58}\text{N}_4\text{O}_{12}$
Molecular weight	822.9 g/mol
Acid dissociation constant (pKa)	1.7

Table 3.2: Continued.

Octanol-water partitioning coefficient (log K _{ow})	4.24
$\lambda_{\max}$ (nm)	334

3.1.2. Characteristic of Wastewater

Real wastewater was collected from the Gebze Organized Industrial Zone in Turkey. The wastewater sample was collected in plastic bottles and transported to the laboratory immediately. It was then stored in the refrigerator at +4°C to prevent any biological activity. Table 3.3 provides details about a wastewater sample.

Table 3.3: Characteristic of wastewater sample.

pH	7.75
Temperature (°C)	23
Electrical conductivity (μs/cm)	1905
COD (mg/L)	60
TOC (mg/L)	16

3.1.3. Reagents

Lanthanum (III) chloride heptahydrate (LaCl₃·7H₂O), zinc chloride (ZnCl₂), potassium peroxydisulfate (K₂S₂O₈²⁻), potassium hydrogen monopersulfate (2KHSO₅·KHSO₄·K₂SO₃, 98%), iron (III) chloride hexahydrate (FeCl₃·6H₂O, ≥ 99%), hydrogen peroxide (H₂O₂, 30%), sodium hydroxide pellets (NaOH, 99%), 1,4-benzoquinone (C₆H₄O₂, 99%), isopropanol ((CH₃)₂CHOH, ≥ 99.5%), ethanol (C₂H₅OH, ≥ 99.5%), hydrochloric acid (HCl, 30%), sodium percarbonate (Na₂CO₃·1.5H₂O₂), sodium nitrate (NaNO₃, 99%), formic acid (HCOOH), N,O-Bis(trimethylsilyl)acetamide (C₈H₂₁NOSi₂), diethyl ether ((C₂H₅)₂O), and nitric acid (HNO₃, 65%), purchased from Merck, Germany. Dow Corning Corporation (USA) supplied the polydimethylsiloxane prepolymer (PDMS, Sylgard 184A) and curing agent (Sylgard 184B). Cube sugar (Dogus cube sugar, 20 mm × 10 mm × 10 mm) was purchased from the local market in Turkey.

3.2. Experimental Procedures

3.2.1. Preparation of ZnFe and LaZnFe LDHs

Following the co-precipitation technique, undoped LDH and LaZnFe LDH were synthesized. For ZnFe LDH, 3 mmol ZnCl_2 and 1 mmol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 120 mL of distilled water under N_2 atmosphere. 0.2 mol/L of NaOH was slowly added to adjust the pH to 8. The solution in the magnetic stirrer was aged for 24 h following pH adjustment. The precipitates were centrifuged and repeatedly washed with distilled water. Finally, powdered ZnFe LDH was obtained after drying for 7 h at 50 °C in an oven.

For LaZnFe LDH synthesis, 3 mmol ZnCl_2 , 1 mmol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ were added to 120 mL distilled water. The remaining synthesis processes are the same as for ZnFe LDH synthesis. The schematic illustration of the preparation procedure of LaZnFe LDH is illustrated in Figure 3.1.

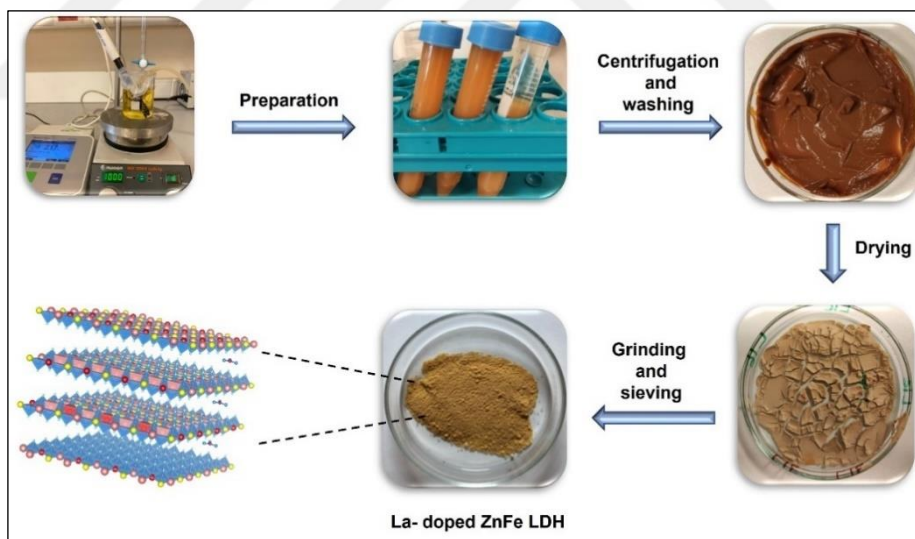


Figure 3.1: Synthesis procedure of LaZnFe LDH.

3.2.2. Preparation of LaZnFe LDH@PDMS Sponges

Firstly, the LaZnFe LDH was added to 1 mg/mL ethanol and exposed to ultrasonication for 15 min to prepare LaZnFe LDH immobilized porous polydimethylsiloxane (PDMS) sponges. This catalyst dispersion was absorbed into

sugar cubes, which were then dried for 24 h at 50 °C in the oven. Around 0.024 g of catalyst on a sugar cube after the catalyst coating procedure was carried out ten times. After repeated coating processes, the catalyst-coated sugar was kept in a vacuum oven for 48 h at 40 °C. In Petri dishes, Sylgard 184A and 184B elastomers were mixed at a ratio of 10:1, respectively. To remove the air bubbles from the catalyst-coated sugar, it was immersed into the PDMS elastomer mixture and then kept in a vacuum at 3 Pa at room temperature for 3 h. The sugar cube used as a template was removed by repeatedly washing it in distilled water heated at 90 °C. Lastly, porous PDMS sponges immobilized with LaZnFe LDH were dried at 50 °C in a vacuum oven for a week. Figure 3.2 depicts the production of the LaZnFe LDH catalyst immobilized on porous PDMS sponges.

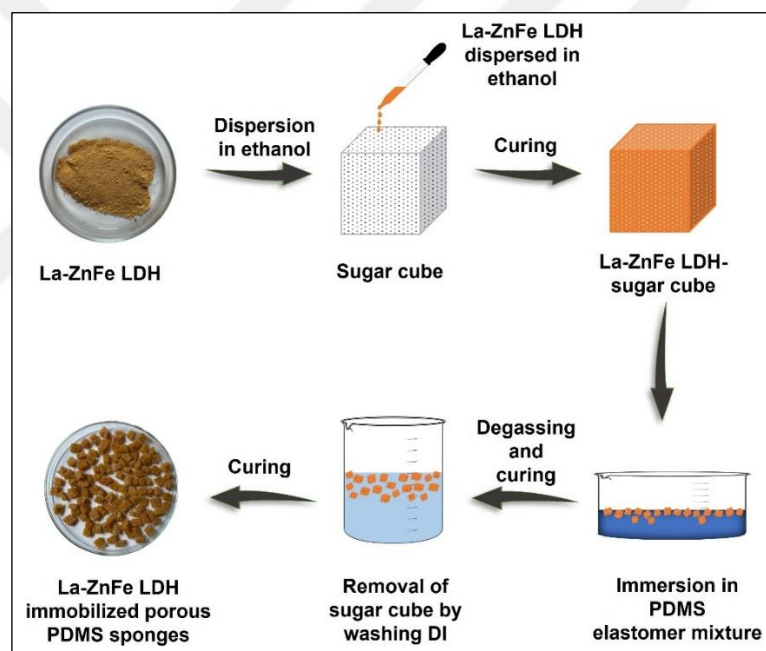


Figure 3.2: Schematic illustration of the preparation of LaZnFe LDH embedded PDMS sponges.

3.2.3. Sonocatalytic Process Procedure

Experiments were carried out in a VWR USC300T model ultrasonic bath. The device has a total volume of 2.8 L and a frequency of 45 kHz with an output power of 120 W. During experiments, the reactor temperature was kept constant at $25 \pm 1^\circ\text{C}$ by the use of ice cubes. An image of the experimental set-up is given in Figure 3.3. For the sonocatalytic degradation process, metribuzin was used as a model pollutant. The

Erlenmeyer was placed into the ultrasonic bath with a volume of 100 mL of metribuzin solution. Before starting the experiment, the distance between the erlenmeyer and the ultrasonic probe was set to 4 cm. Firstly, a predetermined amount of LaZnFe LDH and PDS was added to the solution. For a total of 90 min of the experiment, 5 mL samples were collected every 10 min, and 1 mL of ethanol was added to each sample. Finally, UV-Vis spectrophotometer was utilized to measure the absorbance of the metribuzin solution after the samples were filtered through a 0.22 μm syringe filter. The optimum initial metribuzin concentration, LaZnFe dosage, pH, PDS dosage, and US power were determined based on the efficiency of degradation. The role of reactive oxygen species in the degradation process was determined with scavenger test. The effect of the sonocatalytic process on the degradation of various pollutants, including rifampicin, phenazopyridine, and methylene blue was studied. Additionally, US/LaZnFe LDH/PDS process was studied with real wastewater. Before conducting the experiment, 15 mg/L of metribuzin was added to the wastewater, and the total volume of the solution was adjusted to 100 mL. The experiment was conducted for 360 min under optimal conditions. At intervals of 90 min, 5 mL samples were collected and subsequently subjected to filtration using a 0.22 μm syringe filter. The performance of the process in the wastewater matrix was evaluated by measuring the absorbance of metribuzin in wastewater using a UV-Vis spectrophotometer.



Figure 3.3: Experimental set-up for sonocatalytic process.

3.2.4. Photocatalytic Process Procedure

The experimental setup of the antibiotic degradation process is shown in Figure 3.4. For investigating the photocatalytic activity of the LaZnFe LDH embedded PDMS sponge, a 100 W LED lamp was used as the visible light source. Rifampicin was a

model pollutant for photocatalytic experiments. All experiments were performed under visible light irradiation. All experiments were operated in a 250-mL crystallizing dish under magnetically stirring at room temperature. Before starting the experiment, the sponges were added to the rifampicin solution. The solution was stirred, and a certain amount of PMS was added at predetermined time intervals during the 60-min irradiation. During the experiment period, 3 mL of solution was taken out from the solution at given intervals and 1 mL of ethanol was added to each sample. The residual rifampicin concentration was measured by a UV–Vis spectrophotometer. In this study, the effect of initial rifampicin concentration, LaZnFe LDH@PDMS sponge amount, pH, PMS dosage, and light power were optimized for the effective degradation of rifampicin. The impact of reactive oxygen species on the degradation process was assessed through scavenger experiment. Moreover, the efficacy of the visible light/LaZnFe LDH@PDMS sponge/PMS process was evaluated using actual wastewater. Before the experiment, which was conducted under optimum conditions, 15 mg/L of rifampicin was added to the wastewater, and the volume of the total solution was adjusted to 200 mL. After collecting 5 mL samples every 90 minutes, the efficacy of the process in the wastewater matrix was evaluated by measuring the rifampicin absorbance in the wastewater using a UV-Vis spectrophotometer.

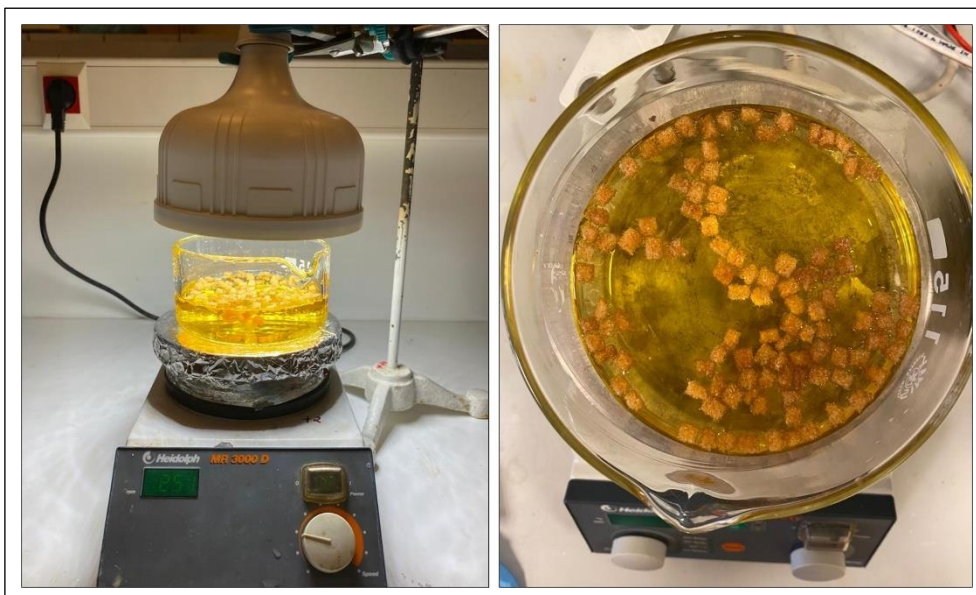


Figure 3.4: Experimental set-up for the photocatalytic process.

3.3. Analytical Procedure

3.3.1. Characterization Methods of As-Synthesized Materials

To determine the crystal structure of samples, XRD Bruker D8 Advance diffractometer (Germany) with and Cu K α source (λ :1.5406 Å) operating at a voltage of 40 kV and Tongda-TD-3700 diffractometer (China) with Cu K α source (λ :1.5406 Å) operating at a voltage of 30 kV was used. The surface functionality of as-prepared materials was evaluated using Fourier Transform Infrared (FTIR) spectrophotometer (Perkin Elmer Spectrum 100, Germany). The surface morphologies of materials were examined via scanning electron microscope (Tescan, MIRA 3, Czech Republic and Philips XL30 SFEG, the Netherlands). was examined with the transmission electron microscope (JEOL JEM-2100 Plus, Japan) operated at 200 kV was utilized to examine the microstructure of catalyst. The elemental composition of samples was analyzed via EDX spectrometer (Philips XL30 SFEG, Netherlands). The optical properties of LaZnFe LDH were analyzed using Ultraviolet–visible (UV–Vis) diffuse reflection spectra (DRS) (Shimadzu UV-2600 spectrophotometer, Japan). The surface chemical states and the compositions of LaZnFe LDH were characterized by X-ray photoelectron spectroscopy (Thermo Scientific Escalab 250Xi+, USA). The surface area and pore volume of samples were determined by analyzing the N₂ adsorption-desorption isotherm with the Brunauer–Emmett -Teller (BET) instrument (BELSORP Mini II, Japan), Finally, inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7800, USA) was utilized to evaluate the leaching of components.

3.3.2. Generating Calibration Curves and Determination of Pollutant Concentration

First, the wavelengths of the model pollutants were scanned in the UV-Visible Spectrophotometer and the maximum absorbance wavelengths (λ_{max}) were determined. The λ_{max} for metribuzin and rifampicin were found as 294 nm and 334 nm, respectively.

Standard solutions of 5,10,15,20,25,30 and 35 mg/L of each pollutant were prepared to generate calibration curves. Using a UV-Vis spectrophotometer, standard solutions of rifampicin and metribuzin were analyzed at 334 nm and 294 nm,

respectively, and concentration-absorbance graphs were obtained. The calibration curve of metribuzin and rifampicin are shown in Figures 3.5 and 3.6.

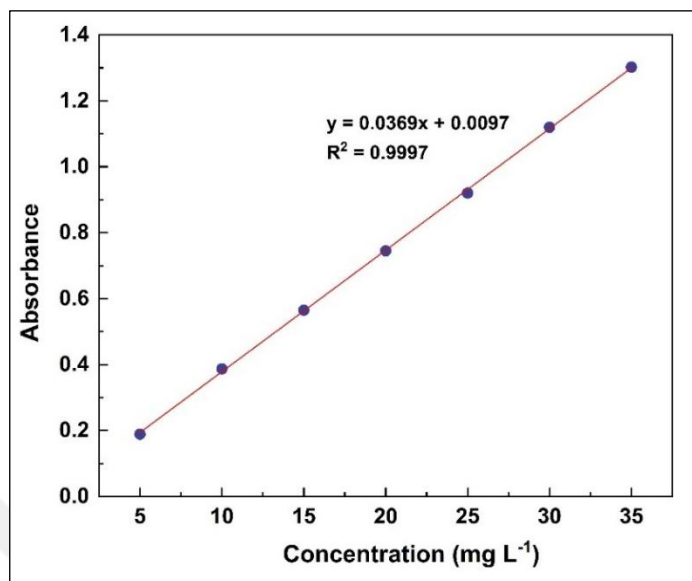


Figure 3.5 The calibration curve of metribuzin at 294 nm.

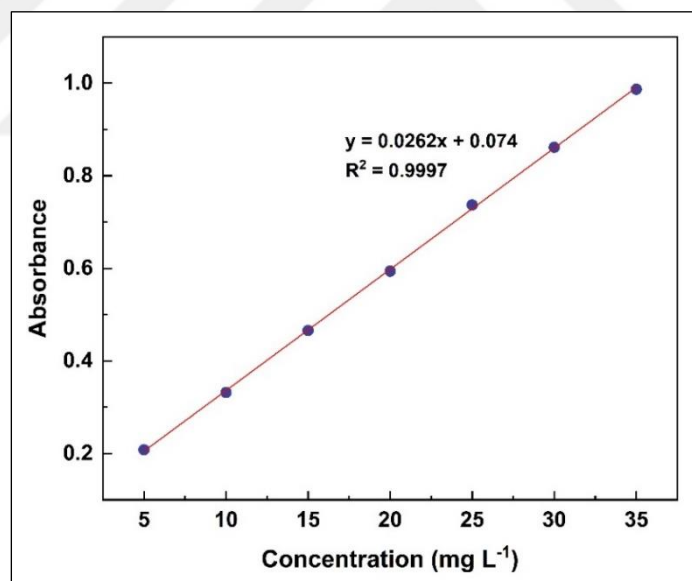


Figure 3.6: The calibration curve of rifampicin at 334 nm.

The degradation rate of pollutants was determined according to the following formula (Equation 3.1) by measuring the absorbance of pollutants at a $\lambda_{\max}$.

$$\text{Degradation efficiency (\%)}: \frac{C_0 - C_t}{C_0} \times 100 \quad (3.1)$$

where, C_0 and C_t are the initial and instantaneous pollutant concentration values after the degradation process, respectively.

3.3.3. Determination of Point of Zero Charge

To determine the pH value at which the net surface area of the catalyst is equal to zero, the zero charge point (PZC) was calculated using the pH drift method. This was accomplished by adjusting the initial pH of the erlenmeyers containing 20 mL of 0.1 mol/L NaNO_3 to 2,4,6,8, and 10. Then, 1 g/L of LaZnFe LDH was added and the erlenmeyer was shaken. After 24 hours of shaking, the solutions' final pH was measured. The catalyst's pH_{pzc} was determined by plotting the initial pH values against the difference between the final and initial pH.

3.3.4. Determination of Intermediates

To detect by-products produced on the sonocatalytic and photocatalytic processes, gas chromatography-mass spectrometer (GC-MS) (Agilent 6890N, USA) was used. Under optimal conditions, metribuzin and rifampicin were treated for 30 min to identify intermediates formed during the photocatalytic degradation of rifampicin and the sonocatalytic degradation of metribuzin. After the solution was filtered through a 0.45 μm filter, organic components were extracted twice with diethyl ether. Diethyl ether was evaporated, and the residual material was dissolved in 100 μL of N,O-bis(trimethylsilyl)acetamide and agitated for 15 min at 60 °C. Finally, the intermediate products produced during the degradation processes were determined by GC-MS analysis.

4. RESULTS AND DISCUSSION

4.1. Degradation of Metribuzin via PDS- Assisted Sonocatalytic Process

4.1.1. Characterization of LaZnFe LDH

The crystalline structure of LDHs was determined with XRD analysis. Figure 4.1 shows the XRD pattern of LDHs before and after La-doping. The characteristic peaks at 2θ : 11.38° , 28.28° , 30.52° , 32.7° , 34.76° , 37.16° , and 58.36° belong to the (003), (110), (101), (009), (012), (015) and (110) plane of ZnFe LDH, respectively (JCPDS 38–0486). LaZnFe LDH had a similar pattern to ZnFe LDH, indicating that the structure of LDH was preserved. Additionally, the peak's position did not change after La-doping, as shown by the magnified region in Figure 4.1. However, the relatively broadened peak demonstrated that the La doping had an impact on LDH's crystallinity and caused a decrease in the crystallinity of the material.

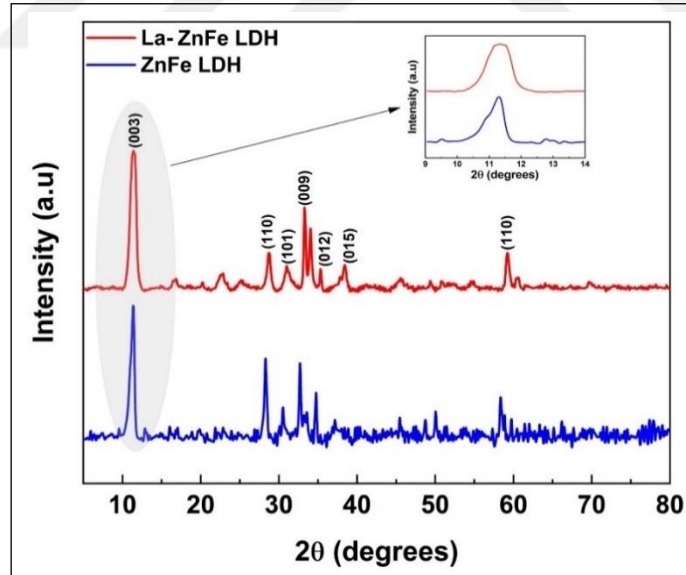


Figure 4.1: The XRD patterns of as-prepared materials.

The interplanar spacing of samples was determined with the Bragg formula:

$$n\lambda = 2d \sin \theta \quad (4.1)$$

where d , n , λ , and θ are interlayer distance, diffraction order, X-ray wavelength (nm), and diffraction angle, respectively. The undoped LDH has an interplanar spacing value of 7.76 Å, whereas LaZnFe LDH has a value of 7.88 Å. La-doping did not affect the distance between cations, which was determined to be 3.14 Å. The distance between the layers for undoped LDH and LaZnFe LDH was determined to be 23.28 Å and 23.64 Å, respectively. The H₂O molecules between the layers can be responsible for the increased distance between the layers. In addition, the main crystallite size of LaZnFe LDH was determined as 17 nm using the Debye–Scherrer Equation [161].

The functional groups of materials were examined via FTIR analysis. As demonstrated in Figure 4.2, the FTIR peaks of undoped LDH and LaZnFe LDH were quite similar. The bands related to the metal-oxygen (M-O) and oxygen-metal-oxygen (O-M-O) stretching vibrations appeared below 1030 1/cm [162]. The bands between 1350 and 1500 1/cm are attributed to the stretching vibration of carbonate anions in the interlayer [163]. The peaks at 1607.5 1/cm corresponded to the bending vibration of the interlayer water molecules [164]. The characteristic absorption peaks at 3455.5 1/cm are associated with the stretching vibration of hydrogen-bonded hydroxyl groups from both the interlayer water and the hydroxyl group in the layers [129].

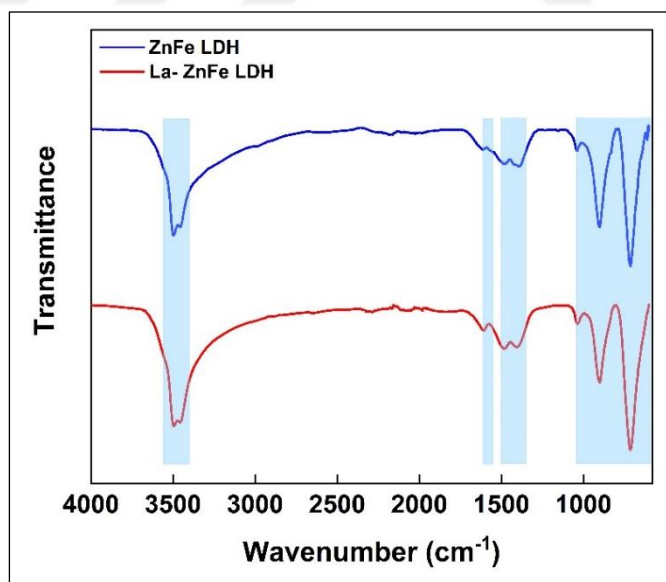


Figure 4.2: The FT-IR spectra of as-prepared materials.

The surface morphology of LaZnFe LDH is shown in Figure 4.3. From the SEM images, it can be observed that the LaZnFe LDH had lamellar structure. In addition,

using ImageJ software, the average thickness of as-synthesized material was determined as 26 nm.

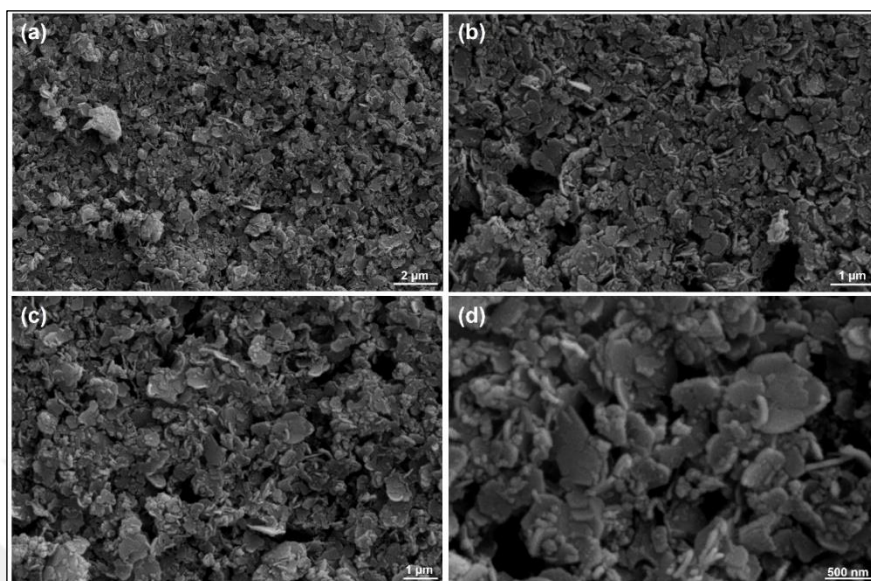


Figure 4.3: The SEM images of LaZnFe LDH at a) 2 μm , b) 1 μm , c) 1 μm , and d) 500 nm.

