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PHOTOCATALYTIC APPLICATIONS OF METAL-ORGANIC FRAMEWORKS

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by

Zeynep AYDIN

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ANKARA

M.Sc.THESIS EXAMINATION RESULT FORM

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PHOTOCATALYTIC APPLICATIONS OF METAL-ORGANIC FRAMEWORKS

ABSTRACT

Metal-Organic Frameworks (MOFs) materials are a new class of crystalline porous materials that have emerged in chemistry and materials science in recent years, in which metals are bonded with covalent bonds and organic binders. MOFs are used in the catalytic degradation of organic dyes due to their semiconductor behaviors, porous structure, pore size, functionality, and excellent mechanical stability. MOFs containing different metal ligands can be produced by adjusting the structure and properties of MOFs with the appropriate choice of building blocks. In this study, the photocatalytic activity of Zr-based MOFs under LED light to decompose methylene blue (MB) was investigated by using polydopamine (PDOP) as initial templates for the production of visible light-sensitive photocatalysts. The chelate formation between Zr^{4+} and (PDOP) led to the nucleation of Zr-O clusters. This cluster nucleation also facilitated the growth mechanism of MOFs on the PDOP. MOF photocatalytic performance was investigated using a LED light source. Also, MOF's physical and chemical properties were investigated using XRD, SEM, and FTIR. Thanks to the newly synthesized catalysts, remarkable photodegradation have been achieved.

Keywords: MOF (Metal-organic framework), PDOP(Polydopamine), Photocatalytic degradation, MB (Methylene blue)

METAL ORGANİK KAFESLERİN FOTOKATALİTİK UYGULAMALARI

ÖZ

Metal Organik Kafes malzemeler son yıllarda kimya ve malzeme biliminde ortaya çıkmış, metallerin kovalent bağlarla ve organik bağlayıcılarla bağlandığı yeni bir kristal gözenekli malzeme sınıfıdır. Organik boyaların katalitik bozunmasında Metal organik kafeslerin (MOF)'lar yarı iletken davranışları, gözenekli yapıları, fonksiyonelliği, mükemmel mekanik stabilite gibi özellikleri nedeniyle kullanılırlar. MOF'ların yapıları ve özellikleri uygun yapıtaşı seçimi ile ayarlanarak farklı metal-ligand içeren MOF'lar üretilebilmektedir. Bu çalışmada, görünür ışığa duyarlı fotokatalizörlerin üretimi için başlangıç şablonları olarak polidopamin (PDOP) kullanılarak, metilen mavisi renklerinin giderilmesi için Zr bazlı MOF'ların LED ışık altında fotokatalitik aktivitesi incelenmiştir. Şelat oluşumu (Zr^{4+} ve PDOP arasında), Zr-O kümelerinin çekirdeklenmesine yol açmıştır. Bu küme çekirdeklenmesi de PDOP üzerinde MOF'ların büyüme mekanizmasını kolaylaştırmıştır. MOF fotokatalitik performansı LED ışık kaynağı kullanılarak, fiziksel ve kimyasal özellikleri ise XRD, SEM ve FTIR kullanılarak araştırılmıştır. Yeni sentezlenen katalizörler sayesinde dikkate değer foto-bozunma oranlarına ulaşılmıştır.

Anahtar Kelimeler*:* Metal organik kafes (MOF), Polidopamin (PDOP), Fotokatalitik bozunma, Metilen mavisi (MB)

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NOMENCLATURE

Abbreviations

µm Micrometer

rpm Rounds per minute

ml Milliliter

Acronyms

MOF: Metal-Organic Framework

PDOP: Polydopamine

$ZrCl_4$: Zirconium IV Chloride

DMF: Dimethylformamide

NH_3: Ammonium Nitrate

H_2O_2: Hydrogen Peroxide

MB: Methylthioninium Chloride, Methylene Blue

SEM: Scanning Electron Microscope

HAuCl: Chloroauric Acid

TSS: Trisodium Citrate Dihydrate

LED: Light-emitting Diode

FT-IR: Fourier Transform Infrared Spectroscopy

XRD: X-ray Diffraction

TiO_2: Titanium Dioxide

ZnO: Zinc Oxide

Fe_2O_3: Iron (III) Oxide

ZrO_2: Zirconia

V_2O_5: Vanadium (V) oxide

Λmax: Max wavelength

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CHAPTER 1

INTRODUCTION

1. Photocatalyst Technology

Population growth and industrialization have brought along problems such as fuel, heavy metals, pesticides, surfactants, and energy problems. This situation has increased the demand for renewable energy. Especially, water contamination is another important problem to be solved in this area [1-2]. Additionally, according to Malato et al., [3], approximately millions of people globally are reported to die due to serious waterborne diseases owing to the consumption of polluted water, and 2.6 billion people have no access to a clean water source. Solar energy is one of the clean, infinite, and important sources [1]. In this manner, renewable solar energy is activated by chemical reactions such as oxidation and reduction (Kudo and Miseki, 2009) [3]. Moreover, photocatalyst converts solar energy which has a spectrum has consisted of UV, visible, and more than near-infrared light, into chemical energy, which will be great hope for future demand [4]. During the past 20 years, photocatalytic technology became a practical interest area and application, such as self-cleaning surfaces, water purification, environmentally friendly surface treatment [5]. In figure 1.1 the comparison of the number of published articles on photocatalysis and its applications in water by years is shown [6]. In addition, photocatalysis holds promising for persistent organic pollutants which one of the most important parts of wastewater treatment (WWT) facilities are aged, can not cope due to the world's population [7].

