

**DETERMINATION OF PHOTOCATALYTIC DEGRADATION
PRODUCTS OF DYE MOLECULES FOUNDED IN TEXTILE
WASTEWATER**

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ABSTRACT

DETERMINATION OF PHOTOCATALYTIC DEGRADATION PRODUCTS OF DYE MOLECULES FOUNDED IN TEXTILE WASTEWATER

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Photocatalytic process is widely applied to remove hazardous organic compounds, microorganisms founded in water, volatile organic compounds and plastics waste by decomposing and destructing them founded in wastes. In this process, oxidation and reduction reactions occur on the surface of photocatalytic materials with the help of conduction band electrons and holes generated on valence band under ultraviolet (UV) or visible light radiation. Among the wastes mentioned above, textile based waste water is so important due to the highly toxic dye contents. Characterization of the degradation products of dye molecules obtained at the end of the process is so important in order to reveal the properties of them. Also characterization of the intermediates is so important to find the degradation pathways.

Degradation products and intermediates can be followed by two different ways. In the first one the color of the solution is followed with UV-vis spectrometry. In the second way the final products can be founded with gas or liquid chromatography coupled with different types of detectors like flame ionization (FID), thermal conductivity (TCD) and mass (MS).

This study is related to find the photocatalytic degradation products of dye molecules founded in textile wastewaters. For this, photocatalytic degradation products of methylene blue (MB) were investigated which are produced in the presence of TiO₂ nanoparticles and palladium nanoparticles added PEDOT (PdNPs/PEDOT) under UV irradiation by using UV spectroscopy and liquid chromatography-mass spectrometry (LC-MS).

The obtained results showed that the initial structure of MB was decomposed under UV light exposure in both the photocatalytic reactions in which TiO₂ nanoparticles and palladium nanoparticles loaded PEDOT (PdNPs/PEDOT) were used. TiO₂ nanoparticles are widely used in photocatalytic dye decomposition reactions and degradation products and pathway are given in literature. The results obtained in this study for the photocatalytic degradation of MB with TiO₂ nanoparticles under UV light exposure are in consistent with the literature. In the case of PdNPs/PEDOT, new catalyst, the main degradation products are similar to those obtained with TiO₂ nanoparticles. So, it can be concluded that photocatalytic degradation of MB by using PdNPs/PEDOT followed the same degradation pathway as TiO₂ nanoparticles under UV light exposure. Besides this work provides a good insight into the decomposition products and pathway for the PdNPs/PEDOT assisted photocatalytic degradation of MB molecules under UV light irradiation.

Keywords: Textile wastewaters, photocatalytic degradation, degradation products, methylene blue, photocatalyst

ÖZ

TEKSTİL ATIKSULARINDA BULUNAN BOYA MOLEKÜLLERİNİN FOTOKATALİTİK BOZUNMA ÜRÜNLERİNİN TAYİNİ

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Fotokatalitik işlem atıklarda bulunan tehlikeli organik bileşiklerin, su kaynaklı mikroorganizmaların, uçucu organik moleküller gibi havayı kirleten maddelerin ve atık plastiklerin gideriminde sıklıkla uygulanmaktadır. Bu işlemde ultraviyole ve görünür ışık altında iletim bandı elektronları ve değerlik bandında oluşan boşlukların yardımı ile fotokatalitik malzemenin yüzeyinde, atık maddelerin parçalandığı yükseltgenme ve indirgenme reaksiyonları oluşmaktadır. Yukarıda bahsedilen atıklar arasında tekstil bazlı atıklar oldukça zehirli boya içeriği sebebi ile dikkate alınmalıdır. Bu işlem sonucunda elde edilen boya moleküllerinin bozunma ürünlerinin karakterizasyonu bunların özelliklerini açığa çıkarmak için çok önemlidir. Ayrıca ara ürünlerin tayin edilmesi de bozunma yolunun bulunması için çok önemlidir.

Bozunma ürünleri ve ara ürünler iki farklı yol ile takip edilebilir. Birincisinde UV-Vis spektrometresi kullanılarak renklerinden takip edilir. İkinci yolda ise elde edilen ürünler alev iyonlaşma (FID), ısı iletkenliği ve kütle (MS) dedektörleri gibi farklı dedektörlerle eşleştirilmiş gaz (GC) yada sıvı kromatografisi (LC) ile bulunabilir.

Bu çalışma tekstil atıksularında bulunan boya moleküllerinin fotokatalitik bozunma ürünlerinin tayin edilmesi ile ilgilidir. Bunun için TiO_2 nanoparçacıklar ve paladyum nanoparçacık eklenmiş PEDOT varlığında ve UV ışığı altında elde edilen metilen mavisinin (MB) fotokatalitik bozunma ürünleri UV-Vis spektroskopisi, ve LC-MS kullanılarak araştırılmıştır.

Elde edilen sonuçlar, metilen mavisinin UV ışınları altında TiO_2 nanoparçacıkların ve paladyum eklenmiş PEDOT (PdNPs/PEDOT) yapılarının kullanıldığı fotokatalitik reaksiyonlarda parçalandığını göstermektedir. TiO_2 nanoparçacıklar fotokatalitik boya bozunması reaksiyonlarında yaygın olarak kullanılmaktadır ve bozunma ürünleri ile bozunma yolu literatürde verilmektedir. Bu çalışmada metilen mavisinin UV ışığı altında TiO_2 nanoparçacıkları ile fotokatalitik olarak bozunması ile ilgili elde edilen sonuçlar literatür ile uyumludur. Yeni katalizör olan PdNPs/PEDOT da ise, elde edilen bozunma ürünleri, TiO_2 nanoparçacıklarla elde edilen ürünler ile benzerlik göstermektedir. Bu sebeple, UV ışığı altında PdNPs/PEDOT ile fotokatalitik olarak metilen mavisinin bozunmasının, TiO_2 nanoparçacıkları ile aynı bozunma yolunu takip ettiği sonucuna ulaşılmaktadır. Ayrıca, bu çalışma, UV ışığı altında metilen mavisi moleküllerinin PdNP/PEDOT destekli fotokatalitik bozunumunun ayrışma ürünlerine ve yoluna iyi bir bakış açısı getirmektedir.

Anahtar Kelimeler: Tekstil atıksuları, fotokatalitik bozunma, bozunma ürünleri, metilen mavisi, fotokatalizör

To my Family

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CHAPTER 1

INTRODUCTION

Dyes used in textile industry and other industrial processes produce a huge waste water known as toxic organic materials. More than 20% (by weight) of total dyes is spreading out to the environment in the form of waste water which causes an increasing environmental risk^{1,2,3}. These colored waste waters are the main source of non aesthetic pollution and their byproducts produced through chemical reactions like oxidation and hydrolysis can be the source of toxic byproducts^{4,5,6}.

Therefore decolorization of dyes founded in waste waters and the removal of the related byproducts has gained great attention. Generally conventional techniques like reverse osmosis, coagulation by using chemicals, ion exchange resins, adsorption on solid surfaces and filtration are used to remove the wastes based on the dye pollutants^{7,8}. Unfortunately these techniques are non-destructive thus organic pollutants only transferred from waste water to another phase. So these processes produce secondary pollution. Besides, regeneration of systems for reuse process and treatment for removal of the solid wastes make these processes so expensive⁹. Biological treatment methods also used for waste water treatment, but they are not so effective for decolorization and decomposition of dye wastes because of the high aromatic content and stability of the dye molecules^{10,11}. Other techniques used for the removal of dye molecules like ozonation and chlorination suffer from slow removal rates and high operating costs besides limited effect on carbon content^{12,13}.

In order to overcome drawbacks mentioned above, new technique known as advanced oxidation processes (AOPs) has become popular. This process includes sonolysis, photofenton, Fenton method, photolysis, and photocatalysis^{14,15}. All mentioned parts included in AOP are useful and have some advantages and disadvantages except photocatalysis. In photocatalytic process, it is possible to obtain decolorization of dye molecules and degrade the organic pollutant with the usage of UV and solar light illumination and proper catalyst^{16,17}.