The element distribution in LDH was provided by EDX analysis. As can be seen in Figure 4.4, O, Cl, La, Fe, and Zn elements appeared in the EDX spectrum with the percentages of atomic 31.04%, 8.74% and 1.52%, 7.17%, and 51.54%, respectively.

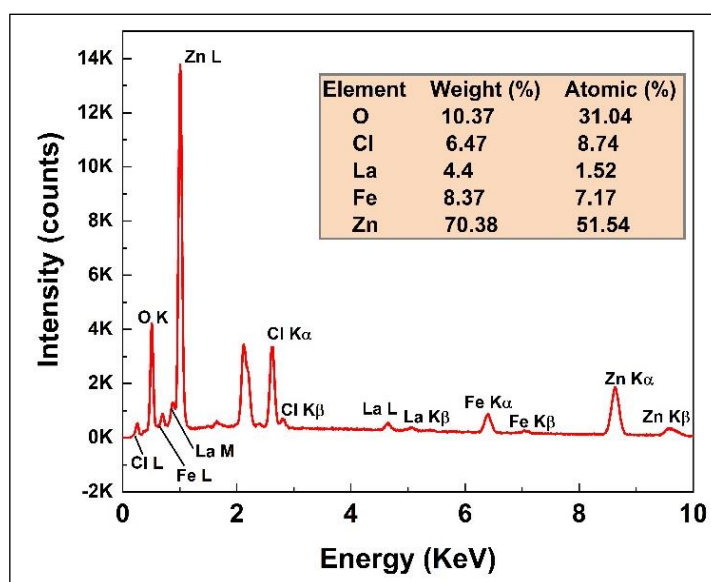


Figure 4.4: The EDX spectrum of LaZnFe LDH.

To determine lattice morphology, TEM and HRTEM analyses were performed (Figure 4.5). TEM images highlighted the lamellar structure of LaZnFe LDH. Furthermore, the HRTEM images indicated the interplanar spacing of 0.32 nm is ascribed to the (110) plane of LaZnFe LDH.

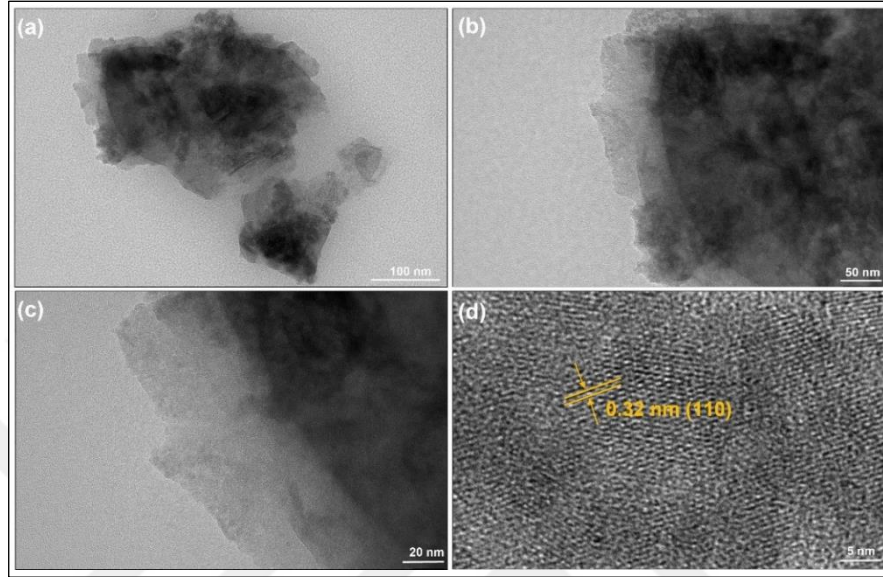


Figure 4.5: TEM and HRTEM images of LaZnFe LDH at a) 100 nm b) 50 nm c) 20 nm, and d) 5 nm.

Textural features of LaZnFe LDH such as specific surface area (S_{BET}), pore volume, and porosity were investigated by N_2 adsorption-desorption isotherms (Figure 4.6). In accordance with the IUPAC standard, the adsorption-desorption hysteresis loop curve revealed a type IV isotherm, indicating that LaZnFe LDH possessed a mesoporous structure. The specific surface area of LaZnFe LDH was found as $110.93 \text{ m}^2/\text{g}$. Besides, the average pore diameter and pore volume (V_{m}) of LaZnFe LDH were found to be 9.67 nm , and $0.27 \text{ cm}^3/\text{g}$, respectively. According to previous studies, the S_{BET} of ZnFe LDH can range from 46.9 to $108.8 \text{ m}^2/\text{g}$. Because La-doping increases surface roughness, LaZnFe LDH has a greater specific area than ZnFe LDH. Increased specific surface area can supply more electroactive sites, thus boosting the charge storage ability of LDH [165]. Moreover, as the S_{BET} improves, active site quantity also increases, leading to an enhancement in the efficiency of the degradation mechanism [166].

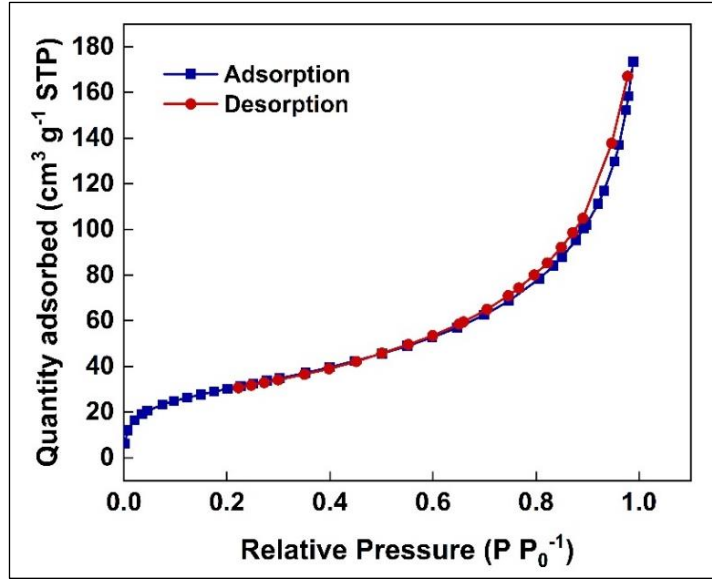


Figure 4.6: N₂ adsorption–desorption isotherm of LaZnFe LDH.

The optical properties of LaZnFe LDH were identified utilizing UV-Vis diffuse reflectance spectroscopy (DRS) with a wavelength range of 200 to 800 nm. Figure 4.7 shows UV–vis DRS spectra and the bandgaps (E_g) of LaZnFe LDH. The LaZnFe LDH shows absorption performance in the UV wavelength region with an absorption peak at nearly 300 nm. From the Kubelka-Munk function (Equation 4.2), the E_g of LaZnFe LDH was calculated:

$$\alpha h\nu: A (h\nu - E_g)^{\frac{n}{2}} \quad (4.2)$$

where α is absorption coefficient h is Planck's constant, ν is light frequency and n is semiconductor type ($n:1$ for direct transition) [167]. The E_g was calculated as 2.40 eV by Kubelka–Munk function.

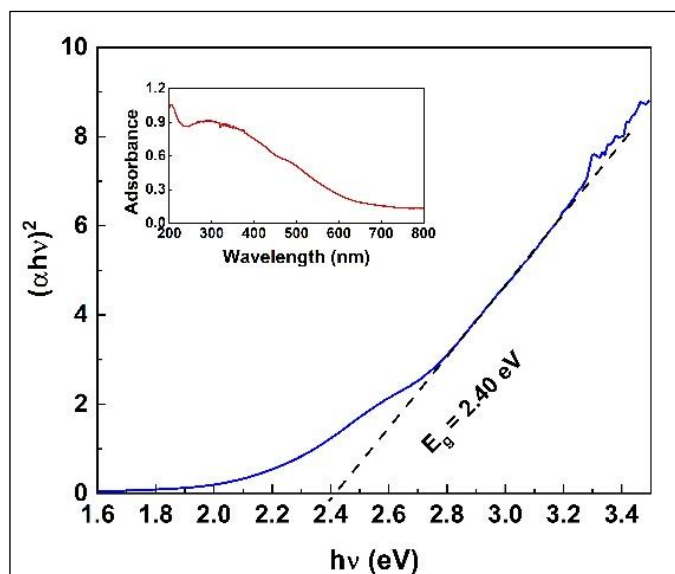


Figure 4.7: Kubelka-Munk transformed function plots for LaZnFe LDH (inset shows the UV-vis absorption spectra).

As illustrated in Figure 4.8, X-ray photoelectron spectroscopy (XPS) was used to evaluate the chemical composition and the chemical bonding state of the catalyst. The survey scan of LaZnFe LDH showed that it contains Zn, Cl, La, Fe, O, and C elements. The binding energy of 1022.10 and 1045.30 eV were respectively for Zn 2p_{3/2} and Zn 2p_{1/2} of Zn 2p. In the high-resolution Fe 2p spectrum of LaZnFe LDH, two peaks at 711.10 and 724.70 eV are attributed to Fe 2p_{3/2} and Fe 2p_{1/2}. Furthermore, three peaks at 704.40, 717.60, and 731.70 eV are assigned to satellite peaks of Fe 2p. The peaks of 198.60 eV and 200.10 eV in the Cl 2p XPS spectrum correspond to Cl 2p_{3/2} and Cl 2p_{1/2}. In addition, the peaks at 835.30 eV and 852 eV are attributed to La 3d_{5/2} and La 3d_{3/2}, respectively. La 3d exhibits satellite peaks at 833.90 and 855 eV.

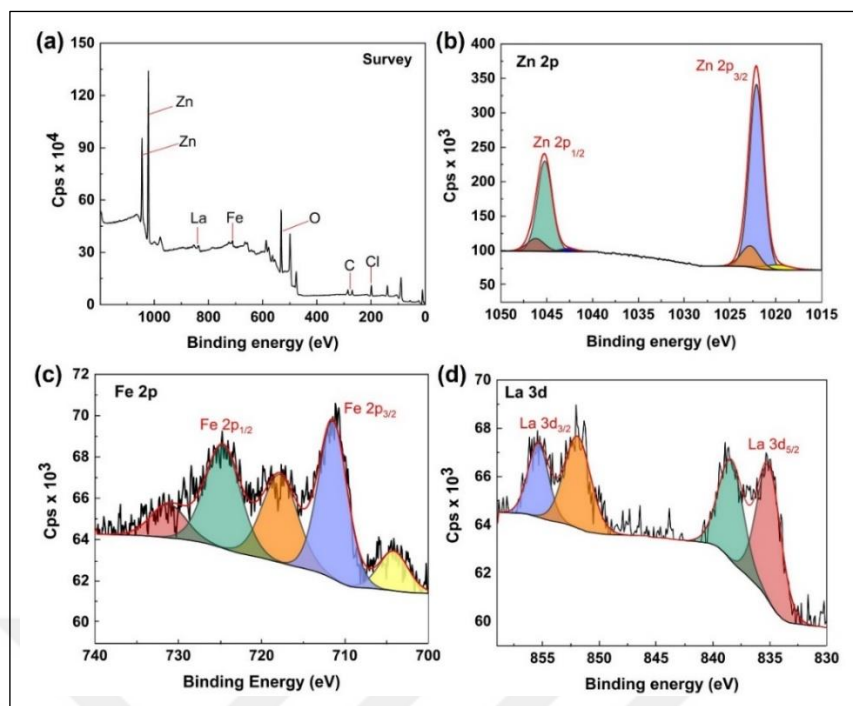


Figure 4.8: XPS spectra of LaZnFe LDH: a) survey and b) Zn 2p, c) Fe 2p, and d) La 3d.

4.1.2. Effect of Operational Parameters on Metribuzin Degradation

To evaluate the performance of the as-prepared material, metribuzin was chosen as the target pollutant. Metribuzin degradation tests were carried out in a variety of processes, including only ultrasonication (US), adsorption, only PDS, US/PDS, US/LaZnFe LDH, and US/LaZnFe LDH/PDS. Moreover, to show the importance of doping, the degradation efficiency of undoped LDH and LaZnFe LDH was compared in the same test conditions. The degradation of metribuzin (15 mg/L) under 120 W ultrasonic power was studied using 1 g/L LaZnFe LDH and 2 mmol/L PDS at its natural pH in a 90-min reaction time. As can be seen in Figure 4.9, PDS solely degraded only 3.2% because it has a low reaction rate, and various strategies are needed to activate it. The efficiency of LaZnFe LDH and US in degrading metribuzin was 12.7% and 19.0%, respectively. The decomposition efficiency improved to 40% when the US activated PDS. The activation of LaZnFe LDH with US boosted the generation of $\cdot\text{OH}$ radicals and improved the metribuzin removal ratio to 55.6%. Furthermore, the degradation efficiency was %64.8 when undoped LDH is introduced to the US/PDS system. This is because the addition of ZnFe LDH increased the number of nucleation sites for cavitation and the number of bubbles [168]. However, when

LaZnFe LDH was introduced, the process's degradation efficiency rose by 14.3%. This is because the La addition increases the number of active sites and electron-hole separation [125]. In addition, The US/LaZnFe LDH/PDS process demonstrated metribuzin degradation efficiency of 90.1% within 360 min, under optimal conditions. Nevertheless, given that the efficiency of 90-min process (79.1%) proved to be adequate, the contact time was maintained at 90 min for subsequent experiments.

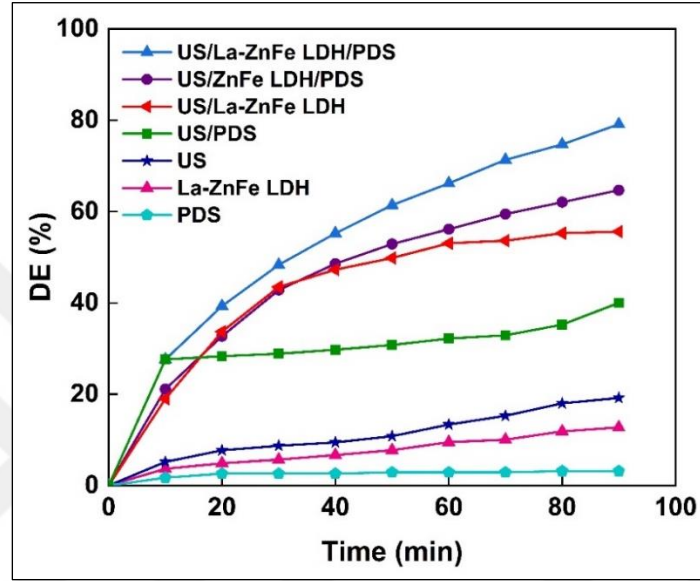


Figure 4.9: Influence of various processes on metribuzin degradation.

The reaction kinetics for sonocatalytic degradation of degradation is investigated by Langmuir–Hinshelwood model and the experimental results can be obtained using pseudo-first-order kinetics based on Equation 4.3 [169].

$$\ln \frac{C_t}{C_i} : kt \quad (4.3)$$

where C_i and C_t refer to the pollutant concentration at time 0 and t (mg/L), respectively, k is the apparent rate constant (1/min), and t is the experimental time (1/min). According to this equation, the reaction rate constants (k_{app}) were 0.0009 1/min, 0.0014 1/min, 0.0022 1/min for only PDS, only LaZnFe LDH, only US process, respectively. Also, the k_{app} values were 0.0111 1/min when LaZnFe LDH was combined with US; 0.0119 1/min when US and ZnFe LDH was combined with PDS; and 0.0168 1/min when US, La-ZnFe LDH, and PDS were combined.

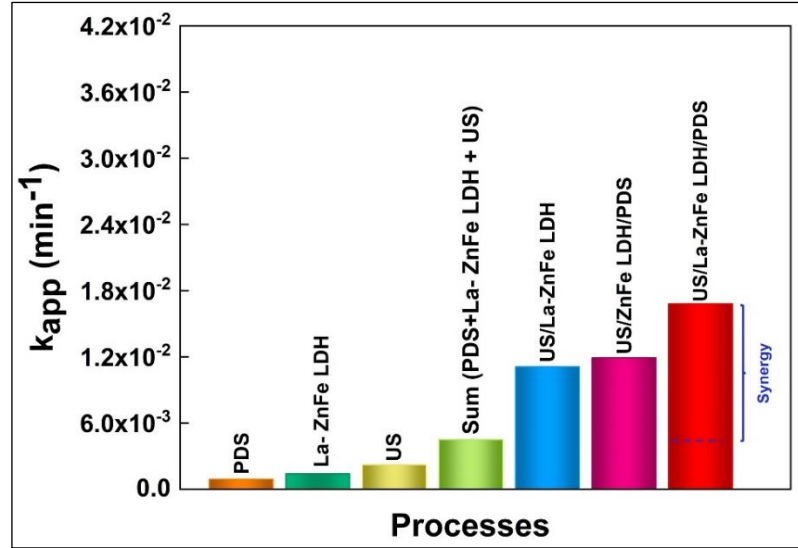


Figure 4.10: Comparison of the k_{app} value of different processes on metribuzin degradation.

The k_{app} for the process involving the combination of US, LaZnFe LDH, and PDS was found to be higher than the sum of the $k_{app}(\text{US})$, $k_{app}(\text{LaZnFe LDH})$, and $k_{app}(\text{PDS})$, as shown in Figure 4.10. This demonstrated the synergistic effect of separate processes when applied together. By calculating the synergy factor, the synergistic relationship between the processes can be better understood. A synergistic factor higher than 1 shows that the combination of processes has a synergistic effect and improves the degradation performance [170]. The synergy factor was determined to be 3.73 using Equation 4.4.

$$\text{Synergy Factor: } \frac{k_{app}(\text{US/ LaZnFe LDH/ PDS})}{k_{app}(\text{US}) + k_{app}(\text{LaZnFe LDH}) + k_{app}(\text{PDS})} \quad (4.4)$$

To determine the impact of catalyst concentration on the US/LaZnFe LDH/PDS degradation process, the experiments were further conducted under catalyst concentrations of 0.1, 0.3, 0.5, 0.7, and 1 g/L. The experiment conducted for 90 min employed metribuzin concentration of 15 mg/L, pH of 6.35 ultrasonic power of 120 W, and PDS concentration of 2 mmol/L. The results showed that the decomposition rate of metribuzin enhanced from 35.9% to 79.1% with the increase in catalyst amount (Figure 4.11). Because as the dosage of LaZnFe LDH increases, a greater number of active sites may be present, thus facilitating the reactive species generation and

increasing the degradation performance [168]. As a result, the optimum dose for the following experiments was determined as 1 g/L.

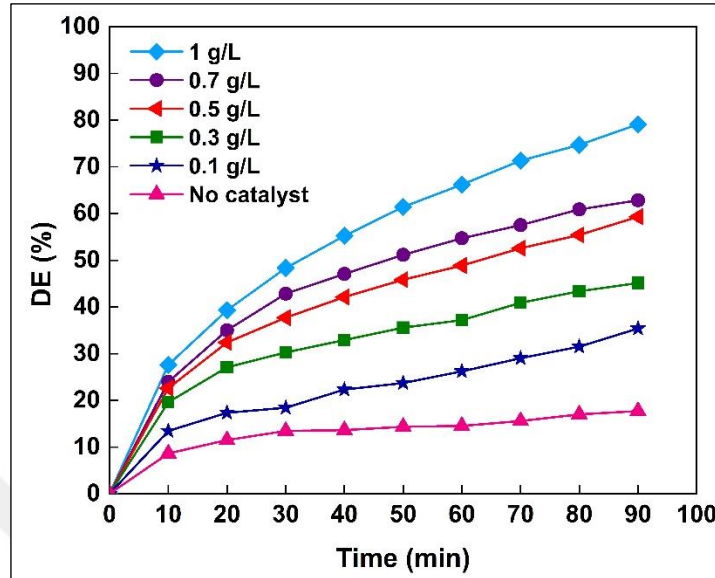


Figure 4.11: Influence of catalyst dosage on the metribuzin degradation by the US/LaZnFe LDH/PDS process.

The role of initial pollutant concentrations of 10–30 mg/L on the US/LaZnFe LDH/PDS was investigated keeping the pH of 6.35, US power of 120 W, and catalyst dosage of 1 g/L. According to Figure 4.12, when the initial amount of metribuzin was 10 mg/L, the degradation efficiency could obtain 81.6% at 90 min. However, the degradation rate gradually decreased as the pollutant concentration increased. The degradation efficiencies of the process were 81.6%, 79.1%, 75%, 71.2%, and 65.1% when the initial metribuzin concentrations were 10 mg/L, 15 mg/L, 20 mg/L, 25 mg/L, and 30 mg/L respectively. This can be attributed to the fact that metribuzin molecules coat the surface of the LaZnFe LDH and prevent the adsorption of heat and energy necessary for the cavitation bubbles to collapse. In addition, coating the surface with metribuzin molecules reduces the number of active sites [171]. ROS are inadequate at high pollutant concentrations for efficient removal, which is another reason [172].

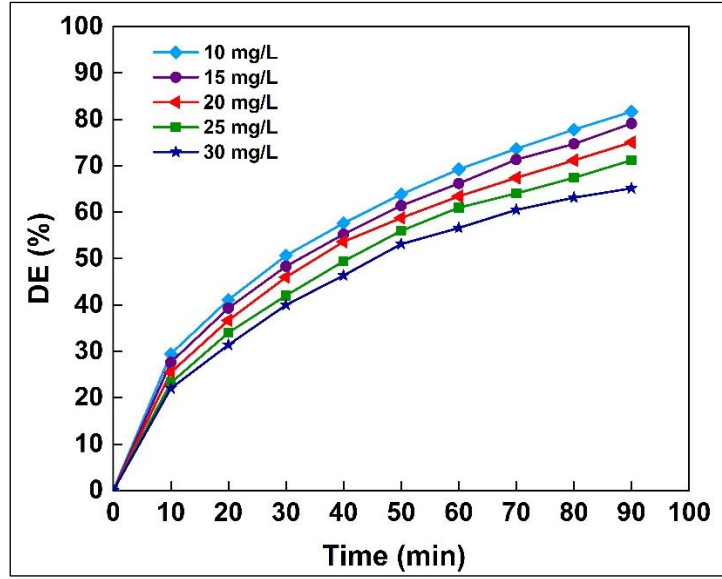
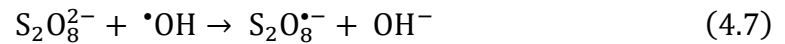
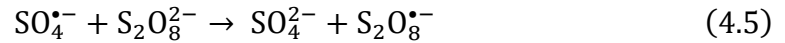


Figure 4.12: Influence of pollutant concentration on the metribuzin degradation by the US/LaZnFe LDH/PDS process.

The effect of PDS concentration (1, 1.5, 2, and 2.5 mmol/L) on the degradation of metribuzin was studied with 15 mg/L metribuzin, 1 g/L of catalyst dosage, pH of 6.35, and 120 W of US power. According to Figure 4.13., the degradation rate was 70.2%, 75%, and 79.1%, when the PDS dosage was 1, 1.5 and 2 mmol/L, respectively. The observed increase in degradation with higher dosages of PDS may be attributed to more ROS production. However, when the excessive dosage of PDS was added (2.5 mmol/L), a decrement in the degradation rate was observed (73.8%). Because when an excess amount of PDS is introduced, it can capture the $\text{SO}_4^{\bullet-}$ produced, induce a radical-radical reaction, or quench $\cdot\text{OH}$ radical (Equations 4.5-4.7) [173]. Therefore, 2 mmol/L was considered the optimum dosage of PDS.



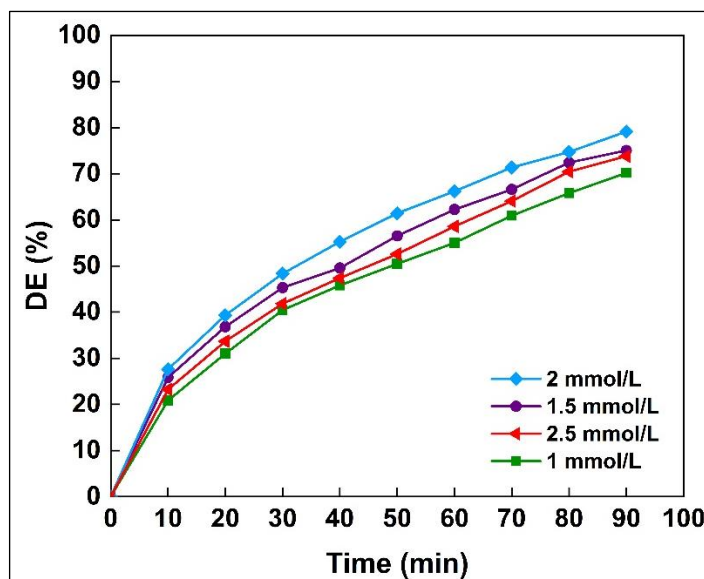


Figure 4.13: Influence of PDS dosage on the metribuzin degradation by the US/LaZnFe LDH/PDS process.