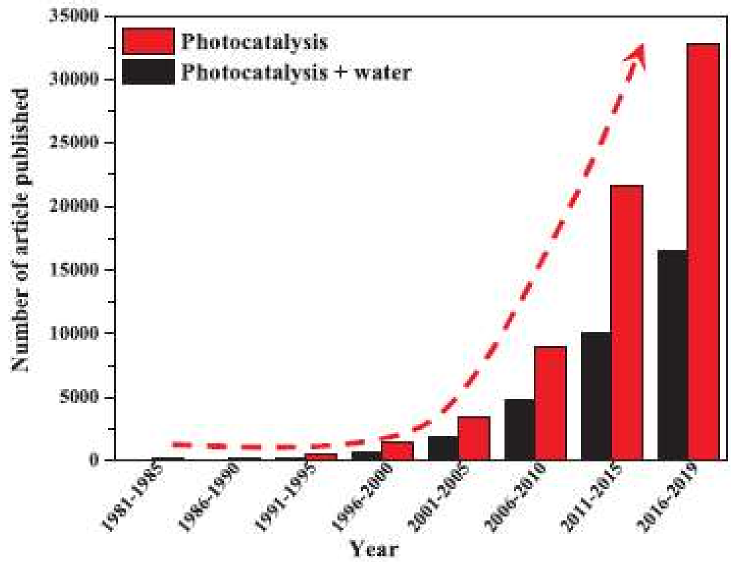

Figure 1.1 The comparison of the number of published articles on photocatalysis and its applications in water by years [6]

As a result of the researches, the photocatalysis method has been a proven option with low cost and high-efficiency features [6]. The efficiency, simplicity, and ability to work in a wide pH range of the photocatalysis method are the most important reasons why photocatalysis is preferred for cleaning organic pollutants [7]. Refractory organic pollutants photocatalytic degradation in aqueous solution have a great many fields. Furthermore, photocatalysis based on MOFs is used as a potential technology [8]. Promising photocatalyst species such as titanium dioxide (TiO_2), zinc oxide (ZnO), iron (III) oxide (Fe_2O_3), zirconia (ZrO_2), vanadium(V) oxide (V_2O_5) are used in many areas, including the field of water contamination [9]. In this study, the photocatalytic degradation efficiency was evaluated by various oxidant experiments by synthesizing Zr-MOF on PDOP used as a template. In line with the thesis, characterization results such as X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectrophotometer (FTIR), UV (Ultraviolet Spectrophotometer) were presented and that is aimed to guide future studies on this subject. Figure 1.2 illustrates the basic photocatalytic degradation mechanism of Zr-MOF@PDOP.

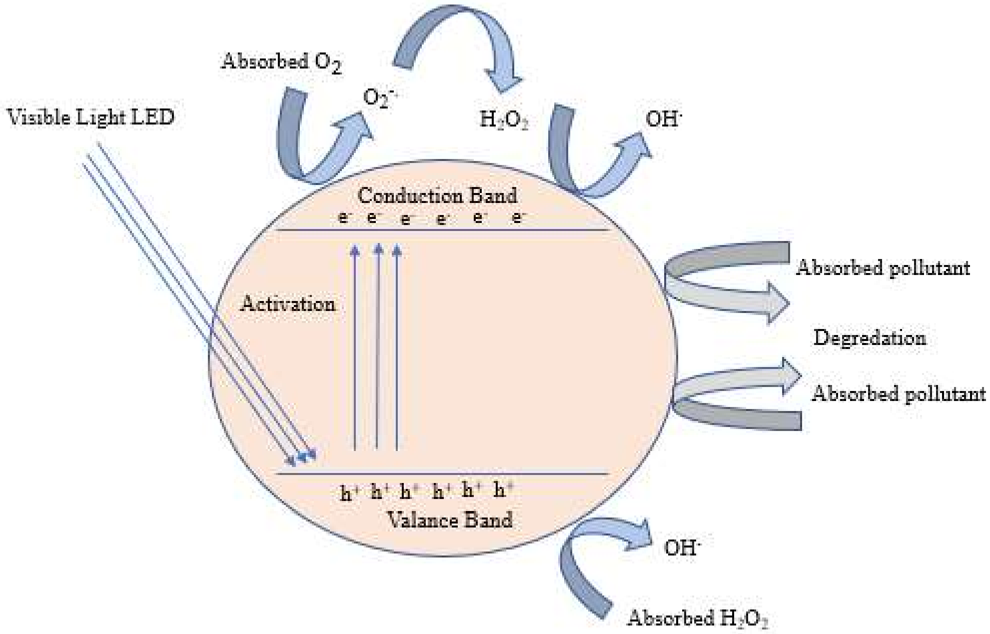

Figure 1.2 Illustration the basic photocatalytic degradation mechanism of Zr-MOF@PDOP [4]

Photocatalyst is defined as the absorption of photon energy by light through the catalyst. Briefly, it is defined as a combination of catalysis and photochemistry. Conventional catalyst technology requires thermal energy while photocatalysis technology requires photon energy. Solar energy is used in the field of renewable energy where photon energy is used as an activation source [2]. Photodegradation activity was started with mechanically stirring suspension of MB and photocatalyst (Zr-MOF@PDOP) in the dark for 30 min. For equilibrium of absorption/ desorption as usual. Electron-hole pairs are created by excitation of the semiconductor with LED. Then e^- is located in the conduction band and the holes (h^+) formed are located in the valance band. Active OH radicals are formed as a result of the reaction of the vacancies in the valance band with H_2O and OH ions. On the other hand, electrons provide OH radicals by reacting with O_2 molecules which are absorbed on the catalyst surface. In addition, the step is continued by the addition of a known concentration of H_2O_2 and O_2 with white LEDs. H_2O_2 is a strong oxidant, and it directly attacks the polluting molecules, causing organic pollutants to break down and the formation of hydroxyl radicals on the surface during the contact of the semiconductor with the beam. Hydroxyl radicals with high oxidizing properties cause the decomposition of impurities [10]. Organic pollutants in an ideal photocatalytic degradation process; ın the presence of species such as Zr-MOF, oxygen, hydrogen peroxide, it is mineralized to CO_2, H_2O, and mineral acids [9].