Nowadays, semiconductor based photocatalysts like TiO_2 , ZnO_2 are widely used in photocatalytic processes. But low recycling rates and photoelectron transfer efficiency besides high band gaps limits the efficient usage of that materials. In order to overcome these drawbacks, studies are performed to find materials with lower band gap and high reuse capacity in the dye removal of waste waters^{18,19}.

1.1 Advanced Oxidation Process

During the last decade, because of the high capability in dyes degradation in wastewater and other aqueous systems, the advanced oxidation processes (AOPs) have a high growing interest compared to traditional techniques. In AOPs, highly reactive species like hydroxy radicals ($\bullet\text{OH}$) are generated. A wide range of organic pollutants are oxidized easily with the help of that reactive species. Nowadays, for decolorization and degradation of dye founded in waste waters, $\text{H}_2\text{O}_2/\text{UV}$ processes²⁰, Fenton and photo-Fenton catalytic reactions²¹, and semiconductor based photocatalysis^{22,23} are widely investigated.

Among the methods mentioned above, semiconductor based photocatalysis, especially TiO_2 in nano form, seems to be most effective way for decolorization and decomposition of dye stuff founded in waste waters ²⁴. Nano form of TiO_2 known as total oxidation catalyst thus may allow complete conversion of all carbon content to CO_2 and it can be applied under atmospheric conditions. Besides, atmospheric oxygen can be used as oxidant with the presence of TiO_2 . Moreover, availability, stability, low cost and non-toxic nature make TiO_2 effective photocatalyst ^{25,26}.

1.2 Mechanism of UV Light Driven Photocatalysis

The general mechanism of photocatalysis under UV light illumination is given in Figure 1.1. According to this, initially, holes (h^+ VB) on valence band (VB) and electrons (e^- CB) on conduction band (CB) generated when semiconductor based photocatalyst interact with UV light and finally absorbs photon which has equal or greater band gap ($h\nu \geq EBG$). The oxidation process of organic species initiates by hydroxyl radical formed with the hole formation and the reduction part is driven with the formation of electrons ^{27,28}.

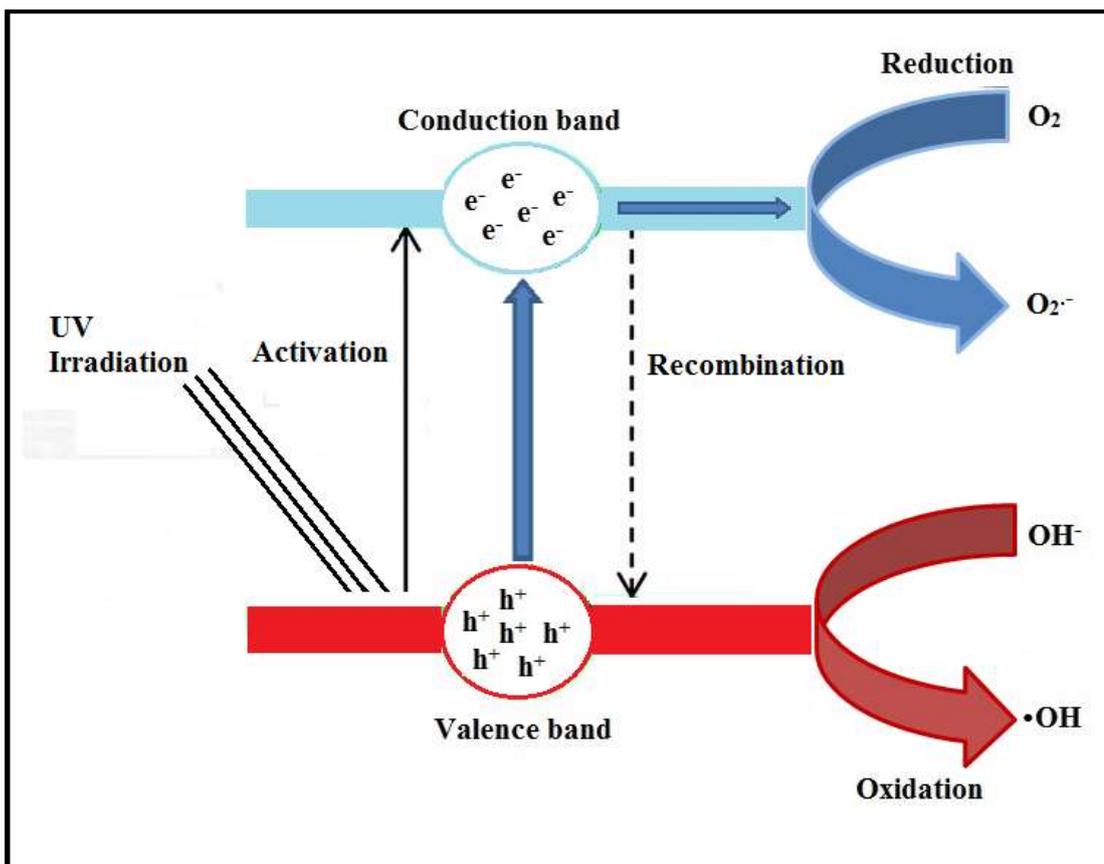


Figure 1.1 General mechanism of the photocatalysis ²⁹

In the whole reaction driven by light illumination, oxidants found in aqueous solution are reduced and the reductants are oxidized with the presence of photocatalytic materials.

Some oxides of the semiconductors like TiO₂, ZnO, MoO₃, ZrO₂, WO₃ and chalcogenides of metals like ZnS, CdS, CdSe shows photocatalytic activity. Unfortunately, in order to meet the thermodynamic requirement, the valence band and conduction band of the semiconductor based photocatalytic materials have certain oxidation and reduction potentials which lie in the band gap ($E^0(\text{H}_2\text{O}/\text{OH}^\bullet) = 2.8 \text{ V vs NHE}$ and $(E^0(\text{O}_2/\text{O}_2^{\bullet-}) = -0.28 \text{ V vs NHE})$).

The band-gap positions of the photocatalytic materials are given in Figure 1.2
30,31,32

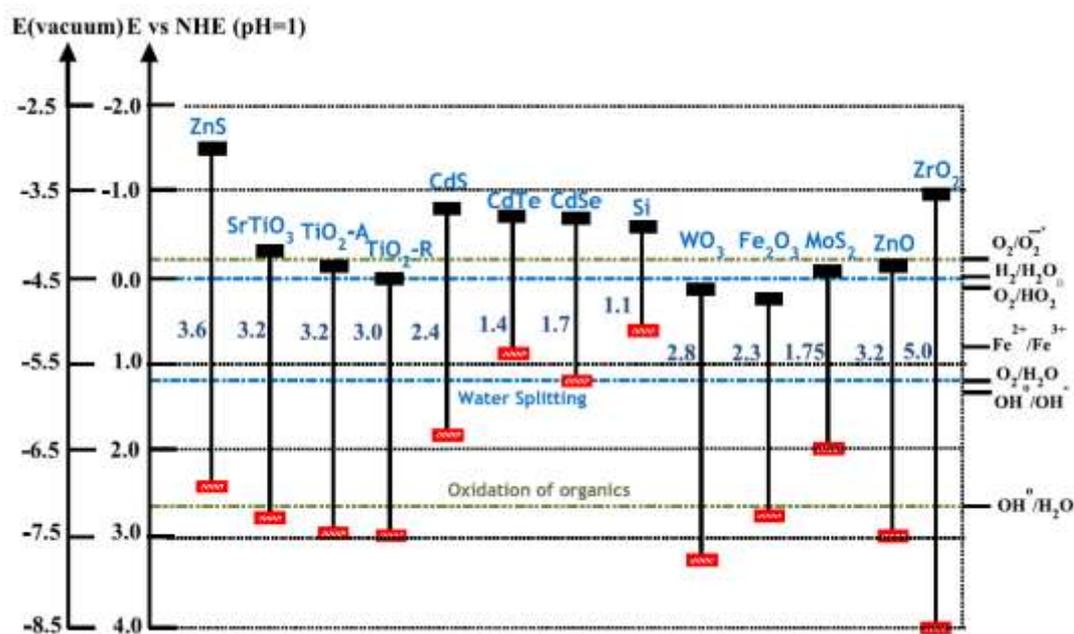


Figure 1.2 Band gap values of different materials³³

It can be concluded from the figure given above that, TiO₂, ZnO, SrTiO₃ and ZrO₂ has favorable band-gap value when compared to the other semiconductors and can be chosen as photocatalyst in the dye removal process under UV light illumination.