To investigate the influence of initial pH on sonocatalytic activity, the initial pH values were adjusted to 4, 6, 8, 10, and 12. The experiment was conducted with metribuzin concentration of 15 mg/L, PDS dosage of 2 mmol/L, and ultrasonic power of 120 W. As illustrated in Figure. 4.14, the lowest degradation rate was found at pH 12, whereas the maximum degradation rate was found at pH 8. To better explain the results, LaZnFe LDH's point of zero charges (pH_{pzc}) was measured. According to Figure 4.15, the pH_{pzc} catalyst was determined as 7.1.

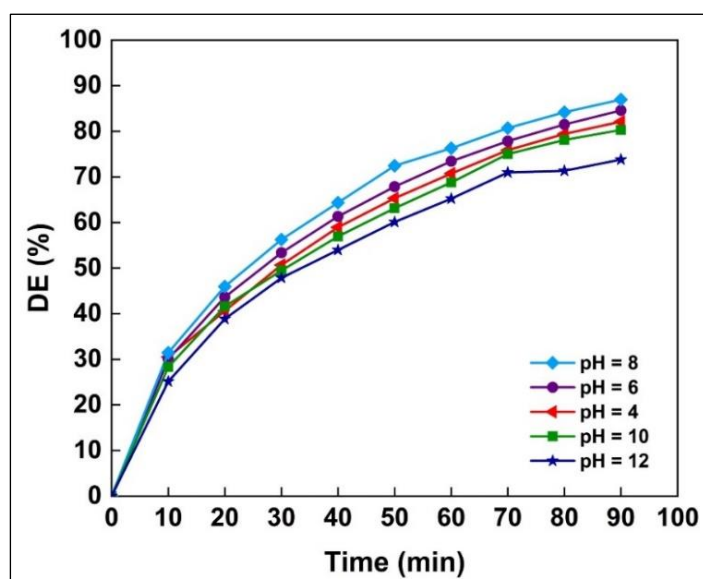


Figure 4.14: Influence of pH on the metribuzin degradation by the US/LaZnFe LDH/PDS process.

The catalyst surface has a negative charge when the pH is higher than pH_{pzc} due to hydroxide anions' adsorption. In contrast, the catalyst surface has a positive charge when the pH is lower than pH_{pzc} due to the adsorption of protons [174]. Additionally, metribuzin has a pK_a of about 1.0, which indicates that the metribuzin molecules are positively charged at pH higher than 1.0 and negatively charged at pH lower than 1.0. As a result, the negatively charged molecules of metribuzin and the surface of the catalyst cause electrostatic repulsion when the pH level is higher than 7.1, which decreases the degradation efficiency [174]. Another reason for the decrease in degradation efficiency at pH 10 and pH 12 is the conversion of $\text{SO}_4^{\cdot-}$ to $\cdot\text{OH}$ with lower redox potential by reacting with OH^- in an alkaline media (Equation 2.28) [175].

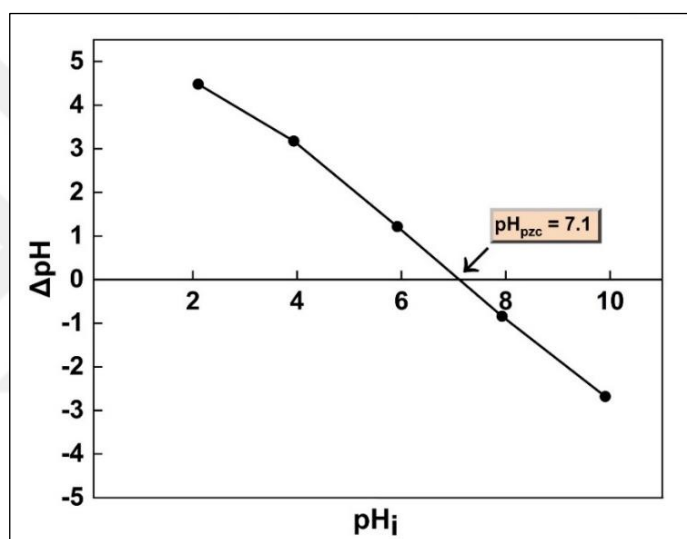


Figure 4.15: Determination of pH_{pzc} of LaZnFe LDH.

The US power is another crucial parameter in the sonocatalytic degradation process. The effect of ultrasonic power on metribuzin degradation was carried out at different ultrasonic power in the presence of 1 g/L catalyst, pH of 6.35, 2 mmol/L of PDS, and 15 mg/L of metribuzin. According to Figure 4.16, 79.1%, 81.2%, and 83.9% of the metribuzin were removed at US power of 120 W, 200 W, and 300 W, respectively. With a rise in US power, the system's turbulence rises, which affects the mass transfer rate [129]. Another reason may be the higher US power leads more ROS to being produced because of the PDS molecule's dissociation [176]. Nevertheless, increasing the power intensity to 300 W resulted in a minor improvement in process performance. Hence, the US power for the following experiment was determined to be 120 W.

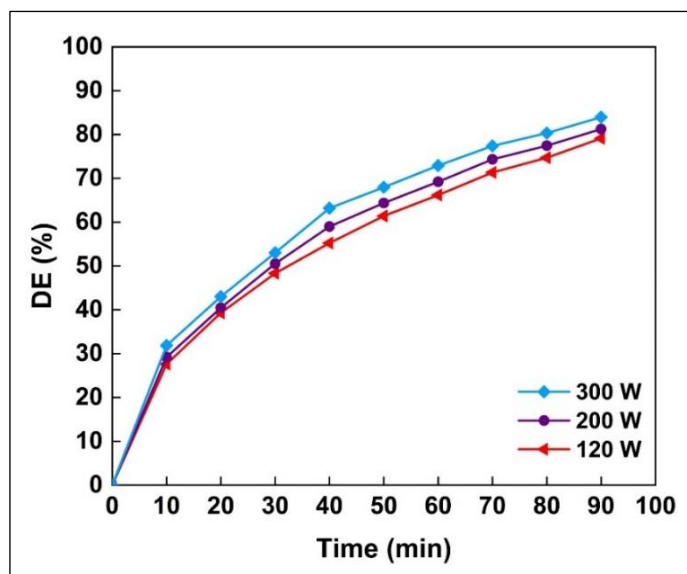
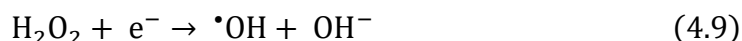
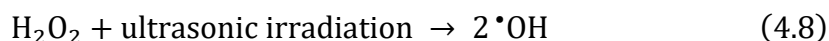
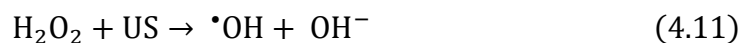
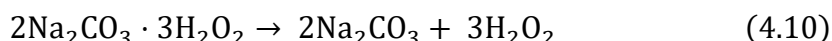


Figure 4.16: Influence of US power on the metribuzin degradation by the US/LaZnFe LDH/PDS process.

The impact of different oxidants such as hydrogen peroxide (H_2O_2), percarbonate (Na_2CO_3), and PDS anion on the sonocatalytic activity was studied. This parameter was studied with 15 mg/L metribuzin, 2 mmol/L of oxidant, 1 g/L of catalyst concentration, pH of 6.35, and 120 W of US power. As illustrated in Figure 4.17, the enhancers increase the degradation efficiency from 55.6% to 63.7%, 74.5%, and 79.1% respectively. The influence of hydrogen peroxide results from the decomposition of H_2O_2 into $\cdot\text{OH}$ during ultrasonic irradiation, according to Equations 4.8 and 4.9 [177].



Based on Equations 4.10 and 4.11, the addition of percarbonate can also increase degradation efficiency owing to the additional $\cdot\text{OH}$ radical generation [178].



Compared to other oxidant agents, PDS has a higher enhancing effect. This is due to the PDS breakdown to $\text{SO}_4^{\bullet-}$ and more $\cdot\text{OH}$ radicals production, as demonstrated by Equations 2.27 and 2.32 [179].

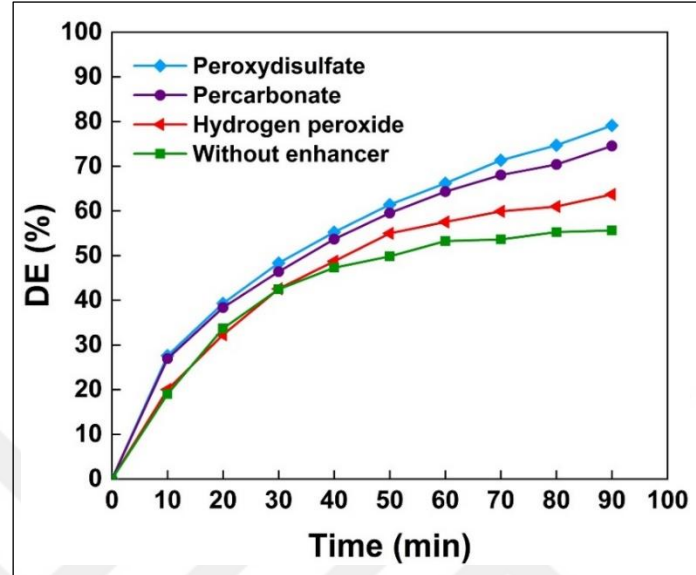


Figure 4.17: Influence of different enhancers on metribuzin degradation by the US/LaZnFe LDH/PDS process.

To determine the role of various free radicals in the degradation process, free radical quenching experiments were carried out. The effect of scavenger on the degradation of metribuzin was studied with 15 mg/L metribuzin, 2 mmol/L of PDS, 1 g/L of catalyst dosage, pH of 6.35, and 120 W of US power. As shown in Figure 4.18, the metribuzin showed good degradation ability without adding a scavenger, and the degradation efficiency reached 79.1%. One of the scavengers, isopropanol is utilized to quench $\cdot\text{OH}$ and has $k_{\text{OH}}:1.9 \times 10^9$ 1/Ms for the reaction between the hydroxyl radical and it [180]. When isopropanol was used as scavenger, the degradation rate decreased to 56.1%. The degradation efficiency decreased to 50.6% after adding formic acid, which is a h_{VB}^+ scavenger. p-benzoquinone ($k_{\text{O}_2^{\bullet-}}:1.2 \times 10^9$ 1/Ms) and phenol ($k_{\cdot\text{OH}}:6.6 \times 10^9$ 1/Ms, $k_{\text{SO}_4^{\bullet-}}:8.8 \times 10^9$ 1/Ms) were utilized as $\text{O}_2^{\bullet-}$ scavenger, and both $\cdot\text{OH}$ and $\text{SO}_4^{\bullet-}$ radicals, respectively ($k_{\text{O}_2^{\bullet-}}:1.2 \times 10^9$ 1/Ms) [181]. The degradation efficiency dropped to 26.6% and 17.3% when p-benzoquinone and phenol were present, respectively. The findings show that $\text{O}_2^{\bullet-}$ and $\text{SO}_4^{\bullet-}$ played significant roles in the degradation process. In the presence of isopropanol and phenol, the removal efficiency decreased by 23% and 61.8%, respectively. It is possible to infer

the impact of the radical on the degradation process from the variation between these two scavenger agents. Because phenol inhibited the degradation process more than isopropanol, the predominant oxidant species were $\text{SO}_4^{\cdot-}$ radicals.

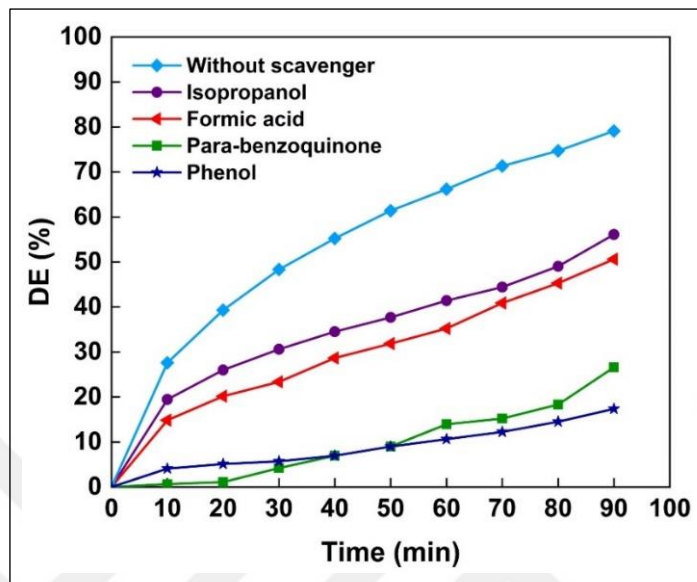
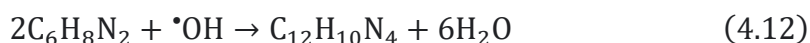


Figure 4.18: Influence of different scavengers on metribuzin degradation by the US/LaZnFe LDH/PDS process.

In addition, to detect $\cdot\text{OH}$ radical in the degradation process, O-phenylenediamine (OPD) was utilized as a probe [182]. The experimental conditions for the experiment were 15 mg/L metribuzin, 2 mmol/L PDS, 1 g/L LaZnFe LDH, 120 W ultrasonic power, and 90 min of reaction time. The reaction between OPD and the $\cdot\text{OH}$ radical results in the formation of a yellow-colored 2,3-diamino phenazine (Equation 4.12). Following an experiment that was conducted under optimum conditions, the OPD-trapped $\cdot\text{OH}$ was identified using a UV-Vis spectrophotometer at a wavelength of 417 nm. Based on these spectra, it can be concluded that the production of $\cdot\text{OH}$ increased with reaction time (Figure 4.19).



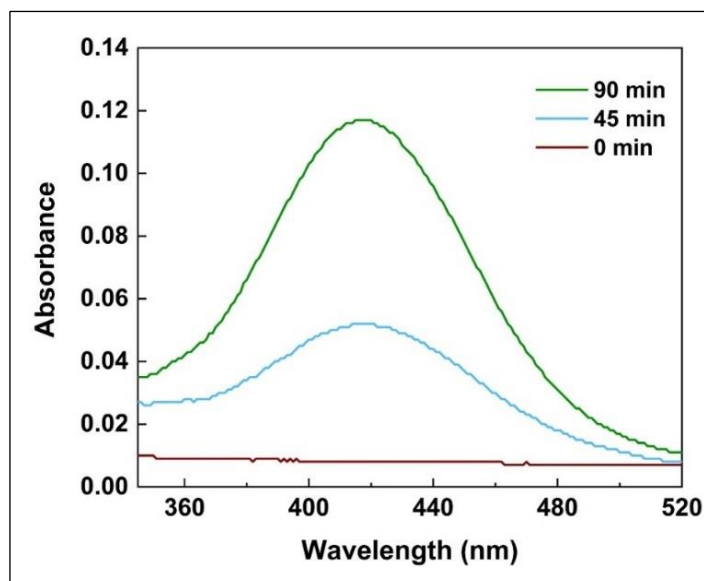


Figure 4.19: Spectra of OPD-trapped hydroxyl radical in metribuzin degradation by the US/LaZnFe LDH/PDS process.

Moreover, methylene blue, rifampicin, and phenazopyridine were chosen as model pollutants to investigate the impact of the US/LaZnFe LDH/PDS process on other pollutants. These experiments were studied by keeping the pollutant concentration of 15 mg/L, the catalyst dosage of 1 g/L, PDS dosage of 2 mmol/L pH of natural, US power of 120 W, and 90 min of reaction time. According to Figure 4.20, The US/LaZnFe LDH/PDS process degraded 52.1%, 43.8%, and 85.4% of methylene blue, rifampicin, and phenazopyridine, respectively. The differences in the molecular structures and chemical compositions of the pollutants may be used to explain why the US/LaZnFe LDH/PDS process has varying efficiency in pollutant removal. For example, when comparing molecular weight, rifampicin ($MW_{\text{rifampicin}}: 822.94 \text{ g/mol}$) > methylene blue ($MW_{\text{methylene blue}}: 319.85 \text{ g/mol}$) > metribuzin ($MW_{\text{metribuzin}}: 214.29 \text{ g/mol}$) > phenazopyridine ($MW_{\text{phenazopyridine}}: 213.239 \text{ g/mol}$). In addition, metribuzin contains a heterocyclic ring, whereas methylene blue contains two aromatic rings and a heterocyclic ring, and rifampicin contains a heterocyclic ring containing naphthoquinone. As a result, US/LaZnFe LDH/PDS process demonstrated that it is successful in degrading various pollutant groups such as dyes, pharmaceuticals, and herbicides.

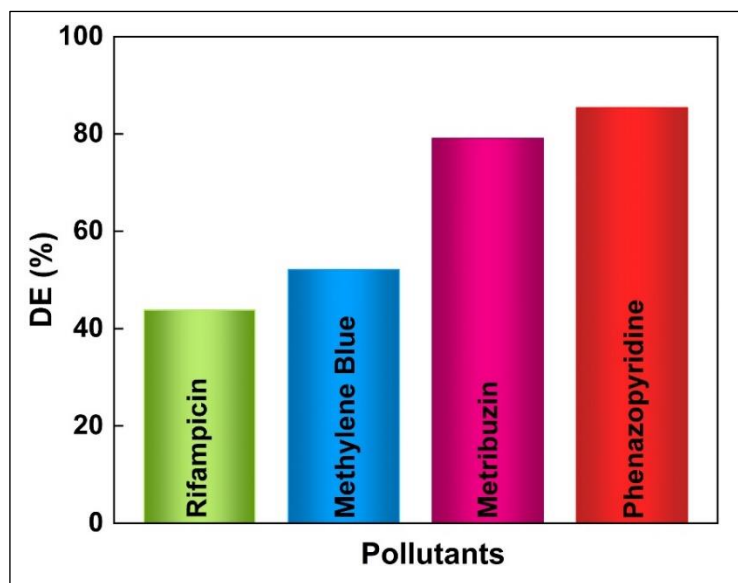


Figure 4.20: Influence of US/LaZnFe LDH/PDS process on the decomposition of different pollutants.

The reusability of the catalyst is crucial for an economic and pilot-scale application. Accordingly, LaZnFe LDH's reusability was examined using PDS dosage of 2 mmol/L, LaZnFe LDH dosage of 1 g/L, pH of 6.35, metribuzin concentration of 15 mg/L, US power of 120 W, and contact time of 90 min. For the reusability experiment of the catalyst, the catalyst was collected after each process, washed with distilled water, dried, and made ready for the next cycle. Accordingly, the retrievability of LaZnFe LDH was examined after 4 consecutive cycles, as shown in Figure 4.21. The degradation efficiencies for the four sonocatalytic cycles of LaZnFe LDH were 79%, 76.6%, 72.4%, and 68.3%, respectively. It was seen that after four cycles, LaZnFe LDH had good recyclability. The decline in efficiency could be caused by degradation intermediates occupying the LaZnFe LDH surface, which reduced active site numbers in the catalyst [183].

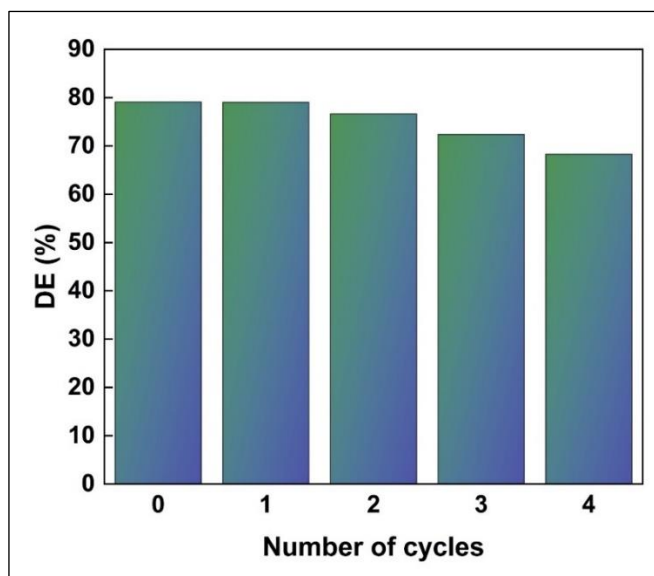


Figure 4.21: Reusability of LaZnFe LDH in US/LaZnFe LDH/PDS process.

Following the reusability test, SEM and XRD analyses were done to examine the changes in the morphological and crystal structure of the catalyst. According to SEM images (Figure 4.22), the catalyst's morphology had not significantly changed. In addition, as shown in Figure 4.23, the used LaZnFe LDH had similar XRD peak positions to the fresh.

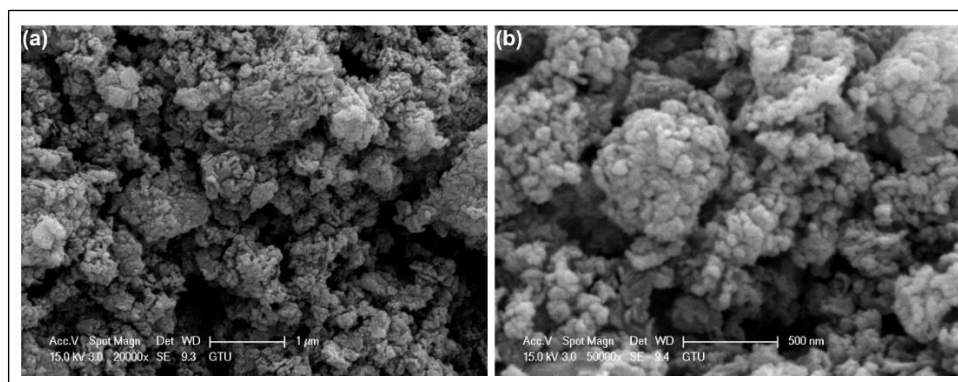


Figure 4.22: The SEM images of the used catalyst at a) 1 μm , and b) 500 nm.

Moreover, to assess the catalyst's stability, a metal-ion leaching analysis was carried out. La and Fe leaching was not found, and only 0.003% of the Zn had leached, according to the ICP-MS analysis. All the information suggested that LaZnFe LDH had excellent reusability and stability and was expected to be an effective catalyst for practical application for degrading refractory pollutants.

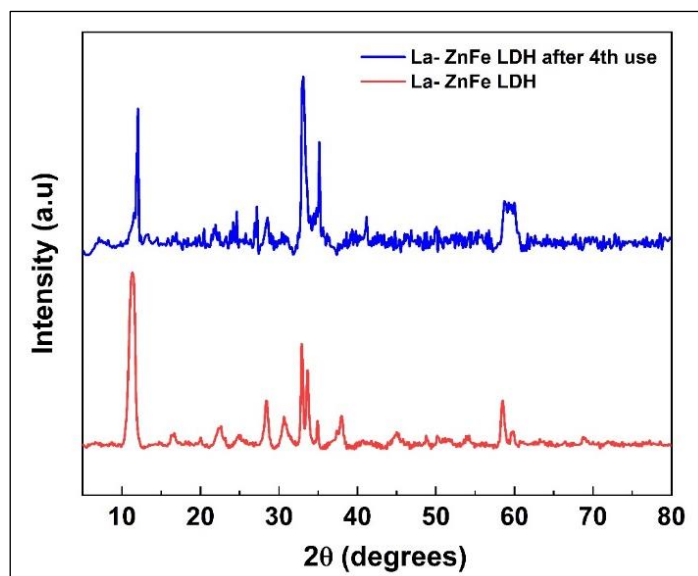


Figure 4.23: The XRD pattern of the used catalyst.

Additionally, US/LaZnFe LDH/PDS process was applied to the metribuzin degradation in the wastewater matrix. The characteristics of wastewater used in the experiment was described in Table 3.3. The sonocatalytic activity was examined in the presence of 1 g/L of LaZnFe LDH, 15 mg/L of metribuzin, 2 mmol/L PDS, and 120 W of ultrasonic power. According to Figure 4.24, US/LaZnFe LDH/PDS system demonstrated 52.8% degradation efficiency of metribuzin in 360 min. Compared to the experiment conducted under the same conditions for 360 min with distilled water, the removal efficacy decreased by 37.3%. This decrease can be ascribed to the existence of various inorganic and organic substances in wastewater, which reduce the activity of the produced ROS [184].

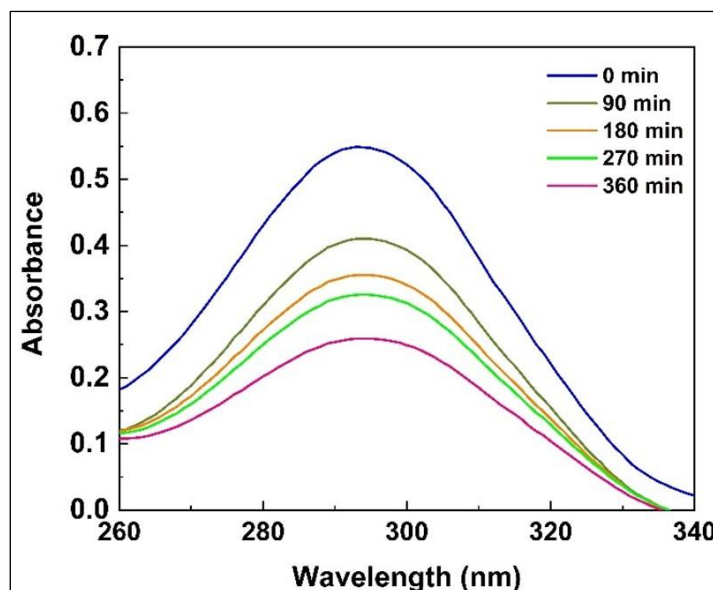
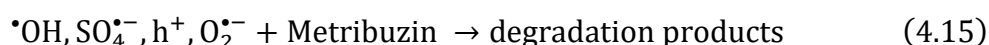
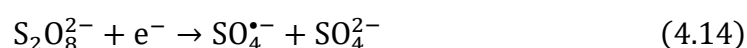


Figure 4.24: UV-Vis spectra of the metribuzin degradation in real wastewater by US/LaZnFe LDH/PDS process.