1.1 Semiconductor

Water purification of pollutants and contaminations of natural and man-made origin, artificial photosynthesis, developing methods of storing the energy of sunlight, and photochemical water decomposition are examples for semiconductor materials areas [11]. Photocatalysis technology which contains semiconductors is one of the promising solutions for environmental and energy pollution [12]. Photocatalysis, with the help of a semiconductor, activated by UV lights and decomposed harmful substances into harmless products. Photocatalysis is also defined as the acceleration of a photoreaction by the presence of a catalyst (Mills, Le Hunte, et al., 1997) which requires light energy [1]. Semiconductor electronic structures are called band theory. Band theory is explained as the function of electronic energy levels. Materials are classified according to the energy gaps found between these bands. According to band theory; the Valance band is the full energy level is in which electrons can be excited by an effect. The conduction band is the energy level that remains empty until the electrons are excited [1]. In conductive materials, the conductivity and valance band are adjacent. However, in insulating materials, there is a large energy difference between the two bands. In Figure 1.3, for semiconductor materials, insulator materials, and conductor materials, the gap between the conduction band and valance band is shown. Photocatalytic oxidation reactions usually consist of heterogeneous catalytic activation of a semiconductor that is irradiated using a light source of appropriate wavelength and based on the band energy of the semiconductor [13-14]. When electrons are activated under photoexcitation with appropriate illumination, semiconductors activate electrons in the valance band and transfer them to the valance band [1].

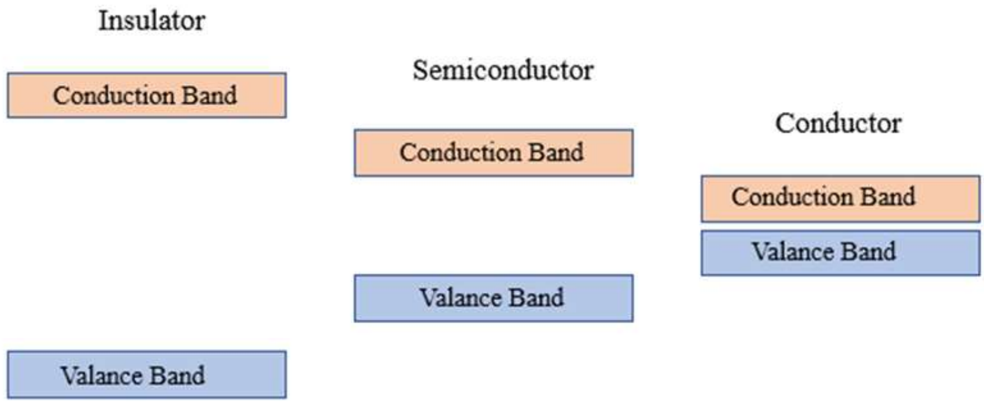

Figure 1.3 Material energy bandgap [1]

1.2 Metal-Organic Frameworks (MOFs)

MOF which has emerged as a new class of crystalline porous materials in the last two decades has become one of the most productive fields in chemistry and material. (Li et al, 1999). MOFs are formed by linking metal ions or groups with organic ligands [15].

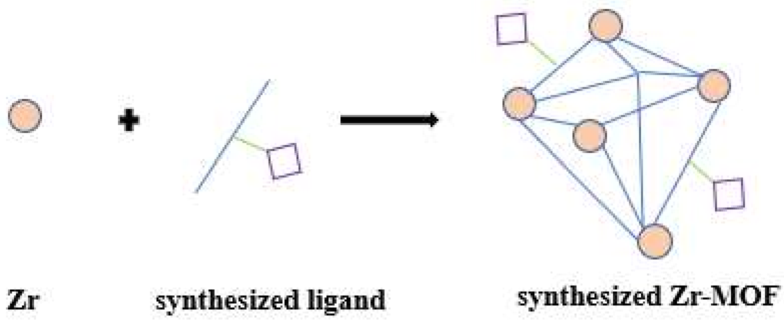

Figure 1.4 Metal-organic framework formation [16]

Kuppler et al. are carried out on MOFs which about potential areas such as gas storage, catalysis, molecular sensing, molecular separation, and drug release [8]. The structures and properties of MOFs can be designed and systematically adjusted with the appropriate selection of building blocks. Zhenqiang Wang and Cohen et al. explained that in addition to the preliminary design in the synthesis, it has been successfully used to adjust the pore properties of MOFs with post-synthesis modifications [17]. Moreover, easy optimization of the pore structure, surface functions, and other properties of MOFs for special applications is possible [15-16]. The finding that MOFs can absorb light has been promising photocatalysts for some reactions [8]. In figure 1.2, the structure of MOF was figured. The elements that determine the topological structure of MOFs are different organic ligands and different metal ions. IR-MOFs (iso-reticular metal-organic frameworks), 55 ZMOFs (zeolitic metal-organic frameworks), MILs (materials ınstitute Lavoisier) are some of the most common MOFs variants. In figure 1.5 MOF types have shown [18-19].

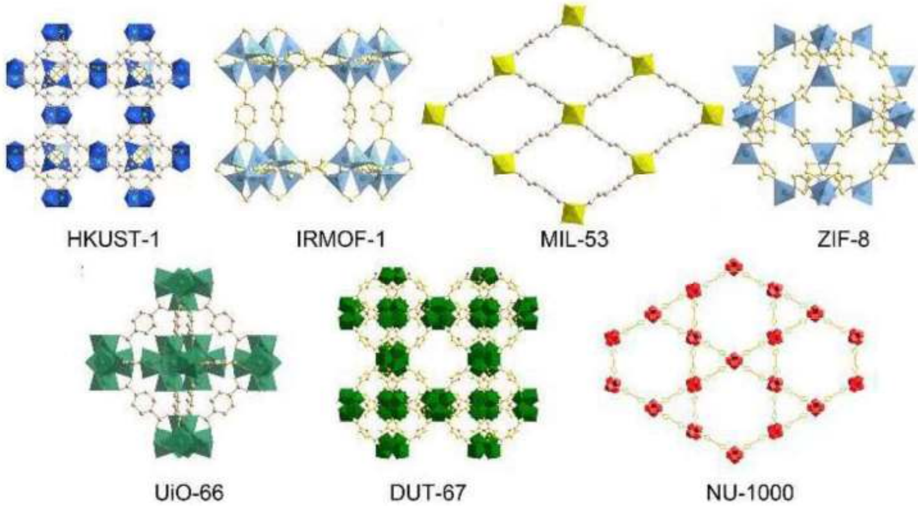

Figure 1.5 Crystal structures of MOFs [17]

Zr-MOF has outstanding stability, especially in the environment of acid and alkali. This is because of the strong link between Zr and O_2. With the addition of functional groups, Zr-MOF becomes superior to other MOF variants [13]. Due to the machinability and mechanical properties of Zr-MOF, it is also considered for industrial applications [20]. The bandgap energy of the semiconductor is the minimum light energy that ensures electrical conductivity. In addition, Zr-MOFs are considered a promising MOF variant due to the rapid and positive results obtained from studies and their inherent advantages [17]. This energy is a fixed value unique to semiconductors and takes a different value for each semiconductor [18]. In figure 1.6 Zr based MOF is shown chemically.