1.3 Dyes

Dyes have wide range of applications in human life. The different applications are such as clothing, dieting beside paper and leather industries. Cosmetics, plastic production, pharmacology and drugs production are other application area of dyes. Among them more than 80% of synthetic dyes are consumed in textile industries approximately. Hard fixation steps of dyes during process cause environmental contaminations such as dyes drainage in the form of liquor contamination, residue unfixed dyes in wastewater etc. which direct dyes as hazardous wastes.

Nearly 10% of dyes are drained into the industrial wastes. Traditional wastewater cleaning operations had steps such as neutralization of acidic and alkaline materials, chemical oxidation and flocculation processes that supplies 70-80% color elimination of wastes. Unfortunately huge part of organic carbon is remaining in wastewater as residue.

The degradation of dye molecules by using UV and visible light exposure are mentined in many publications^{34,35,36} and the important parameters were figured out which affect the degradation rate and the product of the process³⁷. Also effect of the modification of the semiconductor based materials for the degradation of dyes were investigated³⁸.

Dye molecules are classified based on the functional group that composed the dyes, as azoic, indigo, acridine, heteropolyaromatic, aryl, nitro, nitroso, cyanine and stilbene. Among them, due to extensive usage as commercial dye, photocatalytic decomposition and decolorization of azo dyes has been investigated extensively³⁶

For this reason, these type of dye molecules used as test material in the photocatalytic activity measurements of the prepared photocatalyst. Among them, Methylene Blue (MB) is widely used for this aim due to its common usage in industry. It is also known as the common water pollutant in textile indutry. The chemical structure and properties of methylene blue are given in Figure 1.3 and Table 1.1, respectively.

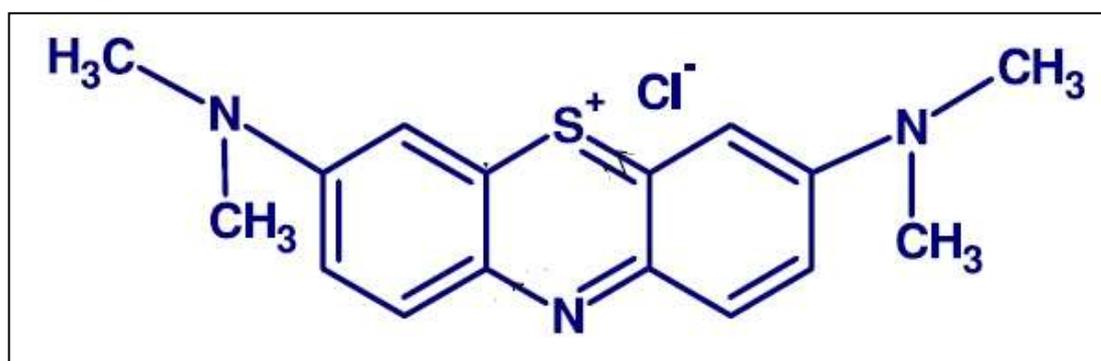


Figure 1.3 Chemical structure of methylene blue

Table 1.1 Physical properties of methylene blue

Dye name	Methylene Blue
Suggested name	Methylene Blue
Abbreviation	MB
C.I. name	Basic Blue 9
C.I. number	52015
Class	Thiazin
λ_{\max}	668 nm
Color	Blue
Empirical formula	$C_{16}H_{18}N_3SCl$
Formula weight	319.9 g/mol
Molecular volume (cm ³ /mol)	241.9
Molecular diameter (nm)	0.80

The decomposition of methylene blue dye molecules is so hard. For this reason it is very important to find the proper catalyst to decompose it both under UV^{39,40} and visible light irradiation. It is possible to find much information about the degradation pathway of methylene blue and degradation products under light illumination by using semiconductor based catalysts^{41,42}. By using this information, it is possible to find degradation products and pathways for new types of catalysts.

1.4 Characterization of the Degradation Product of Dye

The catalytic parameters for the degradation of a dye can be figured out by using percent decolorization measurements during the photocatalytic process. In this measurements, only change in concentration of the target dye molecule can be followed by using its characteristic wavelength.

By performing this measurements, it may be possible to follow the dye intermediates absorb at different wavelengths. But, it is not possible to determine the intermediates and products when they dont have certain color in the range of UV-Vis spectrometer. Also by using this technique it is not possible to follow the removal of the organic carbon content completely with degradation or mineralization and total conversion.

For this reason finding intermediates, degradation products, possible bond cleavages and final products of the dyes during photochemical reaction is so important.

To find the intermediates, remaining portion of trace dye molecules and degradation products quantitatively, generally gas chromatography (GC)^{43,44} and high performance liquid chromatography (HPLC)^{45,46} equipped with different types of detectors like UV, FID and MS⁴⁷. Besides thin layer chromatography (TLC)⁴⁸ can be used in qualitative determination.

1.5 Different Photocatalytic Materials

Because of low energy consumption and less environmental problems, heterogeneous type photocatalytic processes are known as more efficient techniques in photocatalytic reactions in energy and environment issues. Removal of organic contamination can be introduced by photocatalytic mechanism which posses with sufficient yield in elimination of pollutants. The mentioned method because of its progressing in ambient conditions such as atmospheric pressure and room temperature can be selected as proper candidate in organic pollutants elimination⁴⁹.

As mentioned before TiO₂ known as the most effective photocatalyst for the degradation of microorganisms founded in waste water and organic compounds under UV light illumination. Studies are performed to use TiO₂ in the visible region by making modifications of TiO₂ through anion doping and heterostructuring. However, beside TiO₂ researchs are performed to find the materials which show activity in the UV and visible region³³. These type of studies can be considered necessary to find better photocatalysts than TiO₂ in terms of photoactivity and price.

Conjugated polymers⁵⁰, mesoporous materials⁵¹, polyoxometalates (POM)⁵², metal organic framework (MOF)⁵³ compounds, mixed metal oxides (perovskites)⁵⁴, bismuth molybdates, Bi(oxy)halides⁵⁵ can be considered as the examples of new type of photocatalytic materials.

Among them, organic based photocatalysts like conjugated polymers are gained great attention due to their strong light absorption capability, cheap sources and production methods⁵⁶.

1.6 Polymer Type Photocatalytic Materials

Polymeric materials with unsaturated bonds (π), conjugated polymers, can be considered as a new classification of photocatalysts which located in heterogeneous category of photocatalytic materials working under UV and solar light exposures. Generally the photocatalytic processes are introduced with three main factors such as, non-toxicity, efficiency and sensitivity to visible light. These properties are so important for the large scale application. Due to π -bonds of the conjugated materials, they can absorb photons coming from UV and visible light exposures. Due to these properties, conjugated polymers are used commonly in organic electronics and organic photonics^{57,58,59,60}.

The chemical versatility, accessibility and easy modification properties of conjugated polymers make them an interesting candidate in photocatalytic applications. Improvements in the structure can be help to increase the activity of these materials in photocatalytic applications. Some recent study proved that the conjugated polymers can show high catalytic activity in reactions driven by photocatalytic materials^{61,62}.

Conjugated polymers have some advantages when compared with their inorganic counterparts such as cost effective steps of fabrication (cheap processing costs in mass production), easy accessibility, sustainability and possible engineering (functionalization/modification) on structure of the material.

The mentioned properties of polymeric materials make them proper candidates as solar energy convertors in photocatalytic materials^{61,62}. The band gaps of the conjugated polymers with linear structure is lay between 2 to 5 eV depend on the different degrees of conjugation which make them applicable in visible light photocatalytic agents⁶³.

1.7 Aim of the Study

The aim of this work was to investigate the intermediates and degradation products of the methylene blue (MB), a common organic dye, used in textile industry after photocatalytic treatment in the presence of palladium nanoparticles added PEDOT (PdNPs/PEDOT) catalyst under UV light exposure by using UV-Vis spectroscopy and liquid chromatography-mass spectrometry (LC-MS). Besides, photocatalytic degradation of MB with TiO₂ nanoparticles, known as the most common photocatalyst, was also investigated in order to compare the results. Characterization of the catalysts were performed by using SEM, TEM, HR-TEM, EDX, and ICP-OES.