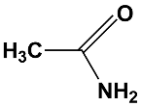
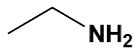
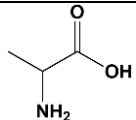
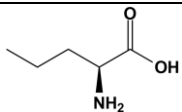
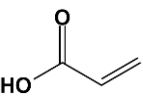
The possible degradation mechanism was proposed for the US/LaZnFe LDH/PDS process on the basis of the results. The sonocatalytic degradation method is based on both the sonoluminescence phenomenon and ultrasonic cavitation effects [185]. The cavitation bubbles first undergo formation, growth, and collapse processes when exposed to ultrasonic irradiation. The high temperature and pressure caused by the cavitation effect result in the breakdown of H_2O , resulting in the formation $\cdot OH$ and $H\cdot$ radicals (Equation 2.7) [186]. At the same time, sonoluminescence e^-/h^+ pairs are produced on the catalyst's surface because of ultrasonic irradiation (Equation 4.13) [187]. Moreover, the US irradiation breaks the chemical bonds in PDS, leading to $SO_4^{\cdot-}$ radicals formation (Equation 2.27) [188]. By reacting with PDS and oxygen molecules, the activated electrons (e^-) generate $SO_4^{\cdot-}$ and $O_2^{\cdot-}$, respectively (Equations 4.14 and 2.23) and [179]. In addition, the holes (h^+) on the surface of the catalyst could react with H_2O and OH^- to generate $\cdot OH$ radical. (Equations 2.21 and 2.22) [129]. As a result, metribuzin and its byproducts are degraded by $\cdot OH$, $O_2^{\cdot-}$, h , and $SO_4^{\cdot-}$ (Equation 4.15) [188].



4.1.3. Intermediates Formed During Metribuzin Degradation

Because of the decomposition of the metribuzin molecular structure, various intermediates were generated during US/LaZnFe LDH/PDS process. To detect the intermediates of metribuzin degradation, GC-MS was applied. Desulfurization and deamination should be the initial steps in the degradation process, based on the metribuzin structure [189], [190]. The degradation of metribuzin is mostly caused by the bond breakage of basic structures like C-C, N-N, C-S, and C-N [191]. According to the detected by-products, the final degradation products of metribuzin are linear compounds, most of which have no more than four carbon atoms. Table 4.1 shows the names, structures, retention times (t_R), and fragments (m/z) of the six by-products that were detected. Some intermediates may not have been detected due to instrumental limitations.

Table 4.1: The detected by-products formed during the degradation of metribuzin.

No.	Compound Names	Structures	t _R (min)	Main fragments (m/z) /(percent)
1	Acetamide		5.603	75.10 (100%), 116.10 (84.12%), 73.10 (13.60%), 117.10(8.32%), 76.10 (7.35%)
2	Ethanamine		6.244	174.10 (100%), 100.10 (58.29%), 73.10 (31.22%), 175.10 (18.67%), 59.00 (17.23%)
3	Alanine		6.307	144.10 (100%), 73.10 (58.62%), 158.20 (34.41%), 59.10 (13.19%), 145.05 (13.14%)
4	L-norvaline		6.312	144.10 (100%), 73.10 (56.34%), 158.10 (34.14%), 59.00 (13.23%), 145.20 (12.57%)
5	2-Propenoic acid		6.976	147.10 (100%), 73.00 (76.74%), 217.20 (21.54%), 188.10 (20.98%), 207.00 (14.45%)

In addition, the ECOSAR model was used to evaluate the toxicity of metribuzin and its intermediates. Indicators such as fish, daphnia, and algae were utilized to assess the acute and chronic toxicity of the by-products. Acute toxicity was expressed by half effective concentration (EC50) and half lethal concentration (LC50), while chronic toxicity was expressed by chronic value (ChV). Based on their toxicity levels, products have been categorized as "not harmful," "harmful," "toxic," or "very toxic" in accordance with the Globally Harmonized System of Chemical Classification and Labeling (GHS) [192]. Consequently, if the EC50, LC50, and ChV values are equal to or greater than 100 mg/L, the compound is non-toxic. If the EC50, LC50, and ChV values range from 1 mg/L to 10 mg/L, the compound is toxic to the organism. If the EC50, LC50, and ChV values are less than or equal to 1 mg/L, the compound is highly toxic to living organisms. According to Table 4.2, the acute and chronic toxicity of metribuzin to fish, daphnia, and algae was very toxic. All identified by-products of the degradation process exhibited lower acute and chronic toxicity compared to metribuzin.

Table 4.2: The acute and chronic toxicities of metribuzin and intermediates.

Compounds	Acute toxicity (mg/L)			Chronic toxicity (mg/L)		
	Fish (LC50)	Daphnia Magna (LC50)	Green Algae (EC50)	Fish (ChV)	Daphnia Magna (ChV)	Green Algae (ChV)
Metribuzin	1.12	2.33	0.914	0.108	0.485	0.108
Acetamide	33600	14200	3170	2320	616	433
Ethylamine	223	20.7	28	27.8	1.33	7.77
Alanine	325000	21700	56400	11000	1010	12300
L-norvaline	96700	7240	15000	2.3300	378	3560
2-Propenoic acid	14900	7310	3000	1230	477	571

4.1.4. Energy Analysis and Degradation Turnover Calculation

For the long-term utilization of the process, it is also essential that it be economically feasible. The expression "electrical energy per order" (EEO) was created to assess the economic feasibility of the process. The electrical energy required to

remove pollution from a specified volume was determined using the following formula [193].

$$E_{EO} : \frac{P \times t \times 1000}{V \times 60 \times \log (C_i/C_f)} \quad (4.16)$$

where P is US power (kW), t is contact time (min), V is the volume of reactor (L), C_0 is the initial pollutant concentration (mg/L), and C_f is the final pollutant concentration (mg/L). Accordingly, the EEO value was determined as 2537.6 kWh/m³order. The EEO values of the sonocatalytic degradation of various pollutants are shown in Table 4.2. The fact that the US/LaZnFe LDH/PDS process has a lower EEO value than other sonocatalytic degradation studies can be attributed to the existence of PDS, which accelerates the degradation reaction.

A degradation turnover (dTON) calculation was performed to further demonstrate the effectiveness of the process. The following formula (Equation 4.17) was used to calculate the degradation turnover rate, which was determined to be 37.5 $\mu\text{mol/hgcat}$.

$$dTON : \frac{[C_0] - [C_f]}{t \times [A]} \quad (4.17)$$

where C_0 is initial pollutant concentration ($\mu\text{mol/L}$), C_f is the final pollutant concentration ($\mu\text{mol/L}$), t is contact time (h), and A is LaZnFe LDH dosage (g/L) [194].

Table 4.3: Comparison of EEO value of different sonocatalytic processes.

Catalyst type	Pollutant	Reaction conditions	kapp (1/min)	EEO (kWh/m ³ order)	Ref.
TiO ₂	2,4-Dichlorophenoxyacetic Acid	[Catalyst] :0.5 g/L, [Pollutant]:75 mg/L, contact time:60 min, and pH:2	-	10791	[195]
TiO ₂	Ofloxacin	[Catalyst] :0.4 g/L, US power:120 W, [Pollutant]:20 mg/L, pH:natural pH, and contact time:120 min	0.0015	7040.6	[196]
ZnO	Ofloxacin	[Catalyst] :0.4 g/L, US power:120 W, [Pollutant]:20 mg/L, contact time:120 min, and pH:natural pH	0.0019	6154.5	[196]
Cu ₂ O/MoS ₂ /rGO	Tetracycline	[Catalyst] :0.3 g/L, US power:120 W, [Pollutant]:20 mg/L, contact time:75 min, and pH:natural pH	0.018	2560	[197]
LaZnFe LDH	Metribuzin	[Catalyst] :1 g/L, US power:120 W, [Pollutant]:15 mg/L, contact time:90 min, and pH:natural pH	0.0168	2537.6	This study

4.2. Degradation of Rifampicin via PMS- Assisted Photocatalytic Process

In this section, the objective was to enhance the stability and reusability of the catalyst. To achieve this, the La-ZnFe LDH catalyst was immobilized on polydimethylsiloxane (PDMS) sponge, which served as a supporting substrate. In addition, the performance of the LaZnFe LDH@PDMS sponge was evaluated using the photocatalytic degradation process under visible light, which is economically feasible.

4.2.1. Characterization of LaZnFe LDH@PDMS Sponge

XRD patterns were used to identify the crystallinity phase of LaZnFe LDH, pure PDMS sponge, and LaZnFe LDH@PDMS samples (Figure 4.25). For LaZnFe LDH typical diffraction peaks at 2θ : 11.38° , 28.28° , 30.52° , 32.7° , 34.76° , 37.16° , and 58.36° were assigned well to (003), (110), (101), (009), (012), (015), and (110) planes, respectively (JCPDS No 38-0486) [194]. A large peak between 10° and 24° in the XRD pattern of the PDMS sponge indicates that the material is amorphous [198]. In addition, the XRD pattern for the LaZnFe LDH@PDMS sponge was quite similar to that of the PDMS sponge.

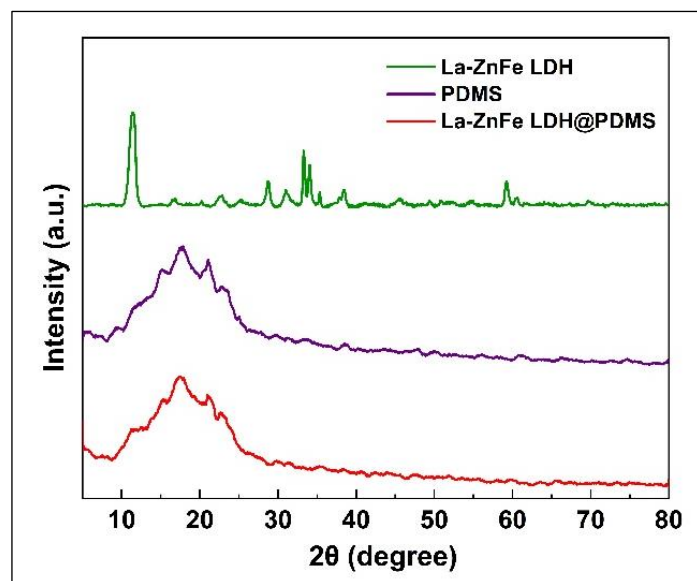


Figure 4.25: The XRD patterns of LaZnFe LDH, PDMS sponge, and LaZnFe LDH immobilized porous PDMS sponges.

FTIR spectra were used to determine the functional classes of materials, and the results are illustrated in Figure 4.26. On the LaZnFe LDH spectrum, the strong peaks at 3455.5 cm^{-1} , 1607.5 cm^{-1} , and below 1030 cm^{-1} can be ascribed respectively to O-H, H-O-H, and M-O stretching vibrations [199]. For the PDMS sponge, the C-H stretching vibration peaks appeared at 2962.6 cm^{-1} . The absorption peak at 1257.3 cm^{-1} and 788.2 cm^{-1} belongs to the Si-CH₃ stretching vibration. Besides, the peak at 1008.3 cm^{-1} corresponds to the Si-O-Si stretching vibration [200]. Moreover, similar peaks are also seen in the LaZnFe LDH catalyst-immobilized porous PDMS sponges.

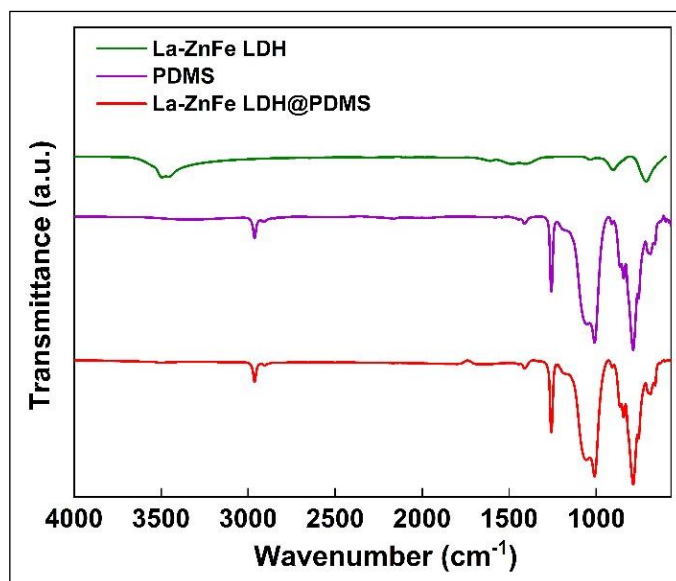


Figure 4.26: The FT-IR spectra of LaZnFe LDH, PDMS sponge, and LaZnFe LDH immobilized porous PDMS sponges.

The SEM images of PDMS and LaZnFe LDH catalyst-immobilized porous PDMS sponges were shown in Figure 4.27. The findings indicate that both the PDMS sponge and the LaZnFe LDH@PDMS sponge displayed an irregular closed-cell structure pore structure. Furthermore, it is observed that the rough structure is enhanced by embedding of LaZnFe LDH on the PDMS sponge.

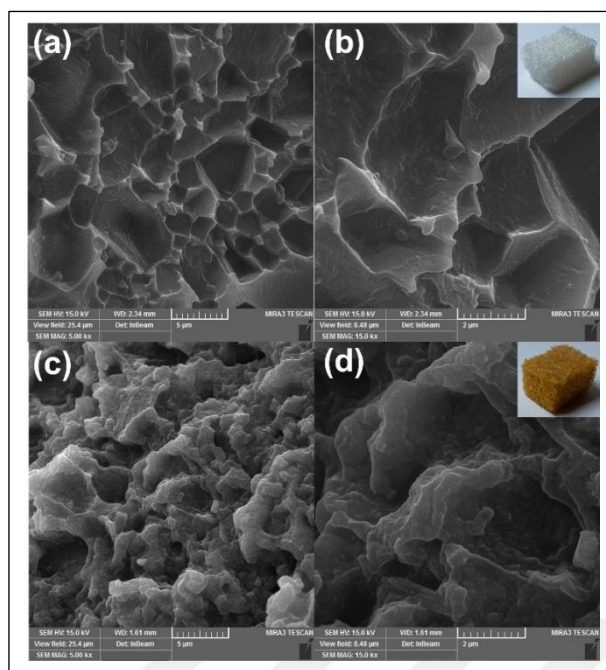


Figure 4.27: The SEM images of a) PDMS sponge at 5 μm , b) PDMS sponge at 2 μm , c) LaZnFe LDH@PDMS sponge at 5 μm , and d) LaZnFe LDH@PDMS sponge at 2 μm .

EDX was used to evaluate the element distribution of LaZnFe LDH catalyst-immobilized porous PDMS sponges. Figure 4.28a shows an SEM image of the area where the elemental distribution is being investigated. As shown in Figure 4.28b. The EDX spectra showed the presence of the elements C, O, Si, Cl, La, Zn, and Fe at atomic percentages of 45%, 27.1%, 23.9%, 0.8%, 0.1%, 2.7%, and 0.4% respectively.

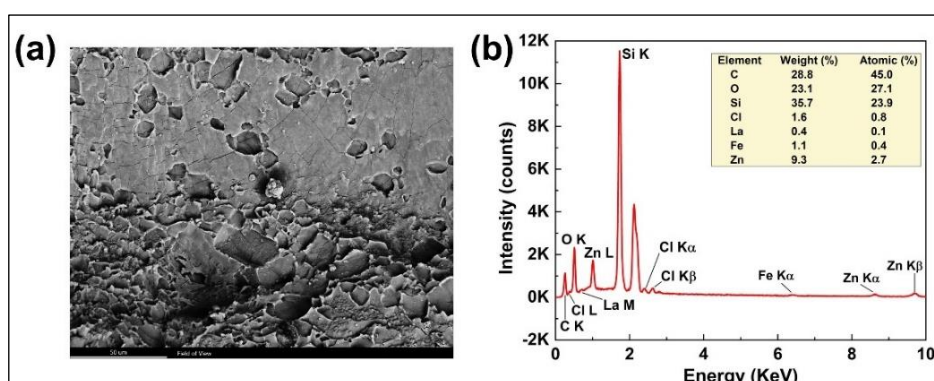


Figure 4.28: SEM-EDX analysis of LaZnFe LDH immobilized porous PDMS sponges: a) SEM images of EDX area, and b) The EDX spectrum.

In addition, the EDX elemental mapping images reveal that C, O, Si, Zn, Fe, and La are uniformly distributed on the LaZnFe LDH@PDMS sponge (Figure 4.29). This demonstrates that LaZnFe LDH was successfully embedded in the PDMS sponge.

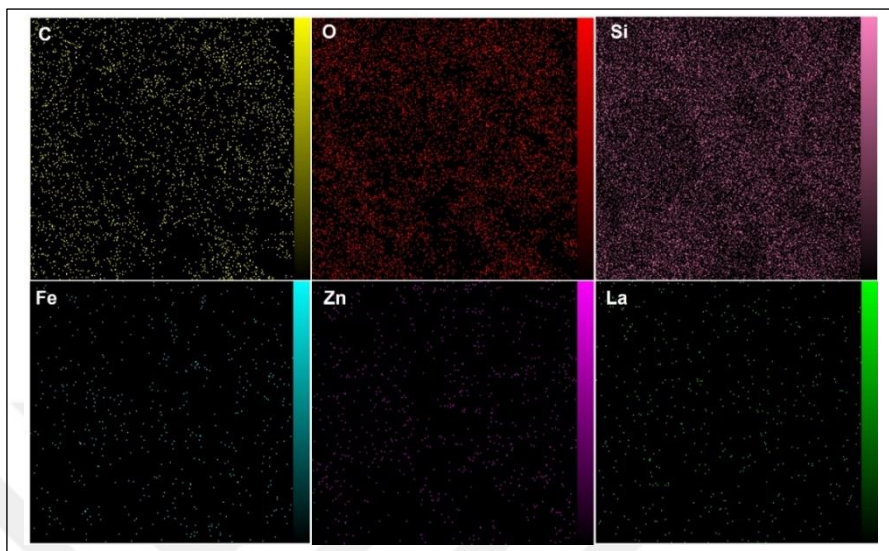


Figure 4.29: The dot-mapping of LaZnFe LDH catalyst immobilized porous PDMS sponges.

Figures 4.30 and 4.31. show the N₂ adsorption-desorption isotherms for PDMS and LaZnFe LDH@PDMS sponges. According to the IUPAC standard, PDMS and LaZnFe LDH@PDMS sponges had the type IV classification with an H3-type hysteresis loop [201], [202]. The findings suggest that both PDMS and LaZnFe LDH@PDMS sponge had the characteristic of mesoporous material.

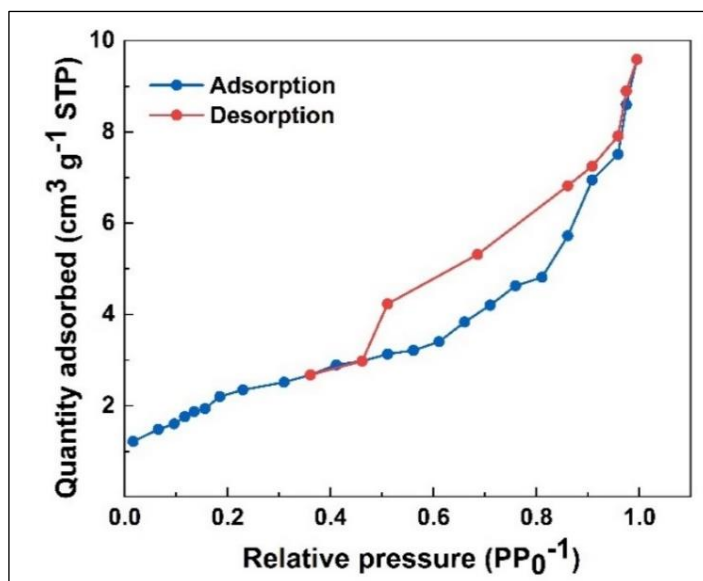


Figure 4.30: N₂ adsorption–desorption isotherm of PDMS sponge.

The BET-specific surface area of PDMS and LaZnFe LDH@PDMS sponges are 7.1 and 5.94 m²/g, respectively. The average pore diameter decreased from 8.13 to 4.89 nm after embedding LaZnFe in the PDMS sponge. At the same time, the pore volume reduced slightly (from 1.63 cm³/g to 1.36 cm³/g). The decline in BET surface area, mean pore diameter, and pore volume is attributable to the filling of the PDMS sponge's porous structure with LaZnFe LDH.

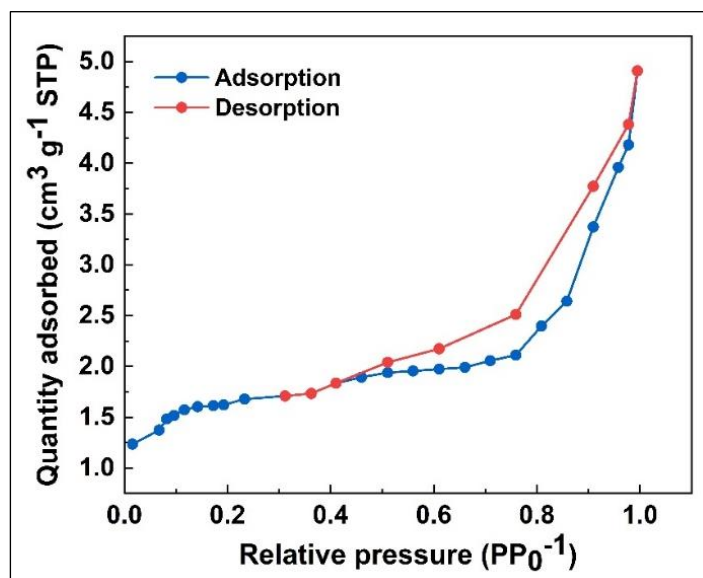


Figure 4.31: N₂ adsorption–desorption isotherm of LaZnFe LDH immobilized porous PDMS sponge.

Contact angle measurement was used to assess the wetting behavior of the surfaces of the prepared samples. The sample is hydrophilic if the contact angle between the water drop and the solid surface is less than 90° , hydrophobic between 90° and 150° , and superhydrophobic above 150° [203]. Figure 4.32a and 4.32b demonstrates the contact angle results of PDMS and LaZnFe LDH@PDMS sponge, respectively. LaZnFe LDH embedding increased the contact angle of the PDMS sponge from 123° to 134° . In another study, it has been found that coating the PDMS sponge with ZnO Rod increased surface hydrophobicity [204]. With the addition of catalyst, the micro-roughness of the surface of the PDMS sponge may have increased, which could be responsible for the increase in contact angle.

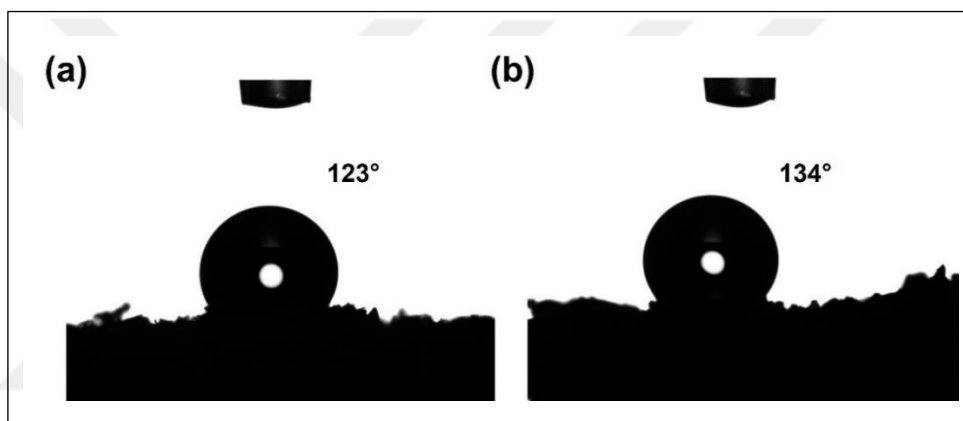


Figure 4.32: Contact angle results of a) PDMS and b) LaZnFe LDH immobilized porous PDMS sponges.

4.2.2. Effect of Operation Parameters on Rifampicin Degradation

Rifampicin was chosen as a model pollutant for assessing the photocatalytic activity of the LaZnFe LDH embedding PDMS sponge. Comparative experiments were carried out to examine the role of various processes in rifampicin removal (Figure 4.33). The experiments were further conducted for 60 min using rifampicin of 15 mg/L, LaZnFe LDH@PDMS sponge of 118 pieces, PMS concentration of 0.2 mmol/L, pH of 8, LED power of 100 W. The degradation efficiency of the adsorption and visible light only processes were 3.7% and 7.2%, indicating that rifampicin was quite resistant to decomposition. PMS demonstrated a removal efficiency of 27% through self-degradation (Equation 2.33) [205]. Notably, the visible light/LaZnFe LDH@PDMS sponge/PMS process achieved degradation efficiency of 59.6% for rifampicin within

60 min. Because the visible light and LaZnFe LDH@PDMS sponge activate the PMS, the PMS can catch the photo-induced electrons and inhibit the carriers of the photocatalysts from recombining. Consequently, more electrons and holes can be involved in forming ROS and the decomposition of rifampicin [206]. In addition, the rifampicin degradation efficiency increased to 92.8% within 360 min, under optimal conditions. However, because the 60-min process was sufficient, the contact time was set to 60 min in subsequent experiments.