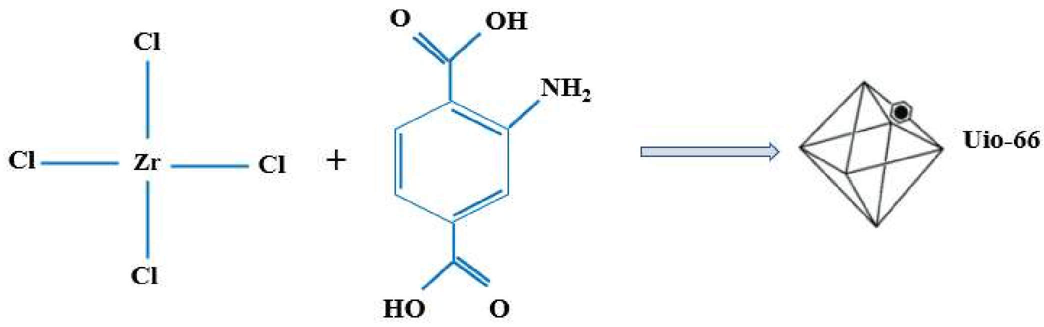

Figure 1.6 Chemical structure of Zr based metal-organic framework [21]

Hydro-thermal and solvothermal production methods are mainly used for a wide variety of MOFs. The main difference between hydrothermal and solvothermal production is that in hydro-thermal production, the synthesis takes place in a water environment whereas, in the solvothermal production method, the synthesis takes place in a solvent environment [22-23].

CHAPTER 2

EXPERIMENTAL PART

2.1 Synthesis of Polydopamine (PDOP)

Polydopamine is a dark brown biopolymer obtained by auto-oxidation of dopamine monomer which has an easy production process and its physical-chemical properties can be controlled by various chemical modifications [24-25]. Figure 2.1 and Figure 2.2 show dopamine and polydopamine structures.

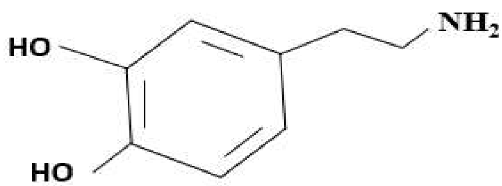

Figure 2.1 Dopamine crystal structure [25]

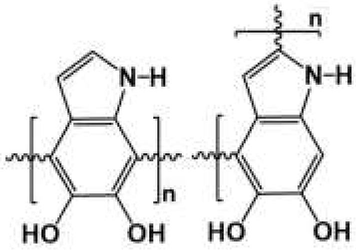

Figure 2.2 Polydopamine crystal structure [26]

Polydopamine has recently emerged as a popular material due to its superior properties thus polydopamine can be easily produced on almost all inorganic and organic substrates. Research and interest in PDOP have increased with the emergence of PDOP's excellent properties and performance in various fields. Areas of application for PDOP include supercapacitor fields, electrocatalysis, photocatalysis, chemo-catalysis, removal of metal and organic dyes, oil-water, and desalination [27-28]. Polydopamine is a type of coating based on the oxidative polymerization of dopamine molecules. Due to its high stability, polydopamine is virtually coated on almost all solid supports. Metallic nanoparticles can be grown on-site on any support without using any reducing agents or metallic seed particles, thanks to polydopamine (PDOP) functional groups [29]. In the first step, 4 ml ethanol, 1.47 ml (%2.47) NH_3, and 7.5 ml distilled water were loaded into respectively and stirred at room temperature for 5 min, then the solution was put into a water bath. Then water temperature of the water-bath mechanism was 70°C. In the second step, DOPHCl (50 mg)-distilled water (1ml) solution was prepared. The solution was stirred at room temperature till the dissolution of DOPHCL in water. The shown in Figure 2.3.

Figure 2.3 Ultrasonic cleaner and vortex

The solution which was prepared in the second step was put into the glass beaker solution with help of Eppendorf. Production of the polydopamine solution waited 17 hours. After 17 hours, polydopamine was centrifugated two times with distilled water.

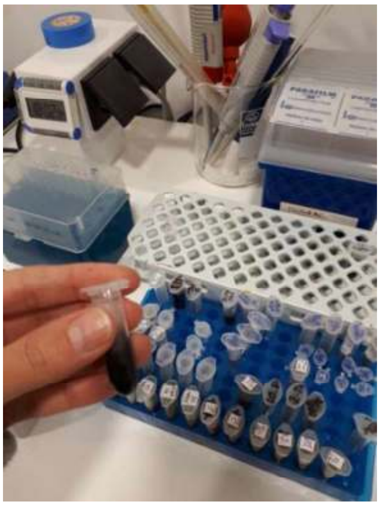

Figure 2.4 The photos of the aqueous dispersion of PDOP

In Figure 2.4 aqueous dispersion of PDOP, and Figure 2.5 amount of synthesized PDOP is shown.