CHAPTER 2

MATERIALS AND METHODS

2.1. Chemicals and Materials

Palladium nitrate ($\text{Pd}(\text{NO}_3)_2 \times \text{H}_2\text{O}$), 3,4 ethelenedioxythiophene (EDOT), iron chloride anhydrous (FeCl_3), sodium borohydride (NaBH_4), chloroform (CHCl_3), methylene blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S} \times 3\text{H}_2\text{O}$, abbreviated as MB) were obtained from Sigma-Aldrich. Titanium dioxide powder, P25, (TiO_2 nanopowder) was supplied by Degussa Co. All reagents were analytical grade (AR) and used through the study without further purification. Deionized water used in experiments was obtained from Milli-Q Water Purification System. All glassware's and magnetic stir bars were cleaned by using water and ethanol before starting to experiments.

2.2. Instrumentation

The initial amount of added palladium ions onto the PEDOT support was investigated by using Perkin Elmer DRC II model inductively coupled plasma mass spectroscopy (ICP-OES).

Scanning electron microscope (SEM) images of the samples were taken by using QUANTA 400F Field Emission Scanning Electron Microscope (FE-SEM). In the SEM sample preparation, solid samples were put onto the carbon tape-coated grids.

In order to find the size of the nanoparticles, JEOL JEM-2010F (FEG, 80-200 kV) high resolution transmission electron microscope (HR-TEM) was used.

Elemental composition of prepared samples was followed by using energy-dispersive X-ray analyzer (EDX) coupled with SEM and TEM.

Dye removal capacity of the prepared catalyst and degradation process were performed by using Labor-UV-reactor-System 2 (UV-RS-2) and ATLAS solar simulator. Removal of methylene blue was observed by using Specord S 600 UV-Vis spectrometer. Degradation products of the MB were also identified by using LC-MS.

2.3. Preparation of Poly (3, 4 ethelenedioxythiophene)

Poly (3, 4 ethelenedioxythiophene) (PEDOT) was prepared by using chemical polymerization of 3, 4 ethelenedioxythiophene (EDOT). The whole procedure is given in Figure 2.1. According to this procedure, 2.60 g anhydrous Iron (III) chloride (FeCl_3) and 10 ml of chloroform (CHCl_3) were mixed in a beaker and stirred 5 min by using magnetic stirrer. In separate beaker 0.568 g EDOT monomer and 10 ml of CHCl_3 were mixed and stirred for 5 min. Then, the mixture which contains FeCl_3 was added drop by drop into the solution contains EDOT monomer. Then the resulting suspension was mixed for 3 hours at room temperature to obtain complete polymerization.

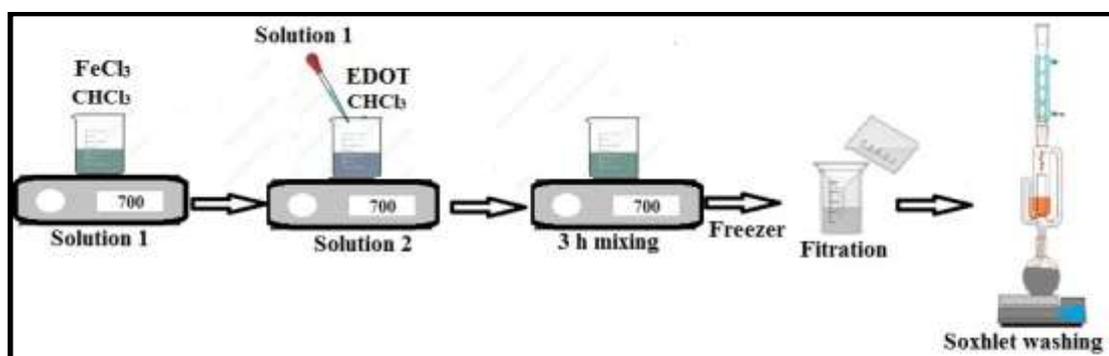


Figure 2.1 Preparation of PEDOT with chemical polymerization of EDOT.

After 3 h period 60 mL of methanol was added to the resulting mixture to obtain solid particles. Then the final mixture put into freezer and was kept for 24 h. After that formed PEDOT particles were filtrated and particles collected onto the filter paper were put into Soxhlet apparatus and the precipitate was washed first with methanol and then dichloromethane for 3 days to remove the monomers and salts deposited onto the structure. Finally PEDOT sample was dried at room temperature.

2.4. Preparation of Palladium Nanoparticles Added PEDOT

In order to add palladium nanoparticles onto PEDOT (PdNPs/PEDOT), initially palladium ions were immobilized onto PEDOT by using wet chemical process known as liquid impregnation. For this, 100 mg PEDOT support material were dispersed into 10 mL water by mixing on magnetic stirrer. After that 5 mg Palladium nitrate were added into the mixture and mixed for 5 h. At the end of this period, palladium ions added PEDOT was isolated from the mixture by using centrifuge. Then the particles were washed several times with water to remove the non-attached palladium ions. The liquid portion of the initial mixture and the washing steps were collected and used for ICP-OES analyses to find the percent loading of palladium ions onto the PEDOT.

Finally palladium ions (Pd^{2+}) were converted to nanoparticles by using NaBH_4 . For this, 50 mg palladium ions added PEDOT was dispersed in 15 mL of water. Then, 50 mg NaBH_4 were added to the solution and mixed until completion of the hydrogen evolution. After that particles were collected by centrifugation and washed several times with water. The obtained particles were dried in oven at 70 °C and used in photocatalytic experiments. The whole procedure is given in Figure 2.2.

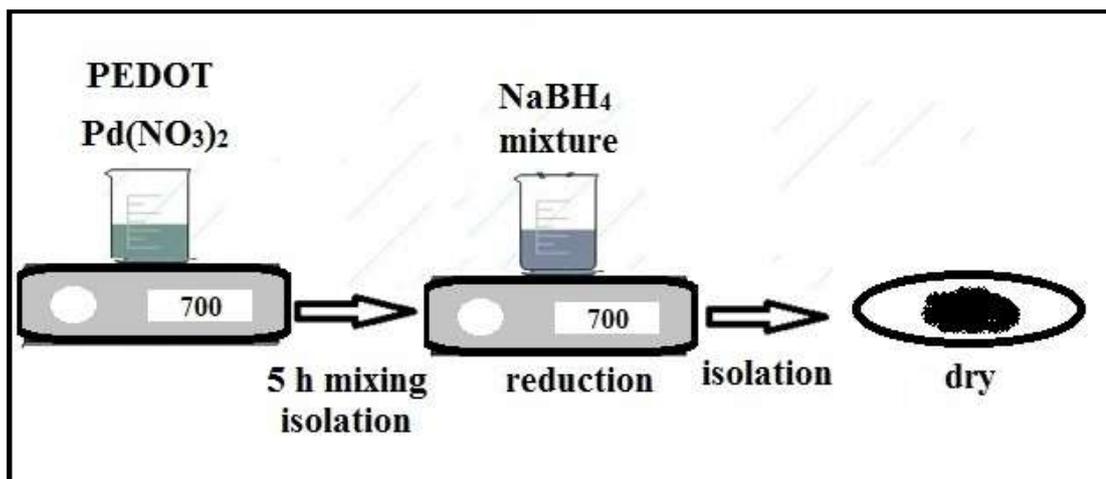


Figure 2.2 Preparation of PdNPs/PEDOT nanocomposite material

2.5. Degradation of Methylene Blue under UV Light Exposure

Photocatalytic degradation of methylene blue in the presence of photocatalysts under UV light illumination was followed by UV-vis spectrometer. For this Labor-UV-reactor-System 2 (UV-RS-2) was used which is coupled with water circulator in order to maintain a constant temperature in the photocatalytic reaction. The reactor and UV source used for photocatalytic degradation and decolorization of MB are given in Figure 2.3.