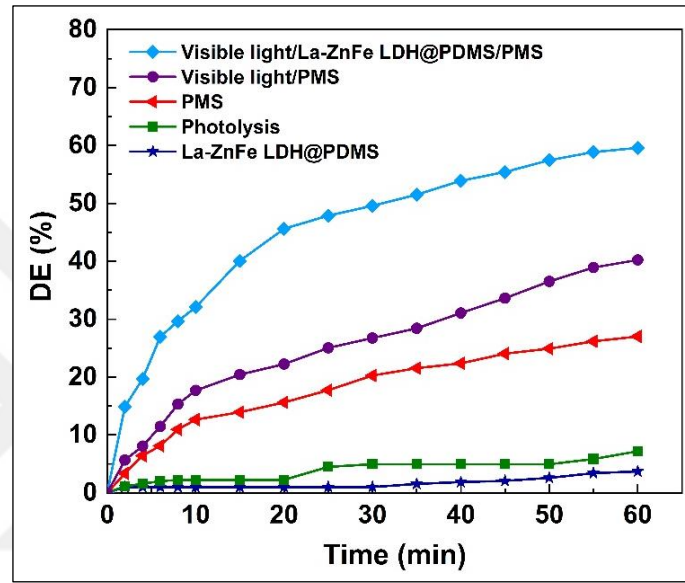


Figure 4.33: Influence of different processes on rifampicin degradation.

The degradation rate can be expressed using a model of pseudo-first-order kinetics. The k_{app} of the process and its components were calculated via Equation 4.3. According to Figure. 4.34, k_{app} follows the order of $k_{\text{visiblelight/LaZnFeLDH@PDMS/PMS}}$ (0.0281 1/min) > k_{PMS} (0.0056 1/min) > $k_{\text{photolysis}}$ (0.0017 1/min) > $k_{\text{adsorption}}$ (0.001 1/min). Moreover, the k_{app} of visible light/LaZnFe LDH@PDMS/PMS process is greater than the sum of the rate constants of the adsorption, photolysis, and PMS processes alone (0.0083 1/min), indicating the synergistic relationship between the processes. To demonstrate the synergistic relationship between the processes, the synergy factor of the degradation process was calculated using Equation 4.4 and found to be 3.38.

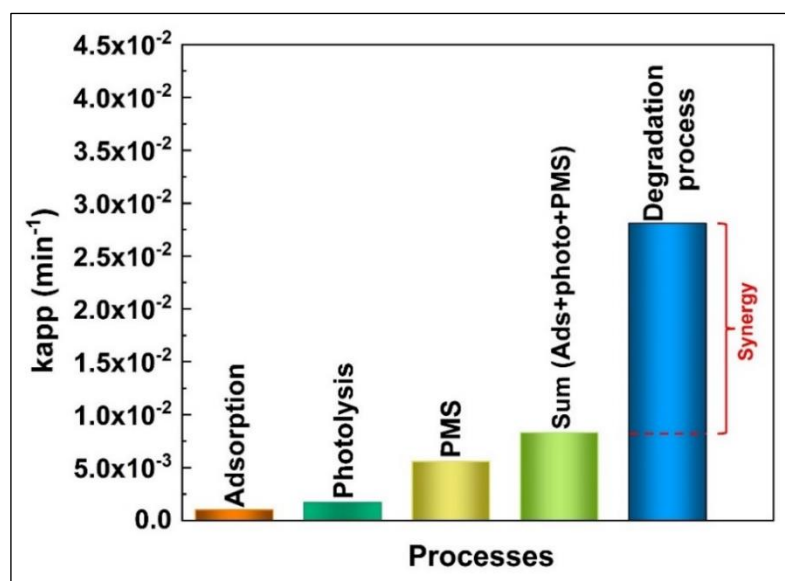


Figure 4.34: Comparison of the reaction rate constant of different processes.

The influence of rifampicin concentration on rifampicin degradation by visible light/LaZnFe LDH@PDMS/PMS process was analyzed using rifampicin concentration of 10 mg/L -30 mg/L. The effect of rifampicin concentration was investigated keeping LaZnFe LDH@PDMS sponge of 118 pieces, PMS concentration of 0.2 mmol/L, pH of 8, LED power of 100 W. According to Figure 4.35, the process achieved 66.5% degradation efficiency in the presence of 10 mg/L rifampicin. When the rifampicin concentration increased to 30 mg/L, the degradation rate decreased to 41.2%. The decline in degradation performance with increasing rifampicin concentration can be ascribed to the occupation of active sites in the LaZnFe LDH@PDMS sponge by rifampicin molecules and inadequate production of reactive oxygen species (ROS). In addition, an increase in rifampicin molecules can decrease the light transmission into the solution [126]. Thus, the optimum rifampicin concentration for the following tests was determined to be 15 mg/L.

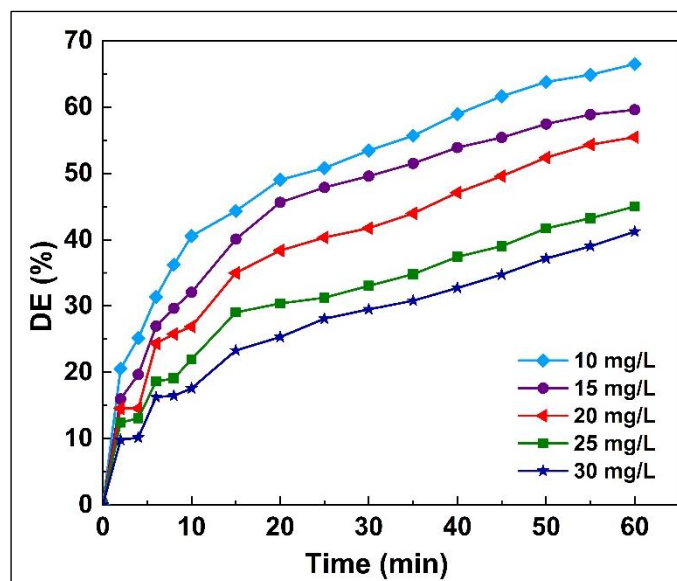


Figure 4.35: Influence of initial rifampicin concentration on the rifampicin photodegradation process using visible light/LaZnFe LDH@PDMS sponge/PMS.

The impact of the number of immobilized sponges on the efficiency of rifampicin degradation was investigated in the presence of LED power of 100 W, rifampicin of 15 mg/L, PMS concentration of 0.2 mmol/L, and pH of 8. Degradation efficiencies were 43.7%, 55.1%, and 59.6% in the presence of 40, 80, and 118 pieces of LaZnFe LDH@PDMS sponges, respectively, according to Figure 4.36. Because as the number of sponges increased, additional active sites for PMS activation became available, increasing the degradation efficiency [207].

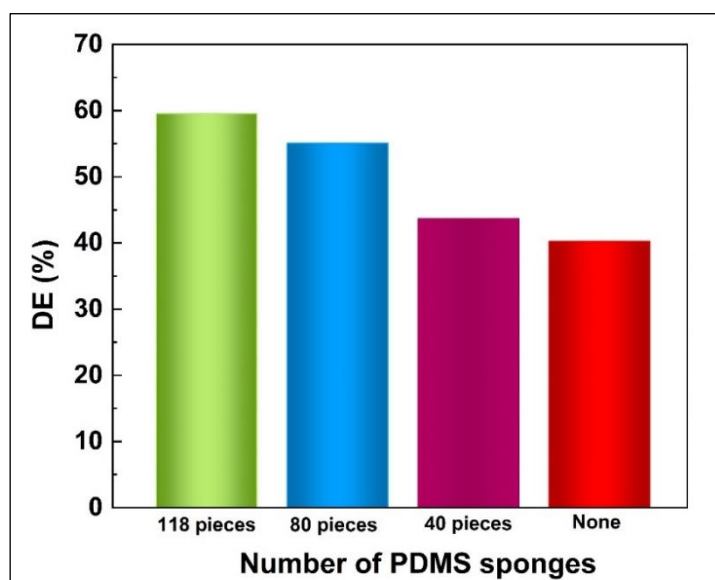


Figure 4.36: Influence of sponge number on the rifampicin photodegradation process using visible light/LaZnFe LDH@PDMS sponge/PMS.

The effect of PMS dosage on rifampicin degradation was evaluated in the range of 0.05–0.3 mmol/L. The experiment was conducted for 60 min in the presence of rifampicin of 15 mg/L, LaZnFe LDH@PDMS sponge of 118 pieces, pH of 8, and LED power of 100 W. According to Figure 4.37, the degradation efficiency improved from 48.6% to 59.6% with an increase in PMS dosage from 0.05 mmol/L to 0.2 mmol/L. Because of the increased PMS dosage, more free radicals were created. When the PMS concentration increased to 0.3 mmol/L, the degradation efficiency reached 61.4%. The limited number of photocarriers may not be sufficient for the activation of excess PMS, which may explain why the removal efficiency does not increase substantially as the PMS dose increases above a given dosage [208]. Therefore, the optimum PMS dosage was selected as 0.2 mmol/L.

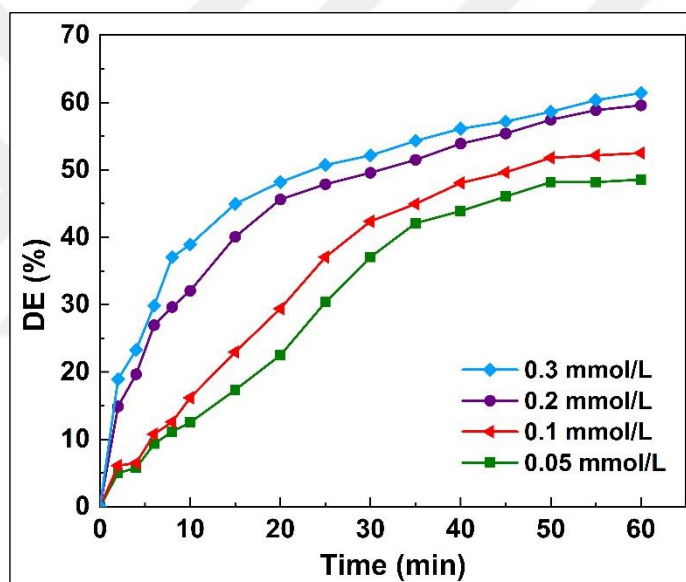


Figure 4.37: Influence of PMS concentration on the rifampicin photodegradation process using visible light/LaZnFe LDH@PDMS sponge/PMS.

The influence of light intensity was examined in the presence of 15 mg/L rifampicin, 118 pieces LaZnFe LDH@PDMS sponge, 0.2 mmol/L PMS, and pH 8. Rifampicin degradation efficiencies of 50.2%, 55.6%, and 59.6% were obtained under 30 W, 50 W, and 100 W LED power, respectively (Figure 4.38). With an increase in light intensity, the generation of electron-hole pairs also increases, which contributes to a boost in decomposition efficiency.

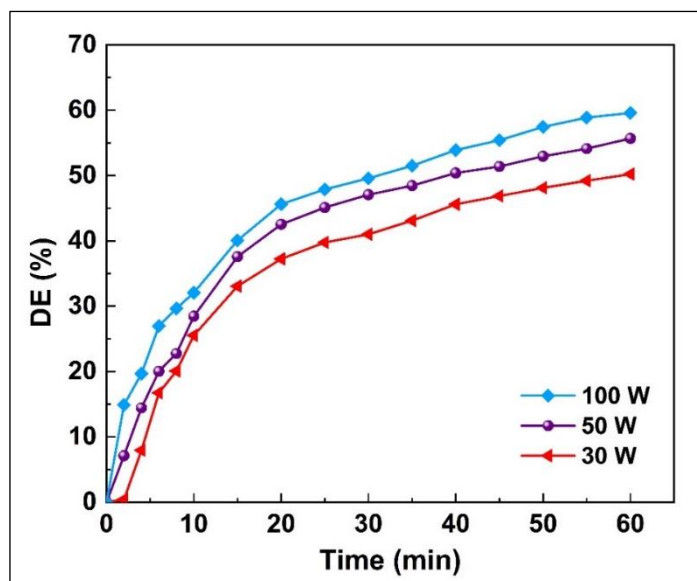


Figure 4.38: Influence of LED power on the rifampicin photodegradation process using visible light/LaZnFe LDH@PDMS sponge/PMS.

To investigate the impact of solution pH was conducted under the same conditions at varying pH levels ranging from 2 to 10. As displayed in Figure 4.39, the greatest degradation efficiency was obtained at pH 8. The least efficiency was obtained at pH 10 and pH 2. This decrease can be explained by pH_{pzc} and the properties of the PDMS sponge. The pH_{pzc} of LaZnFe LDH was calculated as 7.1 in (Figure 4.15). Furthermore, the pK_a value of rifampicin was found to be 1.7 and 7.9 [174]. According to the pH_{pzc} of rifampicin, the catalyst's surface charge is positively charged at pH values lower than 7.1 and negatively charged at pH values above 7.1. On the other hand, The molecule of rifampicin is positive below pH 1.7, negative above pH 7.9, and zwitterion state between pH 1.7 and 7.9 [209]. The decrease in degradation efficiency at pH 10 can be explained by the fact that PDMS sponges are unstable in an alkaline environment [210].

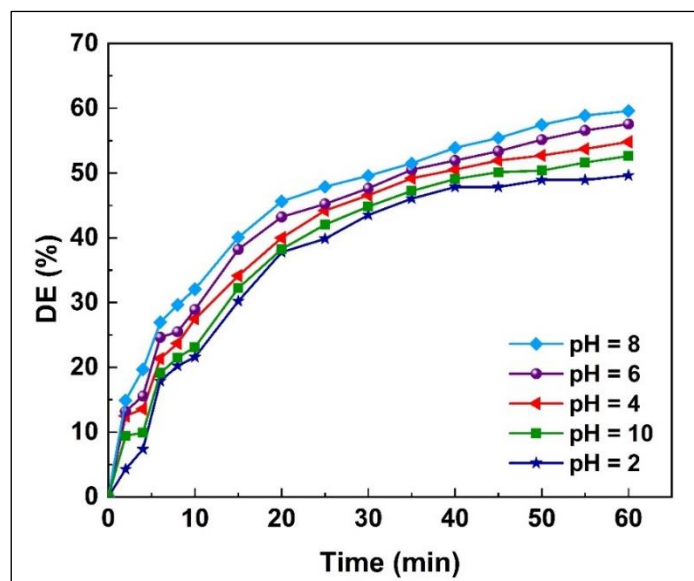
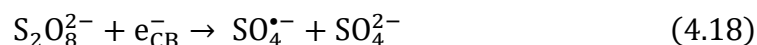


Figure 4.39: Influence of solution pH of the rifampicin photodegradation process using visible light/LaZnFe LDH@PDMS sponge/PMS.

The selection of the oxidant is a crucial determinant in the efficiency of the photocatalytic degradation of the pollutant. The oxidant species of H_2O_2 , PDS, and PMS were employed to examine the influence of oxidant species on the degradation process. The experiments were further conducted using rifampicin of 15 mg/L, LaZnFe LDH@PDMS sponge of 118 pieces, oxidant concentration of 0.2 mmol/L, pH of 8, and LED power of 100 W. As shown in Figure 4.40, the visible light/LaZnFe LDH@PDMS sponge system exhibited a 13.8% removal efficiency of rifampicin in the absence of an oxidizing agent. When H_2O_2 was utilized as the oxidant, it enhanced the removal efficiency to 18.5% by capturing photogenerated electrons and production $\cdot\text{OH}$ radical via Equation 4.9 [211]. Because of its greater O-O bond energy, hydrogen peroxide (H_2O_2) is more difficult to activate than PMS and PDS which likely explains why the system generated with H_2O_2 was less effective in degrading rifampicin [35]. The degradation efficiency of rifampicin increased to 33.5% when PDS was present. PDS can capture photogenerated electrons to produce $\text{SO}_4^{\cdot-}$ radicals (Equation 4.18). In addition, the generated $\text{SO}_4^{\cdot-}$ reacted with H_2O or OH^- to generate the $\cdot\text{OH}$ radical (Equations 2.32 and 2.28) [212]. The lower rifampicin degradation efficiency of PDS compared to PMS can be attributed to the lower energy cleavage of the O-O bond of PMS [194].



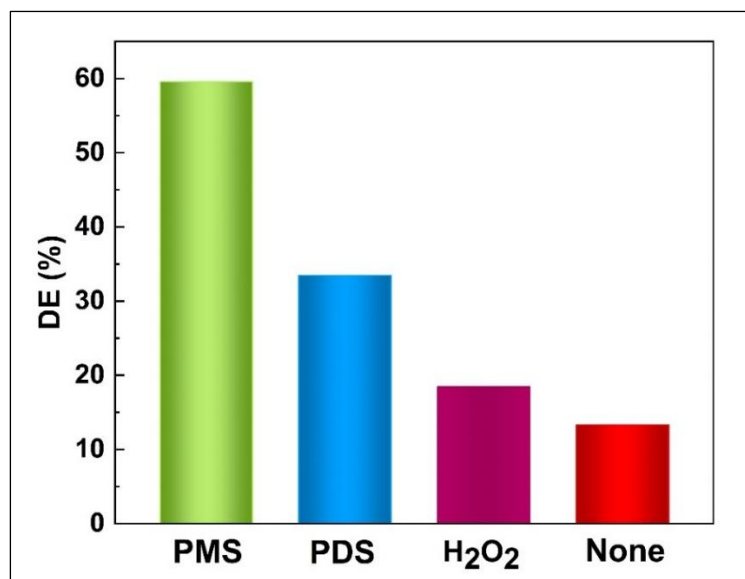


Figure 4.40: Influence of oxidant on the rifampicin photodegradation process using visible light/LaZnFe LDH@PDMS sponge/PMS.

The utilization of an OPD tracer under the sponge number of 118, rifampicin of 15 mg/L, PMS dosage of 0.2 mmol/L, pH of 8, and LED power of 100 W was employed to demonstrate the generation of $\cdot\text{OH}$ radical during the rifampicin photodegradation process. Figure 4.41. indicates that the peak observed at 416 nm can be attributed to the generation of $\cdot\text{OH}$ radicals. The ability of the photocatalytic process to produce $\cdot\text{OH}$ radicals has been demonstrated by the increase in $\cdot\text{OH}$ radical production as the reaction time is increased.

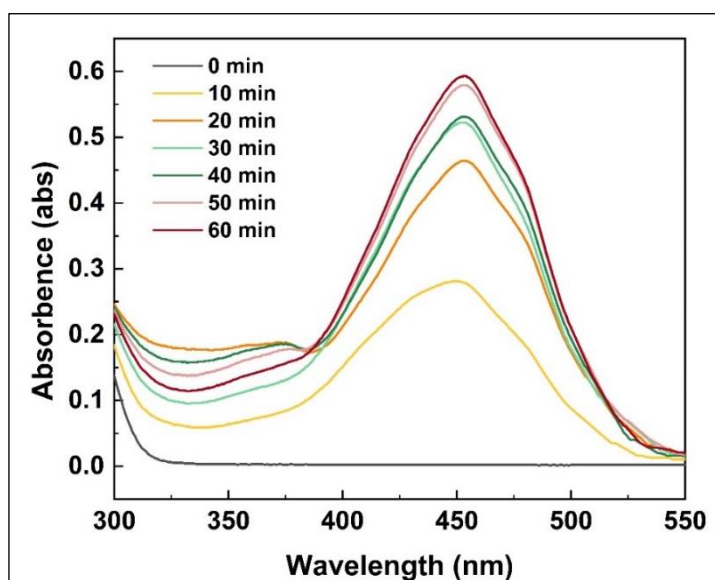


Figure 4.41: Spectra of OPD-trapped hydroxyl radical in rifampicin degradation by visible light/LaZnFe LDH@PDMS sponge/PMS process.

Radical quenching studies were conducted to ascertain the role of active species on the effectiveness of rifampicin degradation in the visible light/LaZnFe LDH@PDMS/PMS system (Figure 4.42). $\cdot\text{OH}$ radicals, both $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ radicals, h^+ , $\text{O}_2^{\cdot-}$ radicals, were quenched using isopropanol (IPA), phenol (pHOH), formic acid, and p-benzoquinone (BQ), respectively. The effect of the scavenger was investigated, keeping rifampicin of 15 mg/L, LaZnFe LDH@PDMS sponge of 118 pieces, PMS concentration of 0.2 mmol/L, pH of 8, LED power of 100 W. The presence of BQ had the greatest inhibiting effect on the photocatalytic degradation of rifampicin by directly removing $\text{O}_2^{\cdot-}$ from the solution, and the removal rate was reduced to 6.5%. On the other hand, degradation decreased from 59.6% to 47.1, 49.1, and 57.62% with the addition of IPA, pHOH, and formic acid scavengers, respectively. According to the findings, the influence of h^+ was quite minor. As a result, $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$, and $\text{O}_2^{\cdot-}$ radicals had a crucial role in the visible light/LaZnFe LDH@PDMS sponge/PMS process.

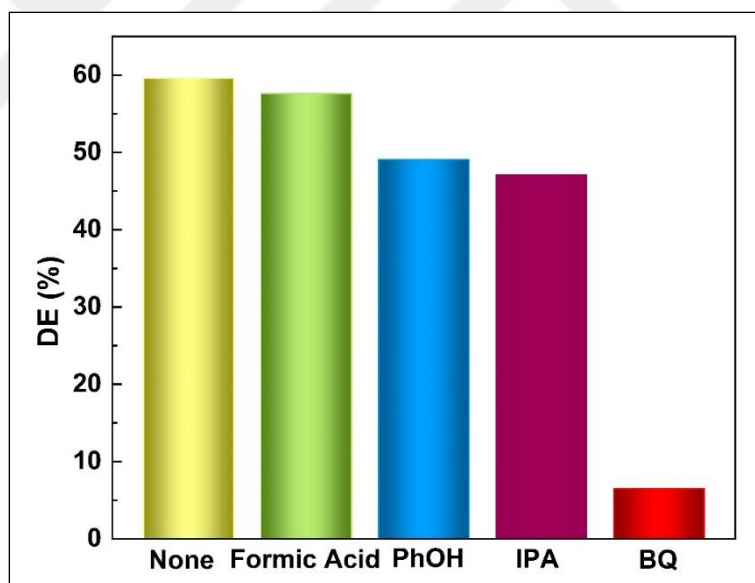


Figure 4.42: Influence of scavenger on the rifampicin photodegradation process using visible light/LaZnFe LDH@PDMS/PMS.

In addition, the visible light/LaZnFe LDH@PDMS sponge/PMS process was tested on the degradation of different pollutants such as methylene blue and metribuzin. These experiments were conducted with pollutant concentration of 15 mg/L, PMS dosage of 0.2 mmol/L, sponge number of 118, and LED power of 100 W under 90 min. According to Figure 4.43, the visible light/LaZnFe LDH@PDMS

sponge/PMS process degraded 32.8%, 37.2%, and 59.6% of methylene blue, metribuzin, and rifampicin, respectively. The highest degradation efficiency of rifampicin can be attributed to the fact that the functional groups of rifampicin can facilitate the binding of rifampicin to metal of the catalyst [213].

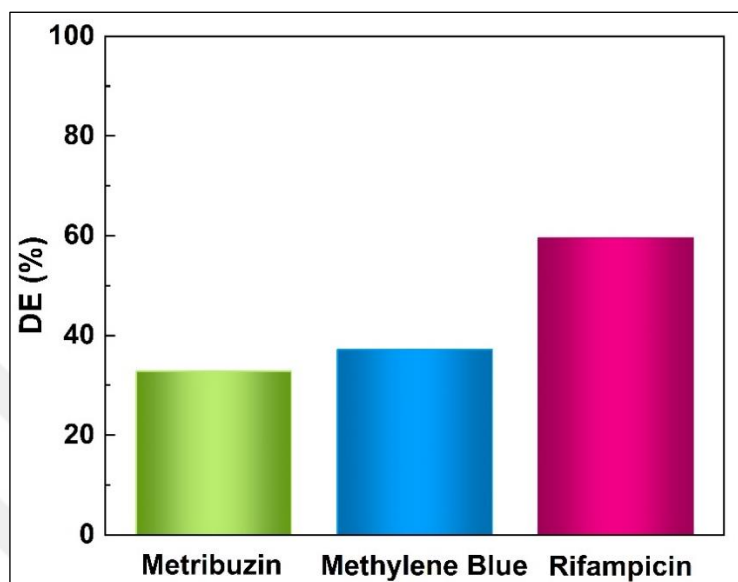


Figure 4.43: Influence of visible light/LaZnFe LDH@PDMS sponge/PMS process on the degradation of different pollutants.

The high stability and reusability of the LaZnFe LDH@PDMS sponge are very important in terms of both economical and practical application. The reusability of the as-synthesized sponge was investigated in visible light/LaZnFe LDH@PDMS/PMS process during seven consecutive cycles under optimum experimental conditions. After each cycle, the sponges were washed with distilled water, dried at 55 °C, and reused in the experiment. As shown in Figure 4.44, the decline in degradation rate from 59.6% to 58% after seven cycles demonstrates that this sponge has great reusability potential.

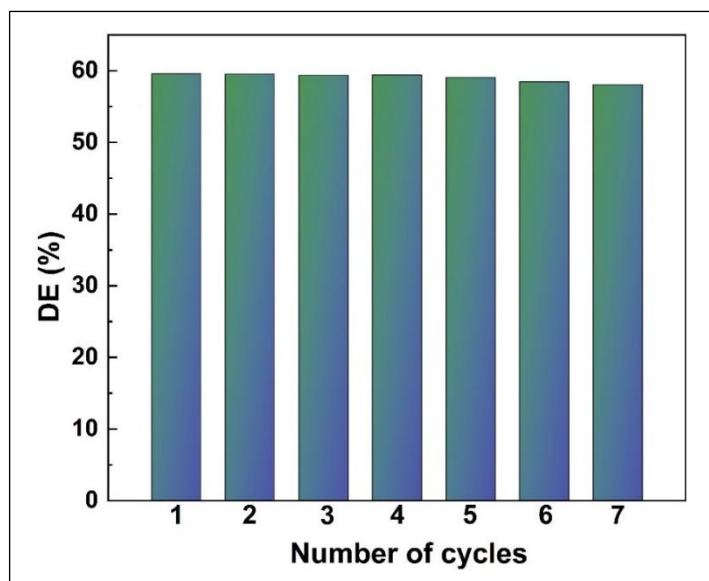


Figure 4.44: Reusability of LaZnFe LDH@PDMS sponge in visible light/LaZnFe LDH@PDMS sponge/PMS process.