Figure 2.5 PDOP synthesis

2.2 Synthesis of Zr-MOF@PDOP

Metal-Organic Framework (MOF) was synthesized according to the process reported elsewhere by material quantity modifications. For optimal Zr-MOF synthesis, various concentrations were tested. In Table 2.1 Zr-MOF synthesis, various concentrations are illustrated. To improve photocatalytic activity, a photocatalyst such as a semiconductor is coated on the surface of a carrier. The recombination of photogenerated electron-hole pairs that occur in photocatalysis reduces the efficiency of the photocatalyst [16]. $ZrCl_4$ (20 mg) and TPA (2 mg) were weighed and added into the glass beaker containing DMF (10 mL). Due to its ability to expand pores and absorb CO_2, DMF material is used as a solvent in the synthesis of Zr-MOF [8]. A mixture of DMF, TPA, and $ZrCl_4$ was sonicated till a clear solution was formed. Then, the synthesis process was performed in laboratory conditions. When the oil bath indicator showed 140 °C, solution of DMF, TPA, $ZrCl_4$ were put into the oil bath and then PDOP (1.0 mg) was added. Before adding, PDOP was sonicated for 1 minute at room temperature. The whole solution process time was 80 minutes. After, cooling of the solution (35-40 min), precipitates were separated by centrifugation (5 min), washed with ethanol two times. Morphological information of PDOP and Zr-MOF@PDOP were characterized by a Scanning Electron Microscope (SEM), (Hitachi, SU5000, Japan). X-ray diffractometer (XRD) (A Miniflex 600, Rigaku Co., Japan) was employed to characterize the X-Ray diffraction patterns (Cu Kα radiation, λ= 0.1546 nm) and also XRD working speed was 2 °C/min. Then UV-Vis spectrometry (Shimadzu UV-1601) was characterized optical properties of photocatalysts with a measurement system that includes a light source and detector mechanism to detect how much light passes through or has been absorbed.

2.3 Photocatalytic Activity Evaluation

Generally, there are two types of photocatalytic applications mechanism. The first type of photocatalysis is hydrogen production, a reaction called water splitting. As the name implies, the reaction separates water molecules into its components: hydrogen and oxygen. Organic pollutant degradation is the name of the second type of photocatalysis referring to processes that break down pollutants in water. Scientists have tried this innovative MOF-based photocatalytic system, with organic pollutants [14-30]. MB is an organic and cationic dye used in the cosmetics and leather industry, resulting in intense water pollution. Moreover, organic dyes which contained in wastewater block sunlight, so both affecting photosynthetic reactions and causing serious harm to human [24]. The most suitable method for removing dyes is photocatalytic degradation (Lai et al.,2019; Tang,2020). To ensure the complete removal of dyes, inorganic catalysts must be used [31]. Many attempts have been made to inhibit electron recombination and increase photocatalytic performance along with surface modification. One of the attempts is the modification of single photocatalyst materials which includes metal or metal oxide nanoparticles to form metal/MOFs heterostructured photocatalysts. MOF-based photocatalysis studies were done under visible light, especially using LED lights, for organic pollutants degradation [8]. Catalytic performance of Zr-MOF was measured with MB ($3.125x10^{-5}$ M) and distilled water (20 mL) solution. Photocatalytic performances of catalysts and various oxidants were evaluated in the photodegradation of MB under visible LED. Visible light is the range of wavelengths from 400-750 nm and also it is visible to the human eye. One of the important reasons for using LED visible light in photocatalysis studies is that it has the most similar wavelength value to sunlight in the light spectrum. LEDs are also preferred due to their long lifetime, economical, low maintenance, and operating cost features. In Figure 2.6 light spectrum is shown [32].

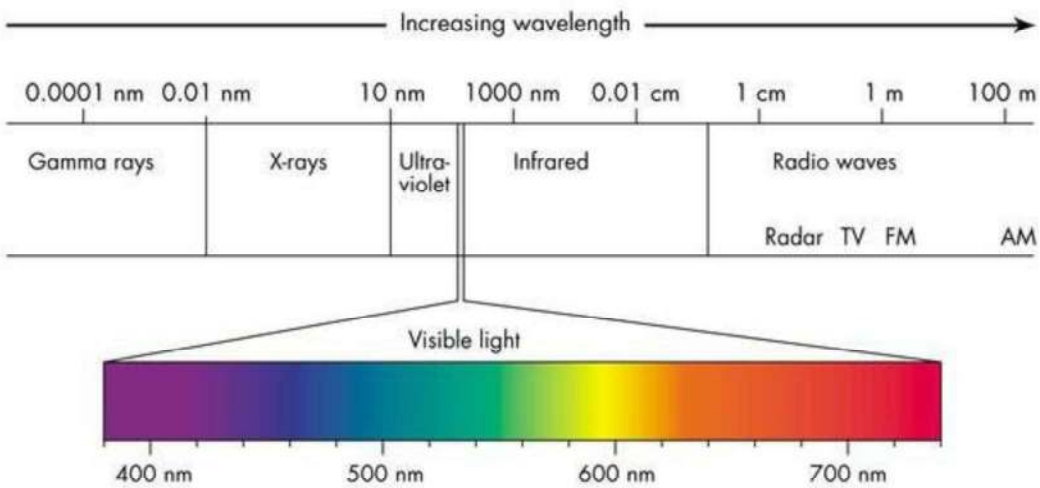

Figure 2.6 Light spectrum [32]

In Figure 2.7 MB solution is shown. After adding Zr-MOF to MB solution, the photocatalytic reaction was started under visible LED light irradiation experiment was started. Light intensity value for the system of LED photoreactor – DC source power properties was 54 mW/cm^2.

Figure 2.7 Pieces of equipment of photocatalytic experiment

Photocatalytic oxidation reactions are heterogeneous catalytic activation that involves the semiconductor band energy and optimum wavelength. Results of activation, electron-hole pairs occur then the electron-hole pairs are found out O_2 radicals which have high activity and $OH^{\cdot}$ groups. One of the most important qualities of OH groups is reactivity. O_2 and $OH^{\cdot}$ radicals are used to facilitate the oxidative degradation of organic-inorganic or metallic contaminants [1]. Summary of reactions on the surface of catalyst shown in Figure 2.8.