Figure 2.3 UV light exposure system used in this study

For monitoring the photocatalytic degradation and decolorisation of methylene blue in the presence of catalyst, 10 mg of catalyst (TiO_2 , PEDOT and PdNPs/ PEDOT, separately) was added to the 1.0×10^{-5} M methylene blue solution. Then the mixture was illuminated with a UV light at constant magnetic stirring. Decolorization of MB was followed by taking 2 mL of solution from the reactor at every 10 min and measuring it by using UV-Vis spectrophotometer given in Figure 2.4.

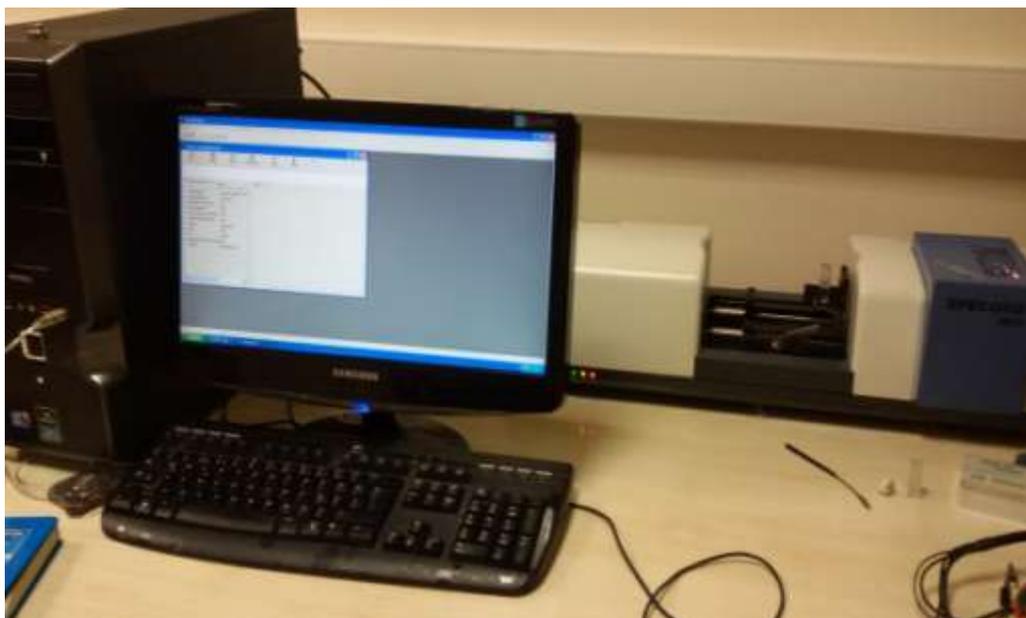


Figure 2.4 UV-Vis spectrometer.

Percent removal of the MB was calculated by following the absorbance maximum at 660 nm and by using Eq. 1 given below.

$$D = (A_0 - A_t) / A_0 \times 100 \% \quad (1)$$

(A_0 =initial absorbance of MB, t = reaction time, A_t =absorbance at time t)

Degradation products of the photocatalytic MB removal reaction were founded by using LC-MS system.

CHAPTER 3

RESULTS AND DISCUSSION

Developed and the developing nations in the world faced with a serious environmental risks due to industries they have. The ecosystem is destroyed by the increase in the amount of air, water and solid waste (plastics) pollution day by day. These pollutions include organic based toxic materials and compounds like dyes, chlorinated and nonchlorinated aromatic and aliphatic compounds, disinfection byproducts, volatile organic compounds, plastics. For this reason, heavy environmental regulations are stated for the use and safe disposal of these types of materials besides removal of their wastes. The most important part of this regulations is related to waste management. Hence, finding proper way to decompose of the wastes and characterize them is so important issue to meet the regulations.

Among the methods used for the removal of wastes from the water, photocatalytic process known as the most effective one. In this process the rate of the chemical reactions (oxidation/reduction) is accelerated with the usage of catalyst under ultraviolet (UV) or visible radiation. Nowadays, great effort has been spent in order to find the proper catalyst and design of effective processes for the decomposition of wastes and the energy generation. Besides, the detailed pathways and degradation mechanism of that kind of materials have not been clear yet.

Therefore, additional studies on the degradation mechanism of the wastes under UV or visible light irradiation is so important to understand the degradation mechanism of toxic molecules and clear out the possible side effects of the degradation products on the environment.

3.1. Preparation and Characterization of Photocatalysts

Due to these unique characteristics like high conductivity, thermal and chemical stability, high transparency and moderate cost Poly(3,4-ethylenedioxythiophene) (PEDOT) is considered as one of the important polymer in the class of conjugated polymers and finds wide range of application areas like in fuel cells, thermoelectric devices, dye-sensitized solar cells, supercapacitors, and organic solar cells.

PEDOT was prepared with 3,4 ethelenedioxythiophene (EDOT) monomer and anhydrous iron chloride by using modified chemical polymerization method explained in details in experimental part. The morphological property of the PEDOT polymer was initially investigated with SEM. The obtained image is given in Figure 3.1.

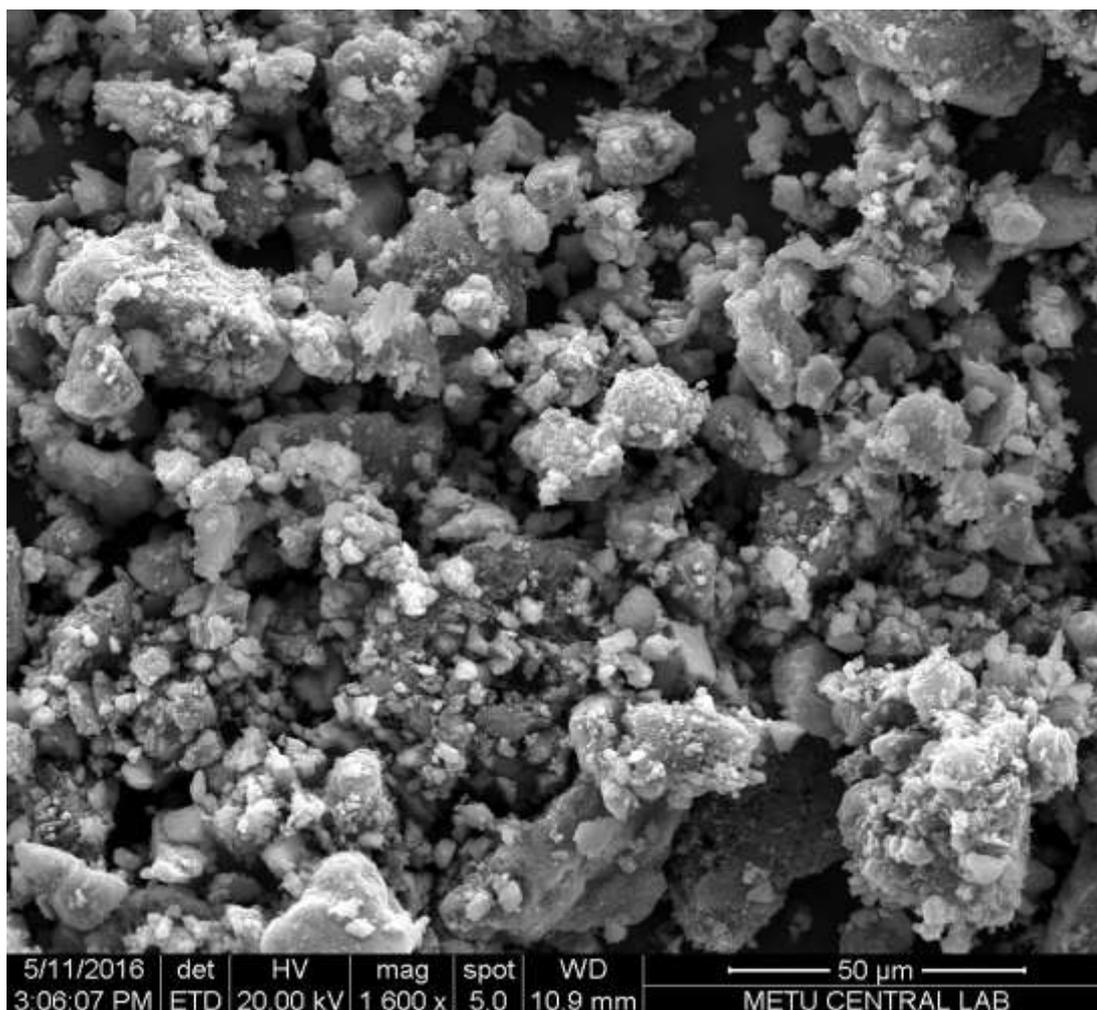


Figure 3.1 SEM image of PEDOT.