Moreover, the images, SEM images, and XRD patterns of fresh and used LaZnFe LDH@PDMS sponges were compared. As illustrated in Figure 4.45, there is a negligible change in the appearance of the sponges.

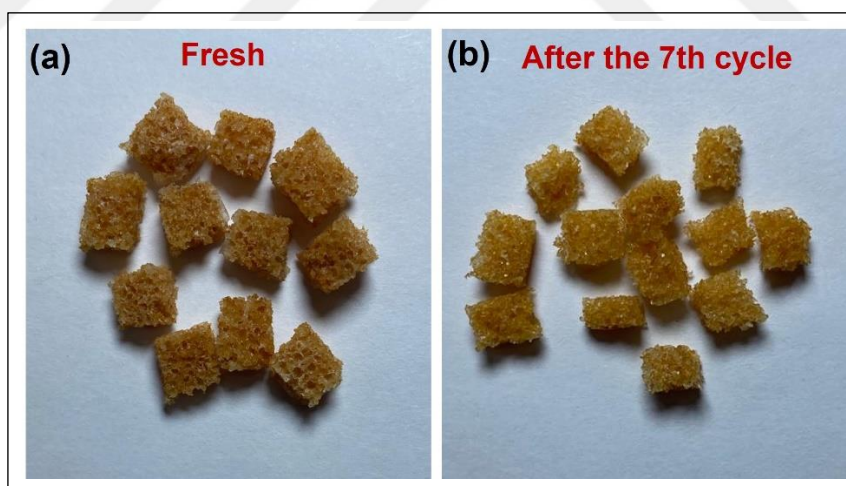


Figure 4.45: The images of a) fresh and b) used LaZnFe LDH@PDMS sponge.

SEM and XRD analysis showed that the morphological structure and structural stability of the sponge used remained almost the same when compared to the fresh sponge (Figures 4.46 and 4.47).

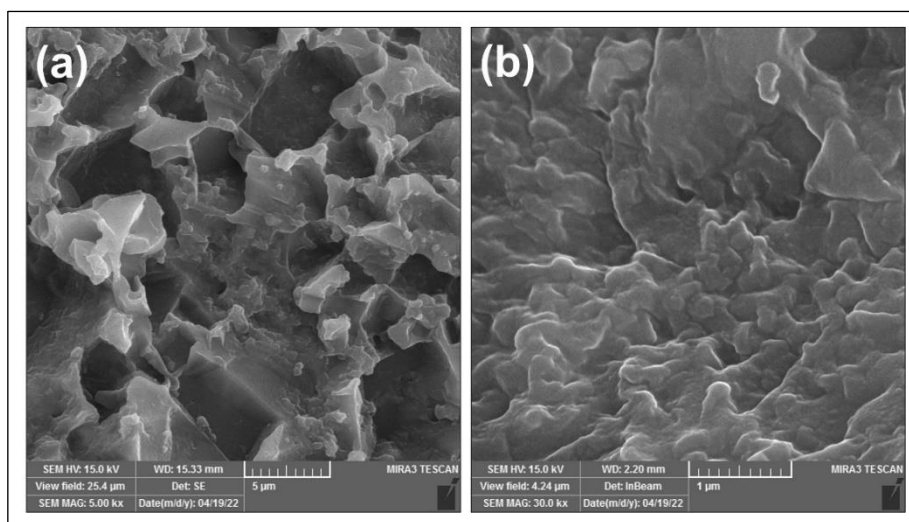


Figure 4.46: The SEM images of used LaZnFe LDH@PDMS sponge at a) 5 μm , and b) 1 μm .

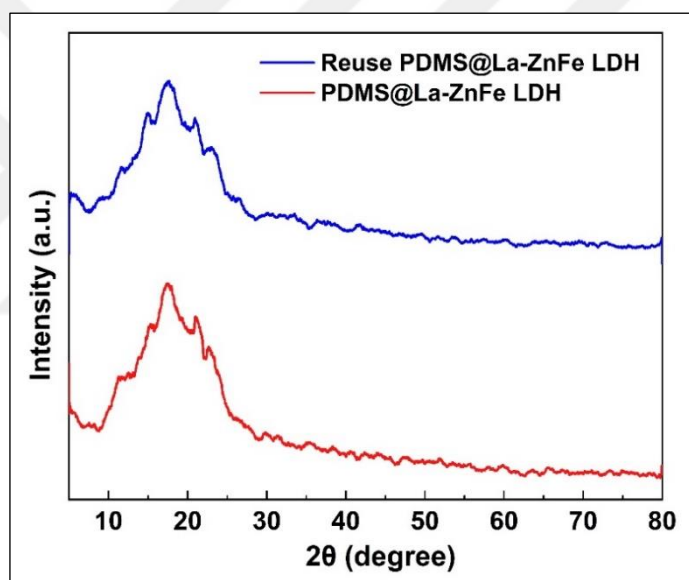


Figure 4.47: The XRD pattern of used LaZnFe LDH@PDMS sponge.

In addition, a leaching test was performed to assess the photocatalyst's stability. According to the ICP-OES results, the leaching concentration of zinc, iron, and silicon was 2.827 mg/L, 0.031 mg/L, and 0.944 mg/L, respectively. These values are below the allowable limit values for potable water determined by the World Health Organization [214].

The visible light/LaZnFe LDH@PDMS/PMS process was further applied to the rifampicin degradation in real wastewater matrix. PMS-assisted photocatalytic degradation of rifampicin was investigated in the presence of 118 pieces of LaZnFe LDH@PDMS sponge, 15 mg/L of rifampicin, 0.2 mmol/L PMS, and 100 W of LED

power. After 360 min of the photocatalytic process, the rifampicin degradation efficiency reached 67.6%, as illustrated in Figure 4.48. Comparing the 360-min treatment of the visible light/LaZnFe LDH@PDMS/PMS process on distilled water and wastewater reveals that rifampicin is degraded 25.2% less from the wastewater. The reason for this decrease in degradation efficiency was the dissolution of organic components and the presence of inorganic anions in the wastewater matrix [215].

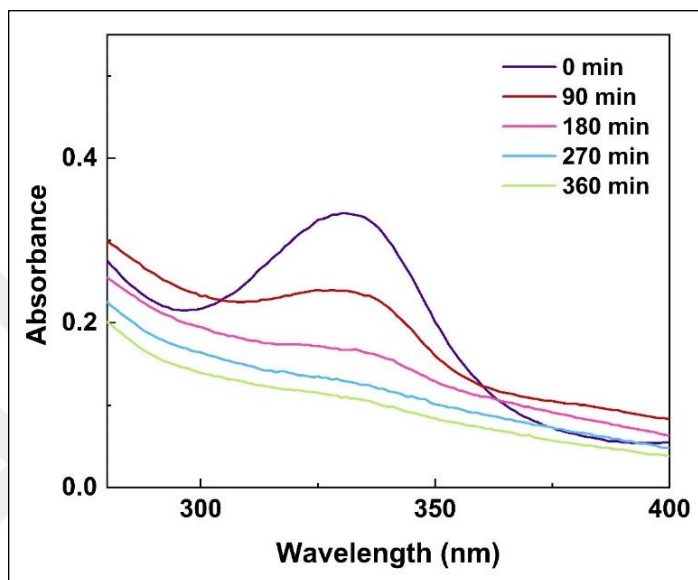


Figure 4.48: UV-Vis spectra of the degradation process of rifampicin in wastewater matrix using visible light/LaZnFe LDH@PDMS sponge/PMS.

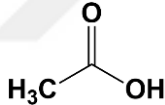
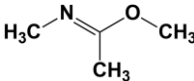
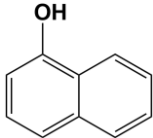
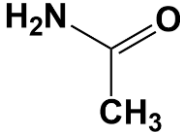
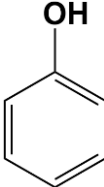
On the basis of the results of the analyses, the mechanism of rifampicin degradation by visible light/LaZnFe LDH/PMS was investigated. Initially, visible light causes the formation of e^-h^+ pairs on the surface of the LaZnFe LDH@PDMS sponge (Equation 2.20). h^+ in the VB of the LaZnFeLDH@PDMS sponge reacts with OH^- or H_2O , leading to the $\bullet OH$ radical generation (Equation 2.21 and Equation 2.22). On the other hand, the e^- located in the CB of the PDMS@LaZnFe LDH sponge exhibits a reaction with O_2 , resulting in the $O_2^{\bullet -}$ formation (Equation 2.23). Simultaneously, upon exposure to light, PMS undergoes reactions with e^- to produce the $SO_4^{\bullet -}$ radical, and with h^+ to generate the $SO_5^{\bullet -}$ radical. Furthermore, the formation of $\bullet OH$ radical occurs through the reaction between $SO_4^{\bullet -}$ and H_2O (Equation 2.32). As a result, rifampicin is converted first to by-products and then to CO_2 and H_2O with the help of h^+ , $SO_4^{\bullet -}$, $O_2^{\bullet -}$, and $\bullet OH$, and species (Equation 4.21).



4.2.3. Intermediates Formed During Rifampicin Degradation

The reaction intermediates generated during the photocatalytic process were detected using GC-MS under optimal conditions. Table 4.4 lists seven intermediates resulting from rifampicin degradation. Breaking bonds like C-C, C-N, and N-N may occur initially, according to the structure of by-products. Then, due to the ring's breakage, lower carbon aliphatic by-products such as acids and amines were produced. These simple structures have the potential to mineralize into the water and carbon dioxide molecules in the last stage. Furthermore, some additional undetected intermediates may have been generated during the degradation of rifampicin.

Table 4.4: The detected by-products formed during the photodegradation of rifampicin.

	Compounds	Structures	Detention time (min)	Main fragments (m/z) / (percent)
1	Acetic Acid		5.609	75.10 (100%), 116.10(83.80), 73.10(14.25%), 117.10(8.43%), 76.10(7.43%)
2	Ethanimidic acid		6.164	147.05 (100%), 73.10(44.58%), 148.05(20.82%), 203.20(18.95%), 188.10(11.30%)
3	1-Naphthalenol		6.318	144.05(100%), 73.05(57.34%), 158.10(34.25%), 145.05(12.39%), 59.05(11.84%)
4	Acetamide		7.045	58.05(100%), 115.00(49.93%), 72.00(26.87%), 100.10(10.13%), 116.00(6.36%)
5	Phenol		14.609	205.15(100%), 220.20(25.13%), 206.20(15.10%), 57.10(11.43%), 145.05(10.18%)

In addition, the acute and chronic toxicity of rifampicin and its intermediates on indicators such as fish, daphnia, and algae were evaluated using the ECOSAR model. In Section 4.1.3, the toxicity classifications of the compounds according to LC50, EC50, and ChV values are detailed. As shown in Table 4.5, both the acute and chronic toxicity of rifampicin to fish, daphnia, and algae was highly toxic. The LC50 and ChV values for acetic acid and acetamide demonstrate that these two intermediates were non-harmful for fish, green algae, and daphnia magna. In addition, ethylamine, 1-naphthalenol, and phenol showed lower acute and chronic toxicity than rifampicin. Consequently, rifampicin can be successfully detoxified using visible light/La-ZnFe LDH@PDMS sponge/PMS process.

Table 4.5: The acute and chronic toxicities of rifampicin and intermediates.

Compounds	Acute toxicity (mg/L)			Chronic toxicity (mg/L)		
	Fish (LC50)	Daphnia magna (LC50)	Green algae (EC50)	Fish (ChV)	Daphnia magna (ChV)	Green algae (ChV)
Rifampicin	0.269	0.148	0.335	0.0084	0.058	0.348
Acetic Acid	25800	1230	4400	2050	732	778
Ethylamine	223	20.7	28	27.8	1.33	7.77
1-Naphthalenol	6.60	3.9	8.56	0.701	0.482	1.49
Acetamide	33600	14200	3170	2320	616	433
Phenol	27.7	9.64	34.4	2.61	0.969	4.53

4.2.4. Energy Analysis

To determine the applicability of a process to real-world applications, it is crucial to calculate the electrical energy consumption. The economic feasibility of the process is assessed through the calculation of the EEO value using Equation 4.16. Accordingly, the EEO value for the rifampicin degradation process was calculated to be 986.17 kWh/m³order. In addition, the EEO values obtained in various photocatalytic removal processes are given in Table 4.6. Since the visible light/LaZnFe LDH/PMS process has a lower EEO value than other photocatalytic processes, it may be more economically feasible.

Table 4.6: Comparison of EEO value of different photocatalytic processes.

Catalyst type	Pollutant	Reaction conditions	kapp (1/min)	EEO (kWh/m ³ order)	Ref.
TiO ₂	Ofloxacin	[Catalyst]: 0.4 g/L, [Pollutant]: 20 mg/L, Light intensity: 125 W, contact time: 120 min, and pH: natural pH	0.0054	1729.5	[196]
PANI-rGO@MnO ₂	Ibuprofen	[Catalyst]: 0.5 g/L, [Pollutant]: 10 mg/L, Light intensity: 18 W, contact time: 120 min, and pH: 4	0.027	1467	[216]
ZnO	Acid Red 37	[Catalyst]: 0.5 g/L, [Pollutant]: 52 mg/L, Light intensity: 13.4 W, contact time: 350 min	0.003	1666.6	[217]
ZnO	Ofloxacin	[Catalyst]: 0.4 g/L, [Pollutant]: 20 mg/L, Light intensity: 125 W, contact time: 120 min, and pH: natural pH	0.0081	1228.2	[196]
LaZnFe LDH@PDMS sponge	Rifampicin	[Pollutant]: 15 mg/L, Light intensity: 100 W, contact time: 60 min, and pH: 8	0.0281	986.2	This study

5. CONCLUSIONS AND RECOMMENDATIONS

In this thesis, the synthesis, and modifications of ZnFe LDH-based nanomaterials to enhance their catalytic performance and applications in AOPs for the degradation of persistent pollutants metribuzin and rifampicin were studied. First, the La element was doped into ZnFe LDH, and utilized for the sonocatalytic degradation of metribuzin via PDS activation. Then, LaZnFe LDH was then immobilized on PDMS sponge to improve its reusability and stability. This immobilized catalyst was used for photocatalytic degradation of rifampicin by PMS activation under visible light irradiation. Various characterization techniques were used to determine the morphological, structural, and optical properties of LaZnFe LDH and immobilized catalyst. The optimum conditions were determined by assessing various parameters including catalyst concentration, oxidant concentration, pH, pollutant concentration, light power, and US power. The results obtained from the studies are as follows:

- The optimum conditions for metribuzin degradation in US/LaZnFe LDH/PDS process were found as catalyst dosage of 1 g/L, metribuzin concentration of 15 mg/L, natural pH, PDS dosage of 2 mmol/L, and ultrasonic power of 120 W during contact time of 90 min.
- Under optimal conditions, US/LaZnFe LDH/PDS process achieved 90.1% metribuzin degradation efficiency within 360 min.
- Comparing the US/ZnFe LDH/PDS process to the US/LaZnFe LDH/PDS process revealed that the addition of La to ZnFe LDH increased metribuzin removal efficiency by 14.3%.
- While PDS solely degraded 3.2% of metribuzin, with the addition of LDH and US, the degradation efficiency was increased to 79.1%. This can be attributed to the activation of PDS by the LaZnFe LDH and ultrasonic irradiation.
- SEM images of the LaZnFe LDH@PDMS sponge reveal that LaZnFe LDH was successfully embedded in the PDMS sponge.
- The optimum operating conditions for the visible light/LaZnFe LDH@PDMS sponge/PMS were determined as 15 mg/L of rifampicin, 0.2 mmol/L of PMS, 100 W of light intensity, and pH of 8, conducting the rifampicin degradation efficiency to 92.8% within 360 min.

- The synergy factor was 3.73 for US/LaZnFe LDH process applied in metribuzin degradation and 3.38 for visible light/LaZnFe LDH@PDMS/PMS process applied in rifampicin degradation, proving the synergistic relationship between process components.
- Scavenger experiments revealed that h^+ , $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$, and $\text{O}_2^{\cdot-}$ contribute to the degradation of metribuzin and rifampicin. However, while $\text{SO}_4^{\cdot-}$ had a major role in the US/LaZnFe LDH/PDS process in which metribuzin is eliminated, $\text{O}_2^{\cdot-}$ had a significant role in the visible light/LaZnFe LDH@PDMS/PMS process in which rifampicin is eliminated.
- The rifampicin degradation efficiency of the immobilized catalyst used in visible light/LaZnFe LDH@PDMS sponge /PMS process decreased by only 1.5% after seven consecutive cycles, indicating high reusability and stability of the immobilized catalyst.
- Metribuzin and rifampicin degradation efficiencies in the wastewater matrix were 52.8% and 67.2%, respectively, after 360 min of contact time for the US/LaZnFe LDH/PDS and visible light/LaZnFe LDH@PDMS sponge/PMS processes. The fact that the removal of pollutants in the wastewater matrix requires more time can be attributed to the inhibitory effect of inorganic anions and organic substances in the wastewater.

The following recommendation can be suggested for future research based on the results:

- Although LDH is quite effective at degrading specific pollutants from an aquatic solution, real wastewater contains many competing anions. Consequently, it is necessary to focus on using LDH to degrade pollutants from real wastewater.
- The immobilization of LDHs on various supporting substrates such as glass, polymers, and carbon nanotubes, and the use of immobilized catalysts in pollutant removal, should be studied further.
- Improving the reusability of LDHs is crucial for the process's long-term application. Various modification techniques should be utilized to improve the reusability and stability of LDHs.

- The use of diverse biopolymers in the synthesis of LDHs can solve the metal leaching problem of some LDHs, which is critical for environmental health.
- It should concentrate on the development and implementation of reactor designs to evaluate the degradation performance of LDHs more accurately.



REFERENCES

- [1] Meng F., Lin C., Song B., Yu L., Zhao Y., Zhao, Y., Zhi, Z., Song, M. (2022), “Synergistic effect of underwater arc discharge plasma and Fe₂O₃-CoFe₂O₄ enhanced PMS activation to efficiently degrade refractory organic pollutants”, *Separation and Purification Technology*, 290, 120834.
- [2] Singh P., Chauhan K., (2021), “Persistent Organic Pollutants (POPs) in Environment and its Health Impact” In: *Management of Contaminants of Emerging Concern (CEC) in Environment*, 71-91.
- [3] Dara D., Drabovich A.P., (2023), “Assessment of risks, implications, and opportunities of waterborne neurotoxic pesticides” *Journal of Environmental Sciences*, 125, 735-741.
- [4] Yang G., Xie S., Yang M., Tang S., Zhou L., Jiang W., Zhou B., Li Y., Si B., (2022), “A critical review on retaining antibiotics in liquid digestate: Potential risk and removal technologies”, *Science of the Total Environment*, 853, 158550.
- [5] Quinn B., Gagné F., Blaise C., (2009), “Evaluation of the acute, chronic and teratogenic effects of a mixture of eleven pharmaceuticals on the cnidarian, *Hydra attenuata*”, *Science of the Total Environment*, 407(3), 1072-1079.
- [6] Cavalier H., Trasande L., Porta M., (2023), “Exposures to pesticides and risk of cancer: Evaluation of recent epidemiological evidence in humans and paths forward”, *International Journal of Cancer*, 152(5), 879-912.
- [7] Hassaan M.A, El Nemr A., (2020), “Pesticides pollution: Classifications, human health impact, extraction and treatment techniques”, *The Egyptian Journal of Aquatic Research*, 46(3), 207-220.
- [8] Büchel K.H., (1983) “Chemistry of Pesticides”, John Wiley & Sons, Inc.
- [9] Rani M., Shanker U., Jassal V., (2017), “Recent strategies for removal and degradation of persistent & toxic organochlorine pesticides using nanoparticles: A review”, *Journal of Environmental Management*, 190, 208-222.
- [10] Mishra S., Pang S., Zhang W., Lin Z., Bhatt P, Chen S., (2021), “Insights into the microbial degradation and biochemical mechanisms of carbamates”, *Chemosphere*, 279, 130500.
- [11] Aswathi A., Pandey A., Sukumaran R.K., (2019), “Rapid degradation of the organophosphate pesticide – Chlorpyrifos by a novel strain of *Pseudomonas nitroreducens* AR-3”, *Bioresource Technology*, 292, 122025.

- [12] Lourthuraj A.A., Hatshan M.R., Hussein D.S., (2022), "Biocatalytic degradation of organophosphate pesticide from the wastewater and hydrolytic enzyme properties of consortium isolated from the pesticide contaminated water", *Environmental Research*, 205, 112553.
- [13] Raj R. S., Krishnan K. A., (2023), "A comprehensive review on the impact of emerging organophosphorous pesticides and their remedial measures: Special focus on acephate", *Environmental Nanotechnology, Monitoring & Management*, 20, 100813.
- [14] Birolli W.G, Dos Santos A., Pilau E., Rodrigues-Filho E., (2021), "New Role for a Commercially Available Bioinsecticide: *Bacillus thuringiensis* Berliner Biodegrades the Pyrethroid Cypermethrin", *Environmental Science and Technology*, 55(8), 4792-4803.
- [15] Liu Y., Tang S., Wang X., Wang X., Tang X., Wu, Q., Huang Z., Ding, J., (2023), "A novel thermostable and salt-tolerant carboxylesterase involved in the initial aerobic degradation pathway for pyrethroids in *Glycomyces salinus*", *Journal of Hazardous Materials*, 451, 131128.
- [16] Velasco E., Ríos-Acevedo J.J., Sarria-Villa R., Rosero-Moreano M., (2021), "Green method to determine triazine pesticides in water using Rotating Disk Sorptive Extraction (RDSE)", *Heliyon*, 7(9).
- [17] Wang M., Zhou M., Tan Q., Yu L., Dong C., Liang R., Liu W., Zhang Y., Li M., Nie X., Jing T., Chen W., (2023), "Triazine herbicides exposure, natural immunoglobulin M antibodies, and fasting plasma glucose changes: Association and mediation analyses in general Chinese urban adults", *Environmental Pollution*, 330, 121833.
- [18] Bilal M., Iqbal H.M., Barceló D., (2019), "Persistence of pesticides-based contaminants in the environment and their effective degradation using laccase-assisted biocatalytic systems", *Science of the Total Environment*, 695, 133896.
- [19] Blaser M.J., (2016), "Antibiotic use and its consequences for the normal microbiome", *Science*, 352(6285), 544-545.
- [20] Etebu E., Arikekpar I., (2016), "Antibiotics: Classification and mechanisms of action with emphasis on molecular perspectives", *International Journal of Applied Microbiology and Biotechnology Research*, 4(2016), 90-101.
- [21] Demeke C.A., Adinew G.M., Abebe T.B., Gelaye A.T., Gemedo S.G., Yimenu D.K., (2021), "Comparative analysis of the effectiveness of narrow-spectrum versus broad-spectrum antibiotics for the treatment of childhood pneumonia", *SAGE Open Medicine*, 9, 1-7.
- [22] Bayan E.M., Pustovaya L.E., Volkova M.G., (2021), "Recent advances in TiO₂-based materials for photocatalytic degradation of antibiotics in aqueous systems", *Environmental Technology and Innovation*, 24, 101822.

- [23] Li S., Wu Y., Zheng H., Li H., Zheng Y., Nan J., Ma J., Nagarajan D., Chang J.S., (2023), "Antibiotics degradation by advanced oxidation process (AOPs): Recent advances in ecotoxicity and antibiotic-resistance genes induction of degradation products", *Chemosphere*, 311(2), 136977.
- [24] Honarmandrad Z., Sun X., Wang Z., Naushad M., Boczkaj G., (2023), "Activated persulfate and peroxymonosulfate based advanced oxidation processes (AOPs) for antibiotics degradation – A review", *Water Resources and Industry*, 29, 100194.
- [25] Murray C.J., Ikuta K.S., Sharara F., Swetschinski L., Aguilar G.R., Gray A., et al., (2022), "Global burden of bacterial antimicrobial resistance in 2019: a systematic analysis", *The Lancet*, 399(10325), 629-655.
- [26] Gogoi D., Das M.R., Ghosh N. N., (2023), "2-D gC3N4 supported CoFe2O4 nanoparticles as an efficient S-scheme catalyst for various antibiotic degradation", *Applied Surface Science*, 619, 156753.
- [27] Salimi M., Behbahani M., Sobhi H.R., Gholami M., Jafari A. J., Kalantary, R. R., Farzadkia M., Esrafil, A., (2019), "A new nano-photocatalyst based on Pt and Bi co-doped TiO2 for efficient visible-light photo degradation of amoxicillin", *New Journal of Chemistry*, 43(3), 1562-1568.
- [28] Kümmerer K., Al-Ahmad A., Mersch-Sundermann V., (2000), "Biodegradability of some antibiotics, elimination of the genotoxicity and affection of wastewater bacteria in a simple test", *Chemosphere*, 40(7), 701-710.
- [29] Nowell L.H., Norman J.E., Moran P.W., Martin J.D., Stone W.W., (2014), "Pesticide toxicity index-a tool for assessing potential toxicity of pesticide mixtures to freshwater aquatic organisms", *Science of the Total Environment*, 476, 144-157.
- [30] Cai F., Lei L., Li Y., Chen Y., (2021), "A review of aerobic granular sludge (AGS) treating recalcitrant wastewater: Refractory organics removal mechanism, application and prospect", *Science of the Total Environment*, 782, 146852.
- [31] Qiu J.L., Li D.W., Jing S.C., Qiu H., Liu F.Q., (2022), "Advanced technique of catalytic ozonation-enhanced coagulation for the efficient removal of low coagulability refractory organics from secondary effluent", *Chemosphere*, 303, 135157.
- [32] Mansas C., Mendret J., Brosillon S., Ayrat A., (2020), "Coupling catalytic ozonation and membrane separation: A review", *Separation and Purification Technology*, 236, 11622.
- [33] Li S., Yang Y., Zheng H., Zheng Y., Jing T., Ma, J., Nan J., Leong Y.K., Chang, J. S., (2022), "Advanced oxidation process based on hydroxyl and sulfate radicals to degrade refractory organic pollutants in landfill leachate", *Chemosphere*, 297, 134214.