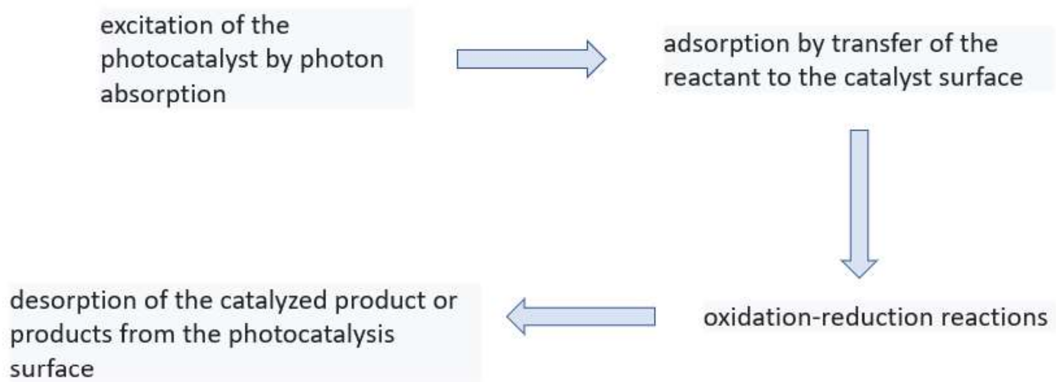

Figure 2.8 Photocatalytic degradation steps [32]

CHAPTER 3

RESULT AND DISCUSSION

3.1 Characterization

3.1.1 Scanning Electron Microscope (SEM) Results

The morphology of nanoparticles was characterized by SEM analysis in Figure 3.1 and Figure 3.2. Scanning electron microscopes are used for spot analysis, wide-area analysis, and composition change detection. Excitation voltage, microscope brand, magnification, diameter, and resolution information are also added to the SEM microscope images [33-34]. The surface morphology of PDOP changed with the addition of additives (Zr doped MOF). The diameter of PDOP particles increased after Zr-MOF formation on the surface. Moreover, Zr-MOF coated on PDOP grew as islet type which is one of the main groups that emerged depending on the thermodynamic parameters of the doping and the surface of the substrate, the initial core, and the growth stages. The other two groups are layer type and mixed type (Stranski-Krastanov) [22-23]. Islets formes caused an increase in photocatalytic activity with increasing the surface area [18]. This can be explained that oxygen-containing functional groups in PDOP combined with Zr^{4+}, inhibiting the crystal growth of Zr-MOF [35].

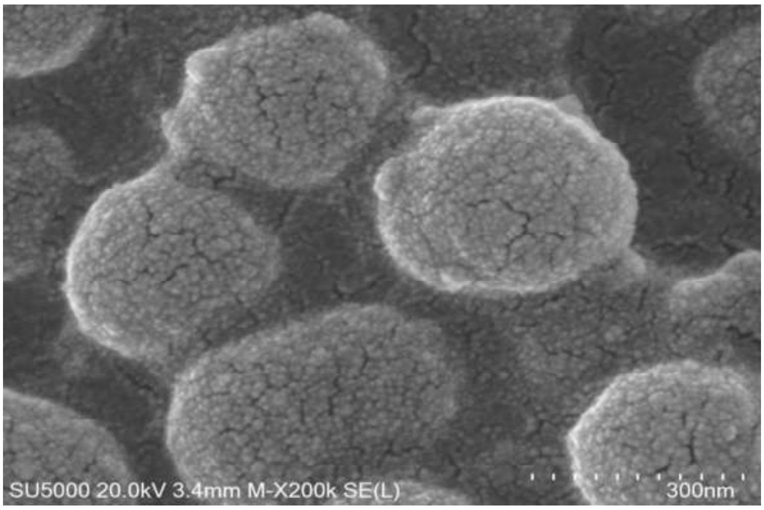

Figure 3.1 SEM image of PDOP

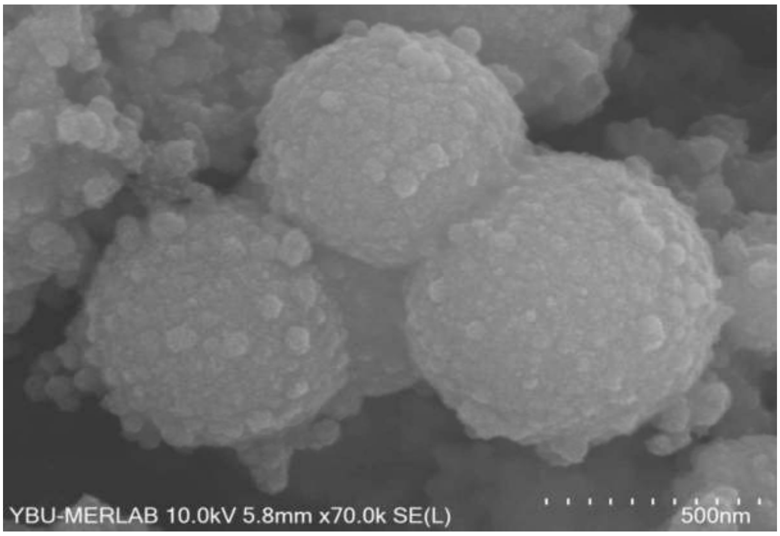

Figure 3.2 SEM image of Zr-MOF@PDOP

3.1.2 X-Ray Diffraction Results

The crystalline structure of samples was analyzed by X-ray diffraction (XRD). The Zr-MOF@PDOP composite material was prepared by the thin layer and amorphous crystal feature of PDOP. As a result, it was observed that the locations of the peaks of the Zr-MOF crystal structure did not change but the peak widths increased due to the PDOP material structure [36]. Depending on the reaction time and peak intensity, characteristic peaks of 7° and 8.45° were obtained for Zr-MOF.(Luv et.al 2015) [37]. As a result of the experiment, the Zr-MOF main diffraction peak at 2θ= 7.26° with the variation of peak intensity was observed. The X-ray diffraction pattern was similar to previous Zr-MOF studies (Lin et al. 2016; Peterson et al. 2014; Shen et al. 2013) [21]. The peak of Zr-MOF (2θ=26.92°) has the same diffraction peak and then as a result of Zr content, a stronger peak intensity proved when compared with literature results, then it was shown in Figure 3.3. Also, peaks at 2θ= 41.5° and 2θ= 43.28° are compatible with literature results. The width of 7.26 and 29.92 peaks is explained in the literature results by parameters such as MOF types, amount of product, and crystal structure changes [35].