From the obtained image, it can be concluded that the size of the resulting PEDOT particles lying between a few hundred nanometers to micrometers with high surface area.

After synthesizing the PEDOT particles, addition of Pd^{2+} ions onto the PEDOT was done by using wet impregnation technique. Detailed procedure is given in experimental part. After the addition of Pd^{2+} ions onto the PEDOT, reduction of palladium ions was performed to obtain palladium nanoparticles (PdNPs) onto PEDOT (PdNPs/PEDOT). After that the addition of PdNPs was revealed by using HR-TEM and EDX coupled to SEM. The results are given in Figure 3.2 and Figure 3.3, respectively.

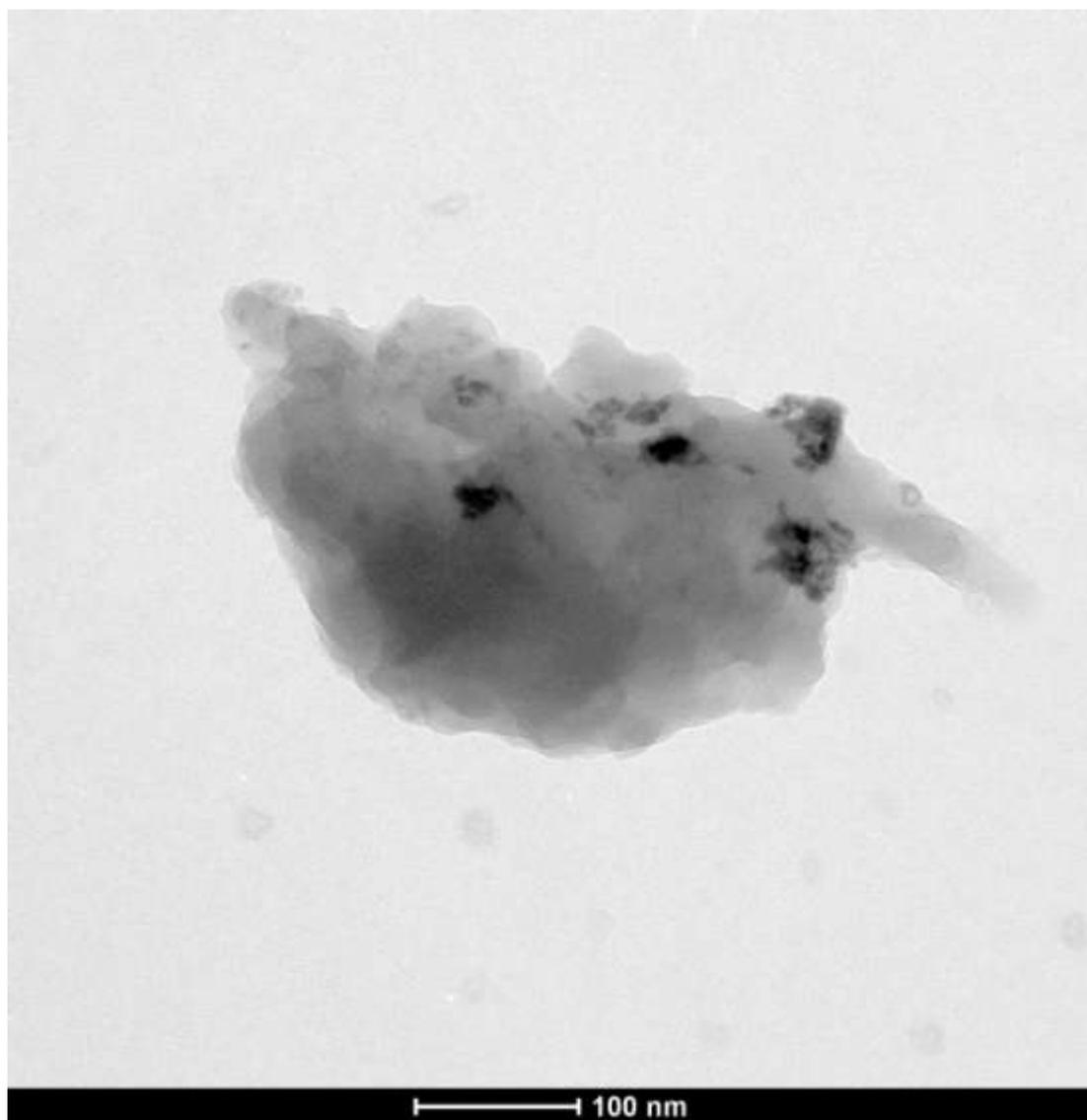


Figure 3.2 HR-TEM image of PdNPs/PEDOT.

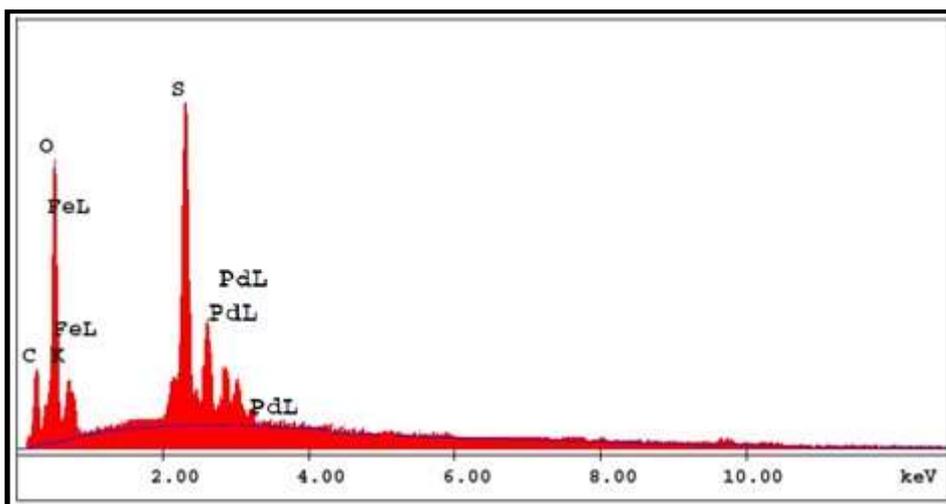


Figure 3.3 EDX pattern of PdNPs/PEDOT.

Addition of palladium nanoparticles can be seen from the Figure 3.2. The size of the palladium nanoparticles was lying between 10-20 nm. The presence of palladium was also proved by taking the EDX pattern. From the EDX pattern given in Figure 3.3, one can state that all framework elements were founded in the final structure of PdNPs/PEDOT nanocomposite material. Besides, percent amount of palladium loaded on PEDOT was investigated with ICP-OES and the percent loading of palladium was founded as 1.03% (w/w).

Finally the morphological characterization of the TiO₂ nanoparticles was performed with TEM. Obtained image is given in Figure 3.4.