- [34] Kim K.H., Ihm S.K., (2011), "Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: A review", *Journal of Hazardous Materials*, 186(1), 16-34.
- [35] Yang Q., Ma Y., Chen F., Yao F., Sun J., Wang, S., Yi K., Hou L., Li X., Wang, D. (2019), "Recent advances in photo-activated sulfate radical-advanced oxidation process (SR-AOP) for refractory organic pollutants removal in water", *Chemical Engineering Journal*, 378, 122149.
- [36] Wang J.L, Xu L.J., (2011), "Advanced Oxidation Processes for Wastewater Treatment: Formation of Hydroxyl Radical and Application", *Critical reviews in environmental science and technology*, 42(3), 251-325.
- [37] Taoufik N., Sadiq M., Abdenmour M., Qourzal S., Khataee A., Sillanpää, M., Barka, N. (2022), "Recent advances in the synthesis and environmental catalytic applications of layered double hydroxides-based materials for degradation of emerging pollutants through advanced oxidation processes", *Materials Research Bulletin*, 154, 111924.
- [38] Deng Y., Zhao R., (2015), "Advanced Oxidation Processes (AOPs) in Wastewater Treatment", *Current Pollution Reports*, 1, 167-176.
- [39] Cuerda-Correa E.M., Alexandre-Franco M.F., Fernández-González C., (2020), "Advanced oxidation processes for the removal of antibiotics from water. An overview", *Water*, 12(1), 102.
- [40] Oturan M.A., Aaron J.J., (2014), "Advanced oxidation processes in water/wastewater treatment: Principles and applications. A review", *Critical Reviews in Environmental Science and Technology*, 44(23), 2577-2641.
- [41] Rekhate C. V., Srivastava J.K., (2020), "Recent advances in ozone-based advanced oxidation processes for treatment of wastewater- A review", *Chemical Engineering Journal Advances*, 3, 100031.
- [42] Gruttadauria M., Liotta L.F., Di Carlo G., Pantaleo G., Deganello G., Meo, P. L., Aprile C., Noto, R., (2007), "Oxidative degradation properties of Co-based catalysts in the presence of ozone", *Applied Catalysis B: Environmental*, 75(3-4), 281-289.
- [43] Khataee A., Farshchi M.E., Fathinia M., Aghdasinia H., (2020), "Photocatalytic ozonation process for degradation of an anthelmintic drug using ceramic coated TiO₂ NPs: CFD simulation coupling with kinetic mechanisms", *Process Safety and Environmental Protection*, 141, 37-48.
- [44] Khataee A., Fazli A., Zakeri F., Joo S.W., (2020), "Synthesis of a high-performance Z-scheme 2D/2D WO₃@CoFe-LDH nanocomposite for the synchronic degradation of the mixture azo dyes by sonocatalytic ozonation process", *Journal of Industrial and Engineering Chemistry*, 89, 301-315.

- [45] Chaparinia F., Soltani C.R.D., Safari M., Godini H., Khataee A., (2022), "Treatment of aquatic medium containing common and emerging contaminants using an aero-electrochemical process based on graphite cathode and three metal oxides alloy as anode: Central composite design and photo/sono-enhancement", *Chemosphere*, 297, 134129.
- [46] Wang G., Liu Y., Duan Y., Ye J., Lin Z., (2023), "Effects of porosity on the electrochemical oxidation performance of Ti₄O₇ electrode materials", *Ceramics International*, 49(10), 15357-15364.
- [47] Moreira F.C., Boaventura A.R., Brillas E., Vilar V.J.P., (2017), "Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters", *Applied Catalysis B: Environmental*, 202, 217-261.
- [48] Fu R., Zhang P.S., Jiang Y.X., Sun L., Sun X.H., (2023), "Wastewater treatment by anodic oxidation in electrochemical advanced oxidation process: Advance in mechanism, direct and indirect oxidation detection methods", *Chemosphere*, 311, 136993.
- [49] Jiad M.M., Abbar A.H., (2023), "Treatment of Petroleum Refinery Wastewater by Electro-Fenton process using a Low Cost Porous Graphite Air-diffusion Cathode with a Novel Design", *Chemical Engineering Research and Design*, 193, 207-221.
- [50] Wang W., Li Y., Li Y., Zhou M., Arotiba O.A., (2020), "Electro-Fenton and photoelectro-Fenton degradation of sulfamethazine using an active gas diffusion electrode without aeration", *Chemosphere*, 250, 126177.
- [51] Garza-Campos B.R., Guzmán-Mar J.L., Reyes L.H., Brillas E., Hernández-Ramírez A., Ruiz-Ruiz, E. J., (2014), "Coupling of solar photoelectro-Fenton with a BDD anode and solar heterogeneous photocatalysis for the mineralization of the herbicide atrazine", *Chemosphere*, 97, 26-33.
- [52] Titchou F.E., Zazou H., Afanga H., Gaayda El J., Akbour R. A., Nidheesh, P. V., Hamdani, M. (2021), "An overview on the elimination of organic contaminants from aqueous systems using electrochemical advanced oxidation processes", *Journal of Water Process Engineering*, 41, 102040.
- [53] Gout E., Monnot M., Boutin O., Vanlout P., Claeys-Bruno M., Moulin P., (2022), "Assessment and optimization of wet air oxidation for treatment of landfill leachate concentrated with reverse osmosis", *Process Safety and Environmental Protection*, 162, 765-774.
- [54] Feng D., Malleret L., Soric A., Boutin O., (2020), "Kinetic study of glyphosate degradation in wet air oxidation conditions", *Chemosphere*, 247, 125930.
- [55] Torres-Palma R.A., Serna-Galvis E.A., (2018), "Sonolysis" In *Advanced Oxidation Processes for Wastewater Treatment, Emerging Green Chemical Technology*, 177-213, Academic Press.

- [56] Rezk A.R., Ahmed H., Ramesan S., Yeo L.Y., (2021), “High Frequency Sonoprocessing: A New Field of Cavitation-Free Acoustic Materials Synthesis, Processing, and Manipulation”, *Advanced Science*, 8(1), 2001983.
- [57] Sathishkumar P., Mangalaraja R.V., Anandan S., (2016), “Review on the recent improvements in sonochemical and combined sonochemical oxidation processes - A powerful tool for destruction of environmental contaminants”, *Renewable and Sustainable Energy Reviews*, 55, 426-454.
- [58] Yusof N.S.M., Anandan S., Sivashanmugam P., Flores E.M.M, Ashokkumar M., (2022), “A correlation between cavitation bubble temperature, sonoluminescence and interfacial chemistry – A minireview”, *Ultrasonics Sonochemistry*, 85, 105988.
- [59] Soltani R. D. C., Mashayekhi M., Khataee A., Ghanadzadeh M. J., Sillanpää M. (2018), “Hybrid sonocatalysis/electrolysis process for intensified decomposition of amoxicillin in aqueous solution in the presence of magnesium oxide nanocatalyst”, *Journal of Industrial and Engineering Chemistry*, 64, 373-382.
- [60] Abdi J., Sisi A.J., Hadipoor M., Khataee A., (2022), “State of the art on the ultrasonic-assisted removal of environmental pollutants using metal-organic frameworks”, *Journal of Hazardous Materials*, 424, 127558.
- [61] de Andrade F. V., Augusti R., de Lima G.M., (2021), “Ultrasound for the remediation of contaminated waters with persistent organic pollutants: A short review”, *Ultrasonics Sonochemistry*, 78, 105719.
- [62] Gholami P., Khataee A., Soltani R.D.C, Bhatnagar A., (2019), “A review on carbon-based materials for heterogeneous sonocatalysis: Fundamentals, properties and applications”, *Ultrasonics Sonochemistry*, 58, 104681.
- [63] Rao Y., Yang H., Xue D., Guo Y., Qi F., Ma J., (2016), “Sonolytic and sonophotolytic degradation of Carbamazepine: Kinetic and mechanisms”, *Ultrasonics Sonochemistry*, 32, 371-379.
- [64] Khataee A., Saadi S., Vahid B., Joo S.W., Min B.K., (2016), “Sonocatalytic degradation of Acid Blue 92 using sonochemically prepared samarium doped zinc oxide nanostructures”, *Ultrasonics Sonochemistry*, 29, 27-38.
- [65] Khataee A., Mohamadi F.T., Rad T.S., Vahid B., (2018), “Heterogeneous sonocatalytic degradation of anazoline sodium by synthesized dysprosium doped CdSe nanostructures”, *Ultrasonics Sonochemistry*, 40, 361-372.
- [66] Eren Z., Ince N.H., (2010), “Sonolytic and sonocatalytic degradation of azo dyes by low and high frequency ultrasound”, *Journal of Hazardous Materials*, 177(1-3), 1019-1024.

- [67] Abdurahman M.H., Abdullah A.Z., Shoparwe N.F., (2021), "A comprehensive review on sonocatalytic, photocatalytic, and sonophotocatalytic processes for the degradation of antibiotics in water: Synergistic mechanism and degradation pathway", *Chemical Engineering Journal*, 413, 127412.
- [68] Qiu P., Park B., Choi J., Thokchom B., Pandit A.B., Khim J., (2018), "A review on heterogeneous sonocatalyst for treatment of organic pollutants in aqueous phase based on catalytic mechanism", *Ultrasonics Sonochemistry*, 45, 29-49.
- [69] Pang Y.L., Lim S., Ong H.C., Chong W.T., (2016), "Synthesis, characteristics and sonocatalytic activities of calcined γ -Fe₂O₃ and TiO₂ nanotubes/ γ -Fe₂O₃ magnetic catalysts in the degradation of Orange G", *Ultrasonics Sonochemistry*, 29, 317-327.
- [70] Hilgenfeldt S., Grossmann S., Lohse D., (1999), "A simple explanation of light emission in sonoluminescence", *Nature*, 398(6726), 402-405.
- [71] Wang G., Cheng H., (2023), "Application of Photocatalysis and Sonocatalysis for Treatment of Organic Dye Wastewater and the Synergistic Effect of Ultrasound and Light", *Molecules* 28(9), 3706.
- [72] Dharman R.K., Shejale K.P., Kim S.Y., (2022), "Efficient sonocatalytic degradation of heavy metal and organic pollutants using CuS/MoS₂ nanocomposites", *Chemosphere*, 305, 135415.
- [73] Akpotu S.O., Oseghe E.O., Ayanda O.S., Skelton A.A., Msagati T.A., Ofomaja, A. E., (2019), "Photocatalysis and biodegradation of pharmaceuticals in wastewater: effect of abiotic and biotic factors", *Clean Technologies and Environmental Policy*, 21, 1701-1721.
- [74] Gowland D.C., Robertson N, Chatzisyneon E., (2021), "Photocatalytic oxidation of natural organic matter in water", *Water*, 13(3), 288.
- [75] Irfan S., Li L., Saleemi A.S., Nan C.W., (2017), "Enhanced photocatalytic activity of La³⁺ and Se⁴⁺ co-doped bismuth ferrite nanostructures", *Journal of Materials Chemistry A*, 5(22), 11143-11151.
- [76] Bai X., Chen W., Wang B., Sun T., Wu B., Wang Y., (2022), "Photocatalytic Degradation of Some Typical Antibiotics: Recent Advances and Future Outlooks", *International Journal of Molecular Sciences*, 23(15), 8130.
- [77] Sun Y., O'Connell D.W., (2022), "Application of visible light active photocatalysis for water contaminants: A review", *Water Environment Research*, 94(10).
- [78] Banerjee S., Pillai S.C., Falaras P., O'shea K.E., Byrne J.A., Dionysiou D. D., (2014), "New insights into the mechanism of visible light photocatalysis", *Journal of Physical Chemistry Letters*, 5(15), 2543-2554.

- [79] Kosera V.S., Cruz T.M., Chaves E.S., Tiburtius E.R., (2017), "Triclosan degradation by heterogeneous photocatalysis using ZnO immobilized in biopolymer as catalyst", *Journal of Photochemistry and Photobiology A: Chemistry*, 344, 184-191.
- [80] Adeyemi J.O., Ajiboye T., Onwudiwe D.C., (2021), "Mineralization of Antibiotics in Wastewater Via Photocatalysis", *Water, Air, and Soil Pollution*, 232, 1-28.
- [81] Ge L., Shao B., Liang Q., Huang D., Liu Z., He, Q., Wu T., Luo S., Pan Y., Zhao C., Huang J., Hu, Y., (2022), "Layered double hydroxide based materials applied in persulfate based advanced oxidation processes: Property, mechanism, application and perspectives", *Journal of Hazardous Materials*, 424, 127612.
- [82] Zawadzki P., (2022), "Persulfate activation by organic compounds: advancements and challenges", *Current Opinion in Chemical Engineering*, 37, 100837.
- [83] Wang J., Wang S., (2018), "Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants", *Chemical Engineering Journal*, 334, 1502-1517.
- [84] Yin R., Guo W., Wang H., Du J., Zhou X., Wu, Q., Zheng H., Chang J., Ren, N., (2018), "Enhanced peroxymonosulfate activation for sulfamethazine degradation by ultrasound irradiation: Performances and mechanisms", *Chemical Engineering Journal*, 335, 145-153.
- [85] Tian K., Shi F., Cao M., Zheng Q., Zhang G., (2022), "A Review of Persulfate Activation by Magnetic Catalysts to Degrade Organic Contaminants: Mechanisms and Applications", *Catalysts*, 12(9), 1058.
- [86] Oyekunle D.T., Gendy E.A., Ifthikar J., Chen Z., (2022), "Heterogeneous activation of persulfate by metal and non-metal catalyst for the degradation of sulfamethoxazole: A review", *Chemical Engineering Journal*, 437, 135277.
- [87] Tang S., Yao Y., Chen T., Kong D., Shen W., Lee H.K., (2020), "Recent advances in the application of layered double hydroxides in analytical chemistry: A review", *Analytica Chimica Acta*, 1103, 32-48.
- [88] Mallakpour S., Hatami M., Hussain C.M., (2020), "Recent innovations in functionalized layered double hydroxides: Fabrication, characterization, and industrial applications", *Advances in Colloid and Interface Science*, 283, 102216.
- [89] Akdağ S., Keyikoğlu R., Karagunduz A., Keskinler B., Khataee A., Yoon Y., (2023), "Recent advances in boron species removal and recovery using layered double hydroxides", *Applied Clay Science*, 233, 106814.

- [90] Mishra G., Dash B., Pandey S., (2018), “Layered double hydroxides: A brief review from fundamentals to application as evolving biomaterials”, *Applied Clay Science*, 153, 172-186.
- [91] Sharma R., Arizaga G.G.C., Saini A.K., Shandilya P., (2021), “Layered double hydroxide as multifunctional materials for environmental remediation: from chemical pollutants to microorganisms”, *Sustainable Materials and Technologies*, 29, e00319.
- [92] Mohapatra L., Parida K., (2016), “A review on the recent progress, challenges and perspective of layered double hydroxides as promising photocatalysts”, *Journal of Materials Chemistry A*, 4(28), 10744-10766
- [93] dos Santos, G. E. D. S., dos Santos Lins P.V., de Magalhães Oliveira L. M. T., da Silva E. O., Anastopoulos I., Erto A., Giannakoudakis D.A., Almeida A.R.K., Duarte J. L .S., Meili L., (2021), “Layered double hydroxides/biochar composites as adsorbents for water remediation applications: recent trends and perspectives”, *Journal of Cleaner Production*, 284, 124755.
- [94] Mittal J., (2021), “Recent progress in the synthesis of Layered Double Hydroxides and their application for the adsorptive removal of dyes: A review”, *Journal of Environmental Management*, 295, 113017.
- [95] Santamaría L., Vicente M.A., Korili S.A., Gil A., (2020), “Progress in the removal of pharmaceutical compounds from aqueous solution using layered double hydroxides as adsorbents: A review”, *Journal of Environmental Chemical Engineering*, 8(6), 104577.
- [96] Li F., Wang Y., Yang Q., Evans D.G., Forano C., Duan X., (2005), “Study on adsorption of glyphosate (N-phosphonomethyl glycine) pesticide on MgAl-layered double hydroxides in aqueous solution”, *Journal of Hazardous Materials*, 125(1-3), 89-95.
- [97] Xie Z.H., Zhou H.Y., He C.S., Pan Z.C., Yao G., Lai B., (2021), “Synthesis, application and catalytic performance of layered double hydroxide based catalysts in advanced oxidation processes for wastewater decontamination: A review”, *Chemical Engineering Journal*, 414, 128713.
- [98] Gama B.M.V.D., Selvasembian R., Giannakoudakis D.A., Triantafyllidis K.S., McKay G., Meili, L., (2022), “Layered Double Hydroxides as Rising-Star Adsorbents for Water Purification: A Brief Discussion”, *Molecules*, 27(15), 4900.
- [99] Huang Y., Liu C., Rad S., He H., Qin L., (2022), “A Comprehensive Review of Layered Double Hydroxide-Based Carbon Composites as an Environmental Multifunctional Material for Wastewater Treatment”, *Processes*, 10(4), 617.

- [100] Karim A. V., Hassani A., Eghbali P., Nidheesh P. V., (2022), "Nanostructured modified layered double hydroxides (LDHs)-based catalysts: A review on synthesis, characterization, and applications in water remediation by advanced oxidation processes", *Current Opinion in Solid State and Materials Science*, 26(1), 100965.
- [101] Barnabas M. J., Parambadath S., Ha C.S., (2017), "Amino modified core-shell mesoporous silica based layered double hydroxide (MS-LDH) for drug delivery", *Journal of Industrial and Engineering Chemistry*, 53, 392-403.
- [102] Zheng Y., Cheng B., You W., Yu J., Ho W., (2019), "3D hierarchical graphene oxide-NiFe LDH composite with enhanced adsorption affinity to Congo red, methyl orange and Cr(VI) ions", *Journal of Hazardous Materials*, 369, 214-225.
- [103] Daneshvar H., Seyed Dorraji M.S., Amani-Ghadim A.R., Rasoulifard M.H., (2019), "Enhanced sonocatalytic performance of ZnTi nano-layered double hydroxide by substitution of Cu (II) cations", *Ultrasonics Sonochemistry*, 58, 104632.
- [104] Lv X., Zhang J., Dong X., Pan J., Zhang W., Wang, W., Jiang G., & Dong, F. (2020), "Layered double hydroxide nanosheets as efficient photocatalysts for NO removal: Band structure engineering and surface hydroxyl ions activation", *Applied Catalysis B: Environmental*, 277, 119200.
- [105] Lestari P.R., Takei T., Kumada N., (2021), "Novel ZnTi/C₃N₄/Ag LDH heterojunction composite for efficient photocatalytic phenol degradation", *Journal of Solid State Chemistry*, 294, 121858.
- [106] Shang S., Hanif A., Sun M., Tian Y., Ok Y.S, Iris, K. M., Tsang D.C.W., Gu Q., Shang, J., (2019), "Novel M (Mg/Ni/Cu)-Al-CO₃ layered double hydroxides synthesized by aqueous miscible organic solvent treatment (AMOST) method for CO₂ capture", *Journal of Hazardous Materials*, 373, 285-293.
- [107] Zhang C., Liang X., Lu Y., Li H., Xu X., (2020), "Performance of CUAL-LDH/GR nanocomposite-based electrochemical sensor with regard to trace glyphosate detection in water", *Sensors*, 20(15), 4146.
- [108] Heidari M., Ghaffarinejad A., (2019), "Electrochemical sensor for L-cysteine by using a cobalt(II)/aluminum(III) layered double hydroxide as a nanocatalyst", *Microchimica Acta*, 186, 1-7.
- [109] Liu H., Li J., Wang M., Liu Y., Liu J., Cui H., (2019), "Controlled microstructure in two dimensional Ni-Co LDH nanosheets-crosslinked network for high performance supercapacitors", *Advanced Powder Technology*, 30(6), 1239-1246.
- [110] Johnston A.L., Lester E., Williams O., Gomes R.L., (2021), "Understanding Layered Double Hydroxide properties as sorbent materials for removing organic pollutants from environmental waters", *Journal of Environmental Chemical Engineering*, 9(4), 105197.

- [111] Chaudhuri H., Yun Y.S., (2022), “Synthesis and environmental applications of graphene oxide/layered double hydroxides and graphene oxide/MXenes: A critical review”, *Separation and Purification Technology*, 297, 121518.
- [112] Baig N., Sajid M., (2017), “Applications of layered double hydroxides based electrochemical sensors for determination of environmental pollutants: A review”, *Trends in Environmental Analytical Chemistry*, 16, 1-15.
- [113] Morel-Desrosiers N., Pisson J., Israeli Y., Taviot-Guého C., Besse J.P., Morel J.P., (2003), “Intercalation of dicarboxylate anions into a Zn-Al-Cl layered double hydroxide: Microcalorimetric determination of the enthalpies of anion exchange”, *Journal of Materials Chemistry*, 13(10), 2582-2585.
- [114] Gautam R.K., Singh A.K., Tiwari I., (2022), “Nanoscale layered double hydroxide modified hybrid nanomaterials for wastewater treatment: A review”, *Journal of Molecular Liquids*, 350, 118505.
- [115] Chaillot D., Bennici S., Brendlé J., (2021), “Layered double hydroxides and LDH-derived materials in chosen environmental applications: a review”, *Environmental Science and Pollution Research*, 28, 24375-24405.
- [116] Song Y., Bai J., Jiang S., Yang H., Yang L., Wei D., Bai L., Wang W., Liang Y., Chen H., (2021), “Co-Fe-Mo mixed metal oxides derived from layered double hydroxides for deep aerobic oxidative desulfurization”, *Fuel*, 306, 121751.
- [117] Nava-Andrade K., Carbajal-Arízaga G.G., Obregón S., Rodríguez-González V., (2021), “Layered double hydroxides and related hybrid materials for removal of pharmaceutical pollutants from water”, *Journal of Environmental Management*, 288, 112399.
- [118] Gao Z., Liang J., Yao J., Zhao Y., Meng Q., He, G., Chen, H., (2021), “Synthesis of Ce-doped NiAl LDH/RGO composite as an efficient photocatalyst for photocatalytic degradation of ciprofloxacin”, *Journal of Environmental Chemical Engineering*, 9(4), 105405.
- [119] Jing C., Dong B., Zhang Y., (2020), “Chemical Modifications of Layered Double Hydroxides in the Supercapacitor”, *Energy and Environmental Materials*, 3(3), 346-379.
- [120] Kaur H., Singh S., Pal B., (2021), “A brief review on modified layered double hydroxides for H₂ production through photoinduced H₂O splitting”, *Environmental Nanotechnology, Monitoring & Management*, 16, 100451.
- [121] Li K., Liu H., Li Q., Yao W., Wu L., Li, S., Wang, Q. (2022), “The role of doped-Mn on enhancing arsenic removal by MgAl-LDHs”, *Journal of Environmental Sciences*, 120, 125-134.

- [122] Kim S., Durand P., André E., Carteret C., (2017), “Enhanced photocatalytic ability of Cu, Co doped ZnAl based mixed metal oxides derived from layered double hydroxides”, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 524, 43-52.
- [123] Goswami K., Ananthakrishnan R., (2019), “Ce-Doped CuMgAl Oxide as a Redox Couple Mediated Catalyst for Visible Light Aided Photooxidation of Organic Pollutants”, *ACS Applied Nano Materials*, 2(9), 6030-6039.
- [124] Wani A.A., Khan A.M., Manea Y.K., Salem M.A.S., (2022), “Enhanced photocatalytic degradation of organic dyes from aqueous environment using neodymium-doped mesoporous layered double hydroxide”, *Journal of Rare Earths*, 40(10), 1554-1563.
- [125] Suárez-Quezada M., Romero-Ortiz G., Suárez V., Morales-Mendoza G, Lartundo-Rojas L, Navarro-Cerón E., Tzompantzi F., Robles S., Gómez R., Mantilla A., (2016), “Photodegradation of phenol using reconstructed Ce doped Zn/Al layered double hydroxides as photocatalysts”, *Catalysis Today*, 271, 213-219.
- [126] Rad T.S., Khataee A., Rad S.S., Arefi-Oskoui S., Gengec E., Kobya M., Yoon Y. (2022), “Zinc-chromium layered double hydroxides anchored on carbon nanotube and biochar for ultrasound-assisted photocatalysis of rifampicin”, *Ultrasonics Sonochemistry*, 82, 105875.
- [127] Chen Q., Wu L., Zhao X., Yang X.J., (2022), “Fabrication of Zn-Ti layered double oxide nanosheets with ZnO/ZnTiO₃ heterojunction for enhanced photocatalytic degradation of MO, RhB and MB”, *Journal of Molecular Liquids*, 353, 118794.
- [128] Gholami P., Khataee A., Soltani R.D.C, Dinpazhoh L., Bhatnagar A., (2020), “Photocatalytic degradation of gemifloxacin antibiotic using Zn-Co-LDH@biochar nanocomposite”, *Journal of Hazardous Materials*, 382, 121070.
- [129] Keyikoglu R., Khataee A., Lin H., Orooji Y., (2022), “Vanadium (V)-doped ZnFe layered double hydroxide for enhanced sonocatalytic degradation of pymetrozine”, *Chemical Engineering Journal*, 434, 134730.
- [130] Rui J., Deng N., Zhao Y., Tao C., Zhou J., Zhao Z., Huang X. (2022), “Activation of persulfate via Mn doped Mg/Al layered double hydroxide for effective degradation of organics: Insights from chemical and structural variability of catalyst”, *Chemosphere*, 302, 134849.
- [131] Li X., Hou T., Yan L., Shan L., Meng X., Zhao Y., (2020), “Efficient degradation of tetracycline by CoFeLa-layered double hydroxides catalyzed peroxymonosulfate: Synergistic effect of radical and nonradical pathways”, *Journal of Hazardous Materials*, 398, 122884.

- [132] Hu J., Sun C., Wu L. X., Zhao G. Q., Liu H. Y., Jiao F.P., (2023), "Halogen doped g-C₃N₄/ZnAl-LDH hybrid as a Z-scheme photocatalyst for efficient degradation for tetracycline in seawater", *Separation and Purification Technology*, 309, 123047.
- [133] Huang X., Xu X., Yang R., Fu X., (2022), "Synergetic adsorption and photocatalysis performance of g-C₃N₄/Ce-doped MgAl-LDH in degradation of organic dye under LED visible light", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 643, 128738.
- [134] Khataee A., Rad T.S., Nikzat S., Hassani A., Aslan M.H., Kobya M., Demirbaş E., (2019), "Fabrication of NiFe layered double hydroxide/reduced graphene oxide (NiFe-LDH/rGO) nanocomposite with enhanced sonophotocatalytic activity for the degradation of moxifloxacin", *Chemical Engineering Journal*, 375, 122102.
- [135] Hasija V., Raizada P., Hosseini-Bandegharai A., Singh P., Nguyen V.H., (2020), "Synthesis and Photocatalytic Activity of Ni-Fe Layered Double Hydroxide Modified Sulphur Doped Graphitic Carbon Nitride (SGCN/Ni-Fe LDH) Photocatalyst for 2,4-Dinitrophenol Degradation", *Topics in Catalysis*, 63, 1030-1045.
- [136] Zhu J., Wang J., He J., Hu L., (2023), "Fabrication of CdS/ZnCr-LDH heterojunctions with enhanced of tetracycline hydrochloride photocatalytic degradation under visible light", *Optical Materials*, 136, 113456.
- [137] Gholami P., Dinpazhoh L., Khataee A., Hassani A., Bhatnagar A., (2020), "Facile hydrothermal synthesis of novel Fe-Cu layered double hydroxide/biochar nanocomposite with enhanced sonocatalytic activity for degradation of cefazolin sodium", *Journal of Hazardous Materials*, 381, 120742.
- [138] Rad T.S., Yazici E.S., Khataee A., Gengec E., Kobya M., (2023), "Tuned CuCr layered double hydroxide/carbon-based nanocomposites inducing sonophotocatalytic degradation of dimethyl phthalate", *Ultrasonics Sonochemistry*, 95, 106358.
- [139] Jácome-Acatitla G., Tzompantzi F., López-González R., García-Mendoza C., Alvaro J.M., Gómez R., (2014), "Photodegradation of sodium naproxen and oxytetracycline hydrochloride in aqueous medium using as photocatalysts Mg-Al calcined hydrotalcites", *Journal of Photochemistry and Photobiology A: Chemistry*, 277, 82-89.
- [140] Wang Y., Wang L., Xiao Z., Liu S., Hu J., Long X., Wu L., Sun C., Chen K., Jiao F., (2022), "Construction of Z-scheme heterojunction of (BiO)₂CO₃/ZnFe-LDH for enhanced photocatalytic degradation of tetracycline", *Journal of Alloys and Compounds*, 900, 163450.
- [141] Khataee A., Arefi-Oskoui S., Samaei L., (2018), "ZnFe-Cl nanolayered double hydroxide as a novel catalyst for sonocatalytic degradation of an organic dye", *Ultrasonics Sonochemistry*, 40, 703-713.

- [142] Rad T.S., Khataee A., Arefi-Oskoui S., Rad S.D, Orooji Y., Gengeç E., Kobya M., (2022), “Graphene-based ZnCr layered double hydroxide nanocomposites as bactericidal agents with high sonophotocatalytic performances for degradation of rifampicin”, *Chemosphere*, 286, 131740.
- [143] Wang X., Wu P., Huang Z., Zhu N., Wu J., Li P., Dang Z., (2014), “Solar photocatalytic degradation of methylene blue by mixed metal oxide catalysts derived from ZnAlTi layered double hydroxides”, *Applied Clay Science*, 95, 95-103.
- [144] Shen J., Shi A., Wu M., Zhang H., Jiang Z., (2022), “Efficient degradation of bisphenol A over facilely optimized ternary Ag/ZnO/ZnAl-LDH composite with enhanced photocatalytic performance under visible light irradiation”, *Solid State Sciences*, 132, 106992.
- [145] Xia G., Zheng Y., Sun Z., Xia S., Ni Z., Yao J., (2022), “Fabrication of ZnAl-LDH mixed metal-oxide composites for photocatalytic degradation of 4-chlorophenol”, *Environmental Science and Pollution Research*, 29(26), 39441-39450.
- [146] Zhang H., Zhang Y., Hou Z., Wu X., Gao H., Su F., Pan H., (2014), “Biodegradation of triazine herbicide metribuzin by the strain *Bacillus* sp. N1”, *Journal of Environmental Science and Health - Part B*, 49(2), 79-86.
- [147] Yang Y., Cui L., Li M., Yao Y., (2019), “Electrochemical removal of metribuzin in aqueous solution by a novel PbO₂/WO₃ composite anode: Characterization, influencing parameters and degradation pathways”, *Journal of the Taiwan Institute of Chemical Engineers*, 102, 170-181.
- [148] Fairchild J.F., Sappington L.C., (2002), “Fate and effects of the triazinone herbicide metribuzin in experimental pond mesocosms”, *Archives of Environmental Contamination and Toxicology*, 102, 170-181.
- [149] Li G., Li D., Rao H., Liu X., (2022), “Potential neurotoxicity, immunotoxicity, and carcinogenicity induced by metribuzin and tebuconazole exposure in earthworms (*Eisenia fetida*) revealed by transcriptome analysis”, *Science of the Total Environment*, 807, 150760.
- [150] Velisek J., Svobodova Z., Piackova V., Novotny L., Blahova J., Sudova E., Maly V., (2008), “Effects of metribuzin on rainbow trout (*Oncorhynchus mykiss*)”, *Veterinarni Medicina*, 53(6), 324.
- [151] Naqvi S.M., Leung T.S., Naqvi N.Z., (1981), “Toxicities of paraquat and metribuzin (Sencor®) herbicides to the freshwater copepods, *Eucyclops agilis* and *Diaptomus mississippiensis*”, *Environmental Pollution Series A, Ecological and Biological*, 26(4), 275-280.
- [152] Štěpánová S., Doleželová P., Plhalová L., Prokeš M., Maršálek P., Škorič M., Svobodová Z., (2012), “The effects of metribuzin on early life stages of common carp (*Cyprinus carpio*)”, *Pesticide Biochemistry and Physiology*, 103(2), 152-158.

- [153] Plhalova L., Stepanova S., Praskova E., Chromcova L., Zelnickova L., Divisova, L., Skoric M., Pistekova V., Bedanova I., Svobodova, Z., (2012), "The effects of subchronic exposure to metribuzin on *Danio rerio*", The Scientific World Journal, 2012.
- [154] Albro P. W., Parker C. A., Abusteit E. O., Mester T. C., Hass J. R., Sheldon Y. S., Corbin F. T., (1984), "Determination of the pKa values of metribuzin and three of its metabolites: A comparison of spectrophotometric and potentiometric methods", Journal of Agricultural and Food Chemistry, 32(2), 212-217.
- [155] Loffredo E., Parlavecchia M., Perri G., Gattullo R., (2019), "Comparative assessment of metribuzin sorption efficiency of biochar, hydrochar and vermicompost", Journal of Environmental Science and Health, Part B, 54(8), 728-735.
- [156] Wehrli W., (1983), "Rifampin: Mechanisms of action and resistance", Reviews of Infectious Diseases, 5(3), S407-S411.
- [157] Jendrzewska N, Karwowska E., (2018), "The influence of antibiotics on wastewater treatment processes and the development of antibiotic-resistant bacteria", Water Science and Technology, 77(9), 2320-2326.
- [158] de Sousa J.F.L., Naves P.L.F., Guilherme L.R., (2023), "Synthesis and evaluation of toxicity and antimicrobial activity of rifampicin associated with iron oxide nanoparticles", Bioscience Journal, 39.
- [159] Taylor A, Anand S, Rose JSM, Shah S, Shah H, et al., (2023), "Rifampin", Reference Module in Biomedical Sciences.
- [160] Kais H., Yeddou Mezenner N., Trari M., (2020), "Biosorption of rifampicin from wastewater using cocoa shells product", Separation Science and Technology, 55(11), 1984-1993.
- [161] Patterson A.L., (1939), "The scherrer formula for X-ray particle size determination", Physical Review, 56(10), 978.
- [162] Zaher A., Taha M., Mahmoud R.K., (2021), "Possible adsorption mechanisms of the removal of tetracycline from water by La-doped Zn-Fe-layered double hydroxide", Journal of Molecular Liquids, 322, 114546.
- [163] Shi Z., Zhu J., Li Z., Xiao Q., Zhu J., (2020), "Sulfur-doped nickel-cobalt double hydroxide electrodes for high-performance asymmetric supercapacitors", ACS Applied Energy Materials, 11, 11082-11090.
- [164] Saeed M., Zafar M., Razzaq A., Khan S.A., Khan Z., Kim W. Y., (2022), Visible-light-active Zn-Fe Layered Double Hydroxide (LDH) for the photocatalytic conversion of rice husk extract to value-added products, Applied Sciences, 12(5), 2313.

- [165] Liao F., Yang G., Cheng Q., Mao L., Zhao X., Chen L., (2022), "Rational design and facile synthesis of Ni-Co-Fe ternary LDH porous sheets for high-performance aqueous asymmetric supercapacitor", *Electrochimica Acta*, 428, 140939.
- [166] Ouyang Y., Zhao L., Deng M., Yang P., Peng G., (2023), "Preparation of diethylenetriamine-functionalized thiosulfate intercalated ZnNiAl-LDHs and its removal behavior and mechanism of U(VI)", *Chemical Engineering Journal*, 452, 139486.
- [167] Li X., Yuan Z., Huang Z., Koso A., Li J., Xie, B., Ni Z., & Xia, S., (2022), "The photodegradation property and mechanism of tetracycline by persulfate radical activated In₂O₃@LDHs Z-scheme heterojunction", *Separation and Purification Technology*, 302, 122077.
- [168] Haddadi S., Khataee A., Arefi-Oskoui S., Vahid B., Orooji Y., Yoon Y., (2023), "Titanium-based MAX-phase with sonocatalytic activity for degradation of oxytetracycline antibiotic", *Ultrasonics Sonochemistry*, 92, 106255.
- [169] Dinari M., Dadkhah F., Azizollahi F., Bateni G., Bagherzadeh F., (2022), "Construction of new recoverable Ag-Fe₃O₄@Ca-Al LDH nanohybrids for visible light degradation of piroxicam", *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, 278, 115630.
- [170] Fathinia M., Khataee A., (2015), "Photocatalytic ozonation of phenazopyridine using TiO₂ nanoparticles coated on ceramic plates: Mechanistic studies, degradation intermediates and ecotoxicological assessments", *Applied Catalysis A: General*, 491, 136-154.
- [171] Dastborhan M., Khataee A., Arefi-Oskoui S., Yoon Y., (2022), "Synthesis of flower-like MoS₂/CNTs nanocomposite as an efficient catalyst for the sonocatalytic degradation of hydroxychloroquine", *Ultrasonics Sonochemistry*, 87, 106058.
- [172] Yi L., Li B., Sun Y., Li S., Qi Q., Qin J., Sun H., Fang D., Wang J., (2020), "Construction of coated Z-scheme Er³⁺: Y₃Al₅O₁₂/Pd-CdS@BaTiO₃ sonocatalyst composite for intensifying degradation of chlortetracycline hydrochloride in aqueous solution", *Separation and Purification Technology*, 250, 117257.
- [173] Li J.Q., Zhou Z. W., Li X., Yang Y. L., Gao J. F., Yu R., Wang H., Wang N., (2022), "Synergistically boosting sulfamerazine degradation via activation of peroxydisulfate by photocatalysis of Bi₂O₃-TiO₂/PAC under visible light irradiation", *Chemical Engineering Journal*, 428, 132613.
- [174] Rad T.S., Yazici E.S., Khataee A., Gengec E., Kobya M., (2022), "Nanoarchitecture of graphene nanosheets decorated with NiCr layered double hydroxide for sonophotocatalytic degradation of refractory antibiotics", *Environmental Research*, 214, 113788.

- [175] Rahmani A.R., Salari M., Shabanloo A., Shabanloo N., Bajalan S., Vaziri Y., (2020), "Sono-catalytic activation of persulfate by nZVI-reduced graphene oxide for degradation of nonylphenol in aqueous solution: Process optimization, synergistic effect and degradation pathway", *Journal of Environmental Chemical Engineering*, 8(5), 104202.
- [176] Hossein Panahi A., Meshkinian A., Ashrafi S.D., Khan M., Naghizadeh A., Abi G., Kamani H., (2020), "Survey of sono-activated persulfate process for treatment of real dairy wastewater", *International Journal of Environmental Science and Technology*, 17, 93-98.
- [177] Ertugay N., Acar F.N., (2014), "The degradation of Direct Blue 71 by sono, photo and sonophotocatalytic oxidation in the presence of ZnO nanocatalyst", *Applied Surface Science*, 318, 121-126.
- [178] Soltani R.D.C., Miraftabi Z., Mahmoudi M., Jorfi S., Boczkaj G., Khataee A., (2019), "Stone cutting industry waste-supported zinc oxide nanostructures for ultrasonic assisted decomposition of an anti-inflammatory non-steroidal pharmaceutical compound", *Ultrasonics Sonochemistry*, 58, 104669.
- [179] Mukhopadhyay A., Tripathy B.K., Debnath A., Kumar M., (2021), "Enhanced persulfate activated sono-catalytic degradation of brilliant green dye by magnetic CaFe_2O_4 nanoparticles: Degradation pathway study, assessment of bio-toxicity and cost analysis", *Surfaces and Interfaces*, 26, 101412.
- [180] Watts R.J., Teel A.L., (2019), "Hydroxyl radical and non-hydroxyl radical pathways for trichloroethylene and perchloroethylene degradation in catalyzed H_2O_2 propagation systems", *Water Research*, 159, 46-54.
- [181] Yang H., Kang J.K., Jeong S., Park S.J., Lee C.G., (2022), "Removal of perfluorooctanoic acid from water using peroxydisulfate/layered double hydroxide system: Optimization using response surface methodology and artificial neural network", *Process Safety and Environmental Protection*, 167, 368-377.
- [182] Fang Y.F., Deng A.P., Huang Y.P., (2009), "Determination of hydroxyl radical in Fenton system", *Chinese Chemical Letters*, 20(10), 1235-1240.
- [183] Ma Q., Nengzi L. chao, Li B, Wang Z, Liu L, Cheng X., (2020), "Heterogeneously catalyzed persulfate with activated carbon coated with CoFe layered double hydroxide (AC@CoFe-LDH) for the degradation of lomefloxacin", *Separation and Purification Technology*, 235, 116204.
- [184] Ouyang F., Li H., Gong Z., Pang D., Qiu L., Wang, Y., Dai F., Cao G., Bharti, B., (2020), "Photocatalytic degradation of industrial acrylonitrile wastewater by F-S-Bi-TiO₂ catalyst of ultrafine nanoparticles dispersed with SiO₂ under natural sunlight", *Scientific Reports*, 10(1), 12379.

- [185] Areerob Y., Cho J.Y., Jang W.K., Oh W.C., (2018), "Enhanced sonocatalytic degradation of organic dyes from aqueous solutions by novel synthesis of mesoporous Fe₃O₄-graphene/ZnO@SiO₂ nanocomposites", *Ultrasonics Sonochemistry*, 41, 267-278.
- [186] Li S., Wang G., Qiao J., Zhou Y., Ma X., Zhang H., Li G., Wang J., Song Y., (2018), "Sonocatalytic degradation of norfloxacin in aqueous solution caused by a novel Z-scheme sonocatalyst, mMBIP-MWCNT-In₂O₃ composite", *Journal of Molecular Liquids*, 254, 166-176.
- [187] Soltani R.D.C., Mashayekhi M., Naderi M., Boczkaj G., Jorfi S., Safari M., (2019), "Sonocatalytic degradation of tetracycline antibiotic using zinc oxide nanostructures loaded on nano-cellulose from waste straw as nanosonocatalyst", *Ultrasonics Sonochemistry*, 55, 117-124.
- [188] Bose S., Tripathy B. K., Debnath A., Kumar M., (2021), "Boosted sono-oxidative catalytic degradation of Brilliant green dye by magnetic MgFe₂O₄ catalyst: Degradation mechanism, assessment of bio-toxicity and cost analysis", *Ultrasonics Sonochemistry*, 75, 105592.
- [189] de Barros A. L. C., da Silva Rodrigues D. A., da Cunha C. C. R. F., das Chagas I. A. S., do Espirito Santo D.R., de Queiroz Silva S., Afonso, R. J. D. C. F. (2021), "Aqueous chlorination of herbicide metribuzin: Identification and elucidation of 'new' disinfection by-products, degradation pathway and toxicity evaluation", *Water Research*, 189, 116545.
- [190] Wang Y., Dong H., Wu Z., Li M., Li J., Qiang Z., (2020), "UV activated monochloramine promotes metribuzin degradation and disinfection by-products formation", *Chemical Engineering Journal*, 385, 123846.
- [191] Kadam S.R., Jadhav N.L., Pandit A.B., Pejaver M.K., (2021), "Degradation kinetics and mechanism of hazardous metribuzin herbicide using advanced oxidation processes (HC & HC+ H₂O₂)", *Chemical Engineering and Processing - Process Intensification*, 166, 108486.
- [192] Li W., Liu K., Min Z., Li J., Zhang M., Korshin G. V., Han J., (2023), "Transformation of macrolide antibiotics during chlorination process: Kinetics, degradation products, and comprehensive toxicity evaluation", *Science of The Total Environment*, 858, 159800.
- [193] Bolton J.R., Bircher K.G., Tumas W., Tolman C.A., (2001), "Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems", *Pure and Applied Chemistry*, 73(4), 627-637.
- [194] Keyikoğlu R., Doğan I. N., Khataee A., Orooji Y., Kobya M., Yoon Y., (2022), "Synthesis of visible light responsive ZnCoFe layered double hydroxide towards enhanced photocatalytic activity in water treatment", *Chemosphere*, 309, 136534.

- [195] Dikmen E., Dogdu G., Yalcuk A., (2022), "Comparison Performances of Hybrid Sonocatalysis and Sonophotocatalysis on the Elimination of 2,4-Dichlorophenoxyacetic Acid in Water: Mineralization and Economic Analysis", *Polish Journal of Environmental Studies*, 31(5).
- [196] Patidar R., Srivastava V.C., (2021), "Mechanistic and kinetic insights of synergistic mineralization of ofloxacin using a sono-photo hybrid process", *Chemical Engineering Journal*, 403, 125736.
- [197] Selvamani P.S., Vijaya J.J., Kennedy L.J., Mustafa A., Bououdina M., Sophia P. J., Ramalingam R. J., (2021), "Synergic effect of Cu₂O/MoS₂/rGO for the sonophotocatalytic degradation of tetracycline and ciprofloxacin antibiotics", *Ceramics International*, 47(3), 4226-4237.
- [198] Nikpour S., Ansari-Asl Z., Sedaghat T., Hoveizi E., (2022), "Curcumin-loaded Fe-MOF/PDMS porous scaffold: Fabrication, characterization, and biocompatibility assessment", *Journal of Industrial and Engineering Chemistry*, 110, 188-197.
- [199] Akdağ S., Rad T.S, Keyikoğlu R., Orooji Y., Yoon Y., Khataee A., (2022), "Peroxydisulfate-assisted sonocatalytic degradation of metribuzin by La-doped ZnFe layered double hydroxide", *Ultrasonics Sonochemistry*, 91, 106236.
- [200] Hamouni S., Arous O., Abdessemed D., Nezzal G., Van der Bruggen B., (2019), "Alcohol and Alkane Organic Extraction Using Pervaporation Process", *Macromolecular Symposia*, 386(1), 1800247.
- [201] Rahman M.M., Muttakin M., Pal A., Shafiullah A.Z., Saha B.B., (2019), "A statistical approach to determine optimal models for IUPAC-classified adsorption isotherms", *Energies*, 12(23), 4565.
- [202] Thommes M., Kaneko K., Neimark A. V., Olivier J.P., Rodriguez-Reinoso F, Rouquerol J., Sing K. S., (2015), "Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)", *Pure and Applied Chemistry*, 87(9-10), 1051-1069.
- [203] Singh A.K., (2022), "Surface engineering using PDMS and functionalized nanoparticles for superhydrophobic coatings: Selective liquid repellence and tackling COVID-19", *Progress in Organic Coatings*, 171, 107061.
- [204] Yang Z. X., Jing L. C., Ming X., Geng W. H., Cao W., Tian, Y., Bin P. S., Bao Z. L., Chang R.Y., Geng, H. Z. (2023), "Preparation and performance study of superhydrophobic layer based on fluffy ZnO rods/PDMS", *Surfaces and Interfaces*, 39, 102968.
- [205] Lu J., Zhou Y., Ling L., Zhou Y., (2022), "Enhanced activation of PMS by a novel Fenton-like composite Fe₃O₄/S-WO₃ for rapid chloroxyleneol degradation", *Chemical Engineering Journal*, 446, 137067.

- [206] Jin C., Kang J., Li Z., Wang M., Wu Z., Xie Y., (2020), “Enhanced visible light photocatalytic degradation of tetracycline by MoS₂/Ag/g-C₃N₄ Z-scheme composites with peroxymonosulfate”, *Applied Surface Science*, 514, 146076.
- [207] Di S., Wang J., Zhai Y., Chen P., Ning T., Shi C., Yang H., Bao Y., Gao Q., Zhu S., (2022), “Efficient activation of peroxymonosulfate mediated by Co(II)-CeO₂ as a novel heterogeneous catalyst for the degradation of refractory organic contaminants: Degradation pathway, mechanism and toxicity assessment”, *Journal of Hazardous Materials*, 435, 129013.
- [208] Shi W., Liu Y., Sun W., Hong Y., Li X., Lin, X., Guo F., Shi, J., (2021), “Assembling g-C₃N₄ nanosheets on rod-like CoFe₂O₄ nanocrystals to boost photocatalytic degradation of ciprofloxacin with peroxymonosulfate activation”, *Materials Today Communications*, 29, 102871.
- [209] Xu Q., Owens G., Chen Z., (2020), “Adsorption and catalytic reduction of rifampicin in wastewaters using hybrid rGO@Fe/Pd nanoparticles”, *Journal of Cleaner Production*, 264, 121617.
- [210] Sosnin I. M, Vlassov S., Dorogin L.M., (2021), “Application of polydimethylsiloxane in photocatalyst composite materials: A review”, *Reactive and Functional Polymers*, 158, 104781.
- [211] Yentür G., Dükkancı M., (2020), “Fabrication of magnetically separable plasmonic composite photocatalyst of Ag/AgBr/ZnFe₂O₄ for visible light photocatalytic oxidation of carbamazepine”, *Applied Surface Science*, 510, 145374.
- [212] Chen D., Xie Z., Zeng Y., Lv W., Zhang Q., Wang F., Liu G., Liu H., (2019), “Accelerated photocatalytic degradation of quinolone antibiotics over Z-scheme MoO₃/g-C₃N₄ heterostructure by peroxydisulfate under visible light irradiation: Mechanism; kinetic; and products”, *Journal of the Taiwan Institute of Chemical Engineers*, 104, 250-259.
- [213] Dang Thi Ngoc T., Thi H. N., Nguyen Duc D, Nguyen Thi S, Nguyen Duc T, Nguyen Hoang N., (2022), “Preparation and Photocatalytic Characterization of Modified Nano TiO₂/Nd/Rice Husk Ash Material for Rifampicin Removal in Aqueous Solution”, *Journal of Analytical Methods in Chemistry*, 2022.
- [214] Kumar M., Puri A., (2012), “A review of permissible limits of drinking water”, *Indian Journal of Occupational and Environmental Medicine*, 16(1), 40-44.
- [215] Mi X., Ma R., Pu X., Fu X., Geng M., Qian J., (2022), “FeNi-layered double hydroxide (LDH)@biochar composite for , activation of peroxymonosulfate (PMS) towards enhanced degradation of doxycycline (DOX): Characterizations of the catalysts, catalytic performances, degradation pathways and mechanisms”, *Journal of Cleaner Production*, 378, 134514.

- [216] Hasan I., Bassi A., Kanungo K., Heun Koo B., (2023), “UV light driven photocatalytic degradation of ibuprofen drug by polyaniline supported rGO@MnO₂ nanocomposite”, *Journal of Photochemistry and Photobiology A: Chemistry*, 444, 114952.
- [217] Elbadawy H.A., Elhusseiny A.F., Hussein S.M., Sadik W.A., (2023), “Sustainable and energy-efficient photocatalytic degradation of textile dye assisted by ecofriendly synthesized silver nanoparticles”, *Scientific Reports*, 13(1), 2302.



BIOGRAPHY

Sultan Akdağ graduated from Istanbul University Environmental Engineering Department in 2019. She started her master's degree in Environmental Engineering at Gebze Technical University in 2021. Since 2021, she has been a research assistant at the Environmental Engineering Department of Gebze Technical University.



APPENDICES

Appendix A: Research Papers Published from This Thesis Study

Akdağ S., Rad T. S., Keyikoğlu R., Orooji Y., Yoon Y., Khataee A., (2022), “Peroxydisulfate-assisted sonocatalytic degradation of metribuzin by La-doped ZnFe layered double hydroxide”, *Ultrasonics Sonochemistry*, 91, 106236.