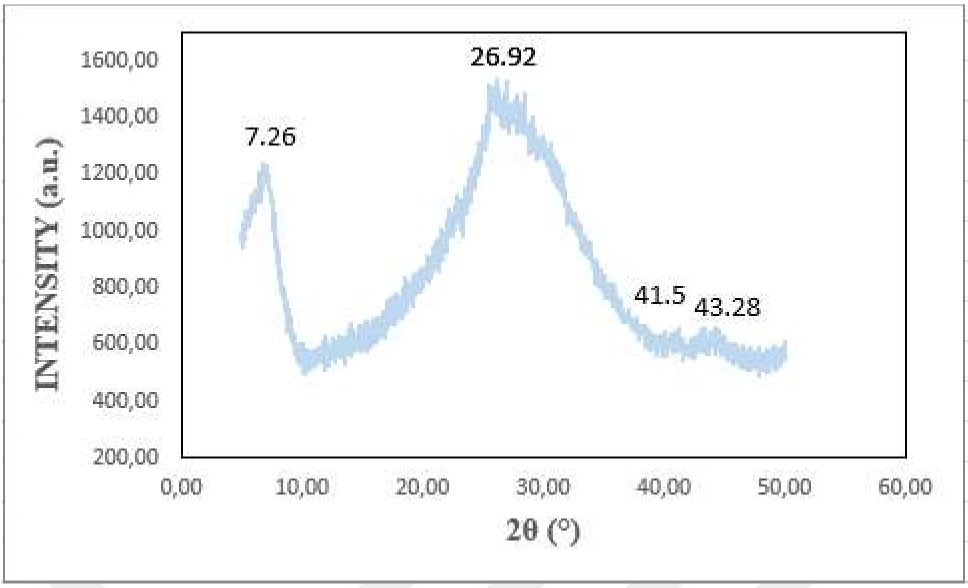

Figure 3.3 XRD result of Zr-MOF@PDOP

3.1.3 FTIR Results

Absorption in the infrared region excites the molecules however this energy can not break the molecular bonds, causing the molecules to vibrate. Changes in the energy level provide information by forming various vibrational spectra [38]. The working principles are based on an interferometer that is fixed in a certain position, sending an excitation pulse on the sample and measuring the IR signals as the time functions. After collecting data for the first position, the movable mirror is positioned for the next position. The detector measures as a function of time for the specified locations. The process is repeated many times and at the end of the process, two-dimensional data is obtained. FTIR gives a time-related spectrum from all mirror positions [31]. PDOP nanoparticles had broadband from 2900-3600 cm^{-1} then the broadband is attributed to the stretching modes of N-H and O-H bonds. The stretching of the aromatic carbon bonds is due to the peak indole 1510 cm^{-1}, furthermore, the peak at 1225 cm^{-1} corresponded to the C-N bending. All the values of wavenumbers concluded that the FTIR spectrum of PDOP proved successful polymerization [25]. Also, the Zr-MOF@PDOP FTIR result was shown in Figure 3.4. The peaks at 1618 cm^{-1} and 1480 cm^{-1} can be attributed to the N-H bending. On the other hand, small changes were observed at 1000 cm^{-1} and 535 cm^{-1}. The reason might be that the introduction of functional groups. When we compared the literature results, the peaks were almost the same and there was a slight decrease in strength [35].

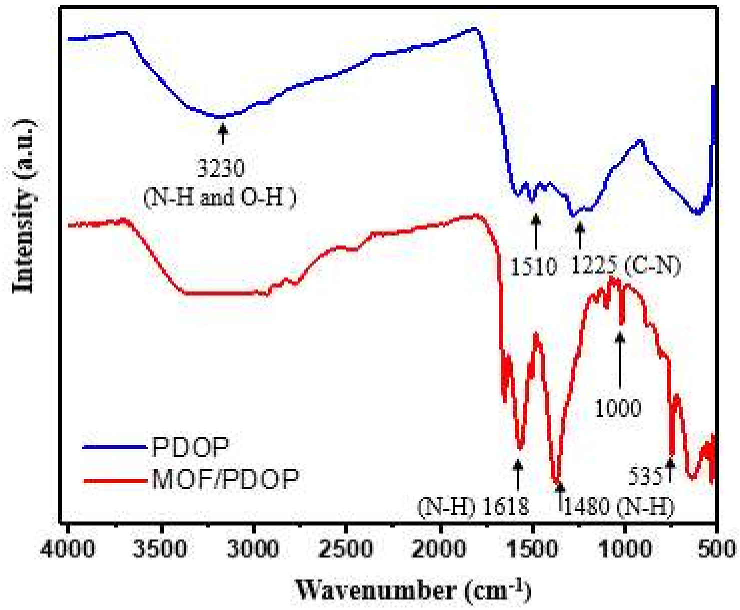

Figure 3.4 FTIR results of PDOP and Zr-MOF@PDOP

3.1.4 UV-Spectrophotometer Results

The effect of light absorption greatly affects the rate of photocatalytic reactions (Curco, 2002) [1]. UV-LEDs have been used in photocatalysis applications for 10 years due to their longevity of 100.000 hours and high quantum efficiency [7]. MB photocatalytic activity was evaluated with reaction time during various processes. The photocatalytic efficiency was investigated in UV spectrometry by looking at the initial and final concentration (C/C_0) value for MB molecule per volume unit. The degradation process which is characterized by a UV spectrophotometer takes place directly by the production of OH radicals without the need for any other chemicals [10]. In Figure 3.5, the synthesized Zr-MOF@PDOP samples were observed in the dark and then in white light. After observing the light effect, to determine the importance of the time parameter under white light and examined in the UV-spectrophotometer. Zr-MOF@PDOP material which did not show any change in the dark environment became sensitive to redox reactions under the light. As a result, when Zr-MOF@PDOP catalyst was exposed to UV light, a strongly oxidizing environment was formed by absorbing the light. Thus chemical reaction was started [10].