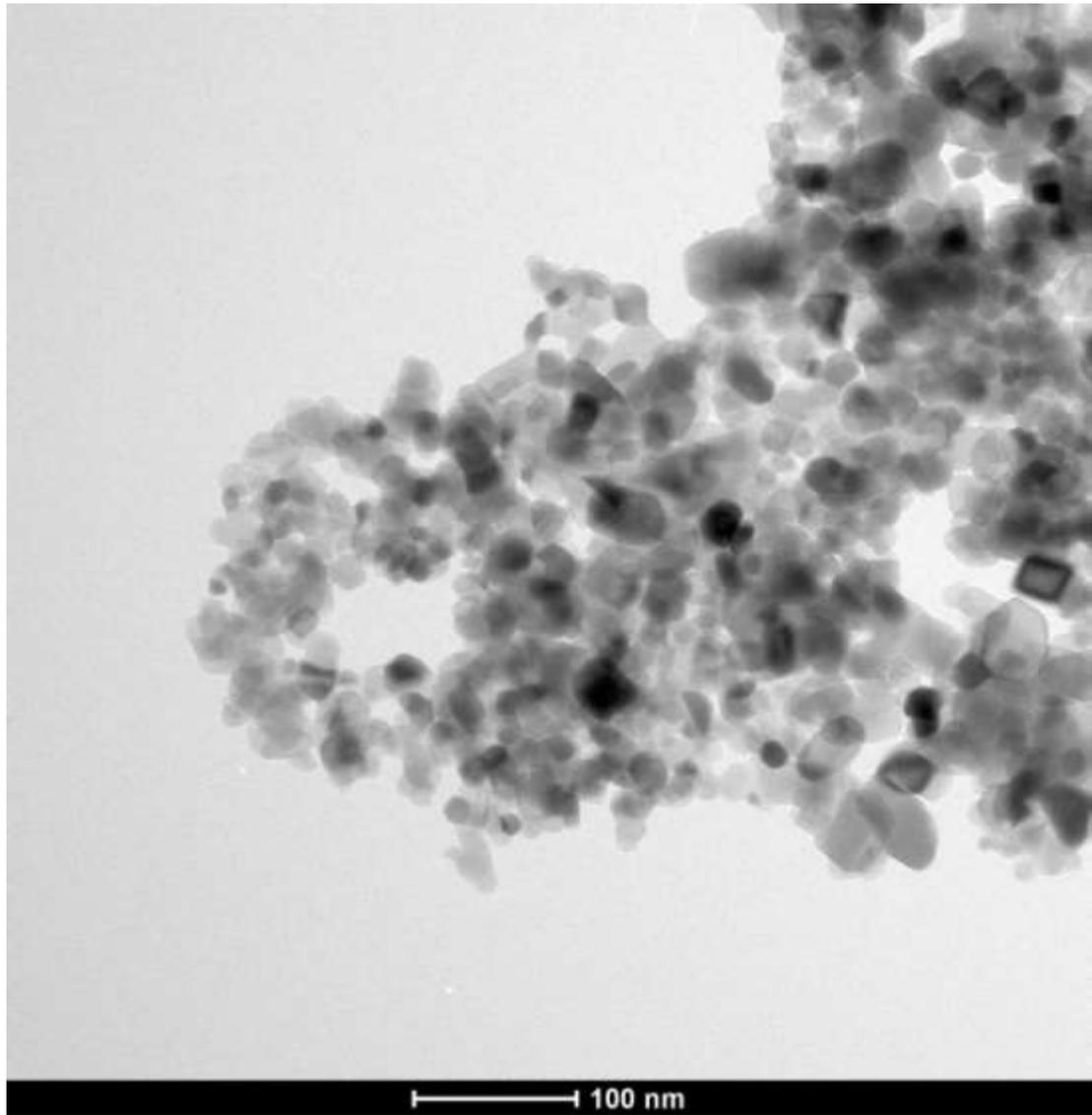


Figure 3.4 TEM image of TiO₂ nanoparticles

The size of the TiO₂ nanoparticles calculated as 25 ± 10 nm from the image given in Figure 3.4.

3.2. Photocatalytic Degradation of Methylene Blue

Photocatalytic degradation of methylene blue, well known organic azo-dye, was performed by using TiO₂ nanoparticles, and PdNPs/PEDOT catalyst under UV light illumination.

Methylene blue was used as a simulant of pollutant in the textile industry, and known as toxic material with a complex structure. Therefore finding decomposition products and pathway is so important. To obtain proper information about the degradation process driven photocatalytically, initially experiments were performed in the absence of catalyst and no degradation was observed. After that decolorization and degradation performance of the catalysts were investigated.

For the reaction initially 0.01 g catalyst was mixed with 10 mL methylene blue solution into the reactor. Then the mixture was stirred at a constant speed under UV light exposure. After that reaction was stopped at certain time period and each time 2 mL sample solution was separated from the mixture by using centrifuge and decolorisation and removal of methylene blue was measured by using UV-Vis spectrophotometer. To find the percent removal, absorbance value at 660 nm was followed. After that by using this absorbance, degradation of methylene blue was calculated with the Eq. 1. This process was repeated until the complete decolorization obtained.

TiO₂ nanoparticles are considered as the reference catalyst which reacts as the total oxidation catalyst in photocatalytically driven reactions. Thus, it is possible to get total decomposition of dye molecules under UV illumination. For this reason photocatalytic experiments were started with the usage of TiO₂ nanoparticles. For this purpose, 10 mg TiO₂ nanoparticles added to 10 mL 1.0×10⁻⁵ M methylene blue and decolorization was obtained under UV light exposure. The result is given in Figure 3.5.

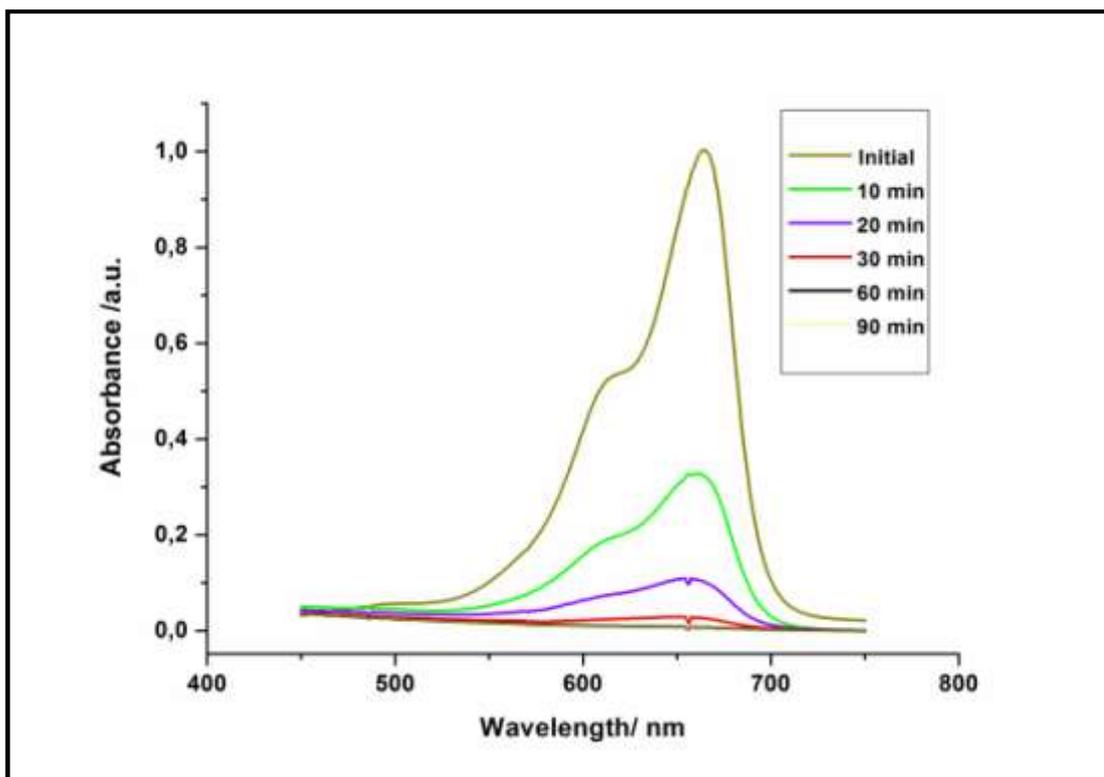


Figure 3.5 UV-Vis spectra related to decomposition of 1.0×10^{-5} M methylene blue by using 10 mg of TiO_2 nanoparticles under UV light exposure

From the Figure 3.5, total removal of methylene blue was calculated and the percent removal results of methylene blue are given in Table 3.1.

Table 3.1 Percent decolorization results of methylene blue at different time with the usage of TiO_2 nanoparticle under UV light exposure.

Time (min)	% decolorization
0	0
10	67.5
20	84.0
30	91.5
60	99.5
90	99.5

From the Figure 3.5, and Table 3.1, it can be concluded that the total decolorization of methylene blue with the usage of TiO₂ nanoparticle as photocatalyst was obtained at 60 min under UV light exposure.

After that decolorization efficiency of the PdNPs/PEDOT was checked by using methylene blue under UV light illumination under same conditions. The obtained spectrum is given in Figure 3.6.

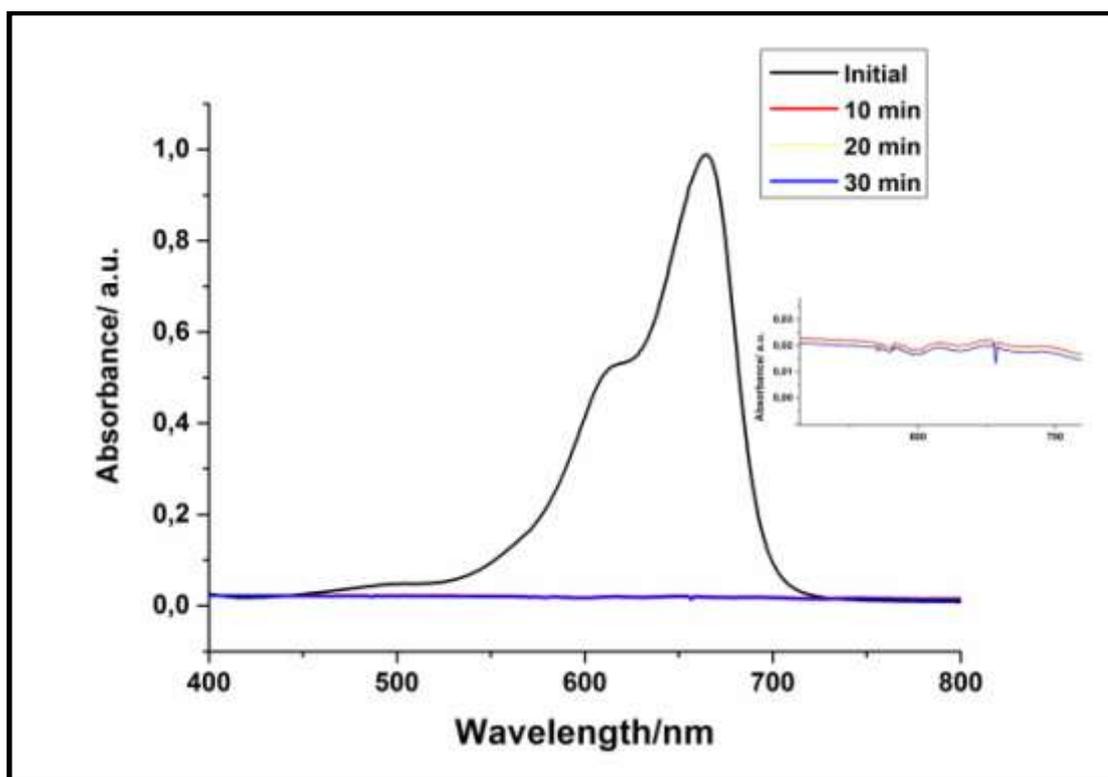


Figure 3.6 UV-Vis spectra related to decomposition of 1.0×10^{-5} M methylene blue by using 10 mg of PdNPs/PEDOT nanocomposite material under UV light exposure

Total decolorization of methylene blue was calculated from the Figure 3.6 and the percent removal results of methylene blue by using PdNPs/PEDOT nanocomposite material under UV light exposure are given in Table 3.2.

Table 3.2 Percent decolorization results of methylene blue at different time with the usage of PdNPs/PEDOT nanocomposite material under UV light exposure.

Time (min)	% decolorization
0	0
10	99.0
20	99.5
30	99.5
60	99.5

From the given results above, total decolorization of methylene blue by using PdNPs/PEDOT nanocomposite material under UV light exposure was almost obtained in 10 minutes. As can be seen from the results, PdNPs/PEDOT nanocomposite material can be considered as more effective photocatalytic material than TiO₂ nanoparticle in the decolorization of methylene blue under UV light illumination.

3.3.Finding the Degradation Products of Methylene Blue

In the previous part, decolorization efficiency of the PdNPs/PEDOT in the removal of methylene blue under UV light was investigated by comparing the data obtained with TiO₂ nanoparticle which is known as one of the most efficient semiconductor based photocatalyst under UV light. The decomposition pathway of methylene blue with the usage of TiO₂ nanoparticle was studied in literature^{64,65}. According to that information, positive hole in the valence band and electron in the conduction band of TiO₂ nanoparticle are generated with UV light irradiation. After that, generated positive hole can oxidize hydroxide ions (or water molecule) adsorbed on the surface of TiO₂ particles to produce hydroxyl radical. The superoxide radical anions, which react with a proton to form hydroperoxyl radical, can be produced with the reaction of oxygen and conduction band electrons⁶⁴. So the data obtained from the usage of TiO₂ nanoparticle as photocatalyst for the decomposition of methylene blue was used as reference to find the intermediates and final products of decomposition of methylene blue with the usage of PdNPs/PEDOT as photocatalyst under UV light.

For this purpose initially, methylene blue was investigated prior to ultraviolet exposure by LC-MS Spectroscopy and the data was used to prove the decomposition of methylene blue with the photocatalytic reaction by using TiO₂ nanoparticles and PdNPs/PEDOT as photocatalyst. The corresponding MS data of the methylene blue before the reaction is given in Figure 3.7.

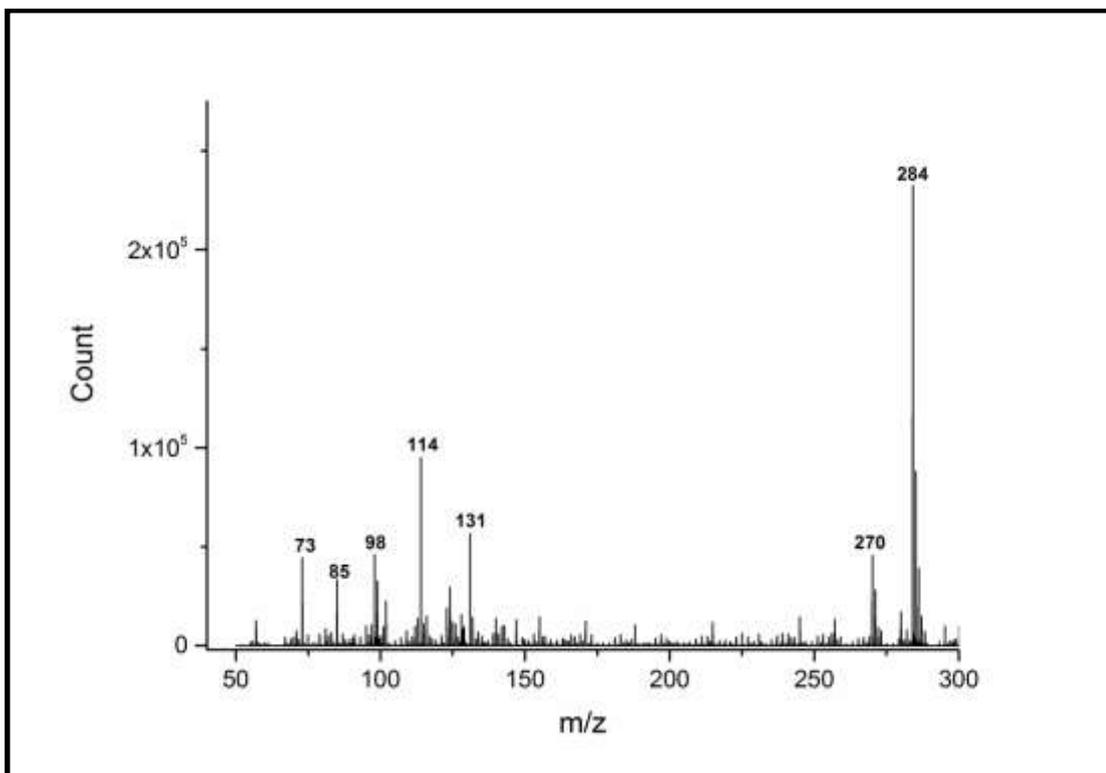