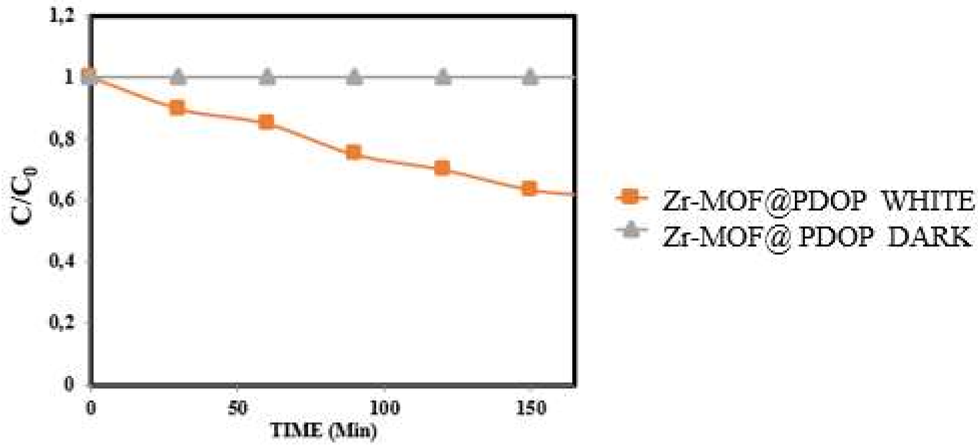

Figure 3.5 UV- spectrophotometer results of Zr-MOF@PDOP

3.1.4.1 Oxidants Results on MOF@PDOP

After the importance of oxygen radical formation on photocatalysis was stated, the first experiment was carried out with H_2O_2. Then after the first sample was taken half an hour later, samples were taken at half-hour intervals under white light and compared with the results of the Zr-MOF@PDOP sample which under the same conditions in Figure 3.6. H_2O_2 increased the efficiency because of that the possible H_2O_2 photolysis induced by incident light increased [39].

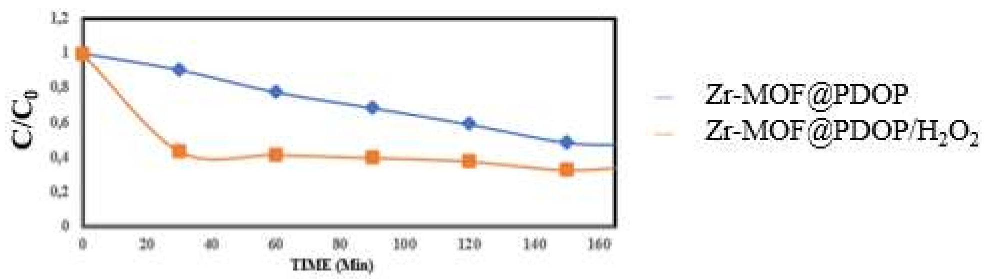

Figure 3.6 Spectrophotometer results of Zr-MOF@PDOP and Zr-MOF@PDOP with H_2O_2

In the last study of photocatalytic degradation, the effect of H_2O_2 +O_2 dosage on MB degradation over Zr-MOF@PDOP system was investigated under given reaction conditions and results are shown in Figure 3.7. Catalyzed degradation kinetic enhancement of MB over Zr-MOF@PDOP was more significant in the presence of both H_2O_2 and O_2 under visible light (%91 efficiencies). When H_2O_2, H_2O_2 (X2), and H_2O_2+O_2 efficiency results are compared, the O_2 λmax value enables faster decolorization and degradation of aromatic structures, is greater than H_2O_2. As a result, H_2O_2+ O_2 photocatalytic degradation was occurred faster [10].

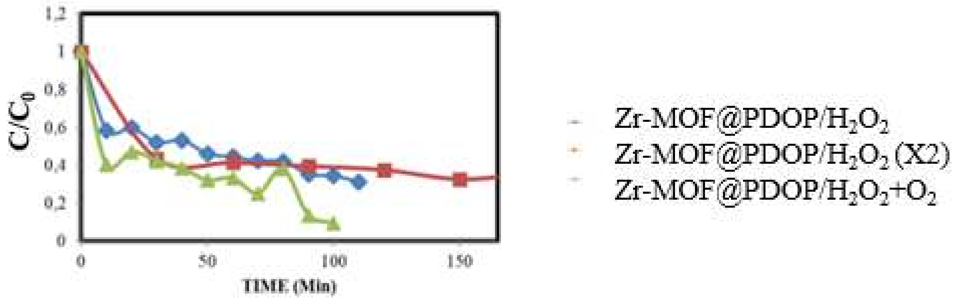

Figure 3.7 UV- spectrophotometer results of Zr-MOF@PDOP with H_2O_2 and O_2

CONCLUSION

Photocatalysis technology which is one of the self-purification cleaning mechanisms is a promising technology for organic pollutants. Many studies have been carried out on photocatalysis technology and these studies continue today. Zr-MOFs have started a new era in many areas such as photocatalysis, gas adsorption, gas purification, bio-medical applications, and hydrogen storage. There is a positive relationship between photocatalysis and Zr-MOFs. While Zr-MOF creates a solution for the degradation of organic dyes, the different oxidants are used for increasing the efficiency of the solution. In this study, the effect of photocatalysis on organic pollutants was investigated with different oxidants such as H_2O_2 and O_2 together with Zr-MOF. Experimental results were also evaluated by characterization methods such as XRD, SEM, FTIR, and UV-spectrophotometer. Light effect and oxidant type were the most important variables affecting the study. Firstly, Zr- doped MOF synthesized by the hydrothermal method was coated on PDOP. MB degradation was analyzed under dark/white LED light under and under white LED light according to light durations. The photocatalytic performance of Zr-MOF@PDOP under white LED light was better than dark MOF@PDOP. As a result of the experiments, it was observed that Zr-MOF samples were compatible with previous literature studies and there was no degradation in the dark environment. To measure the photocatalysis activity efficiency; H_2O_2, H_2O_2 (x2), H_2O_2+O_2 were included in the experiment, respectively. It has been observed that studies with H_2O_2 oxidants give better results by increasing OH radicals than only Zr-MOF studies. As a result, the photocatalytic degradation efficiency of the samples followed; H_2O_2+O_2 (%91)> H_2O_2 (x2) (%72) >H_2O_2 (%71)> Zr-MOF@PDOP (%62). The experiments and results within the scope of the thesis were examined and it was concluded that it will be a guiding study in future studies in photocatalysis applications containing Zr-MOF to be used for organic pollutants.

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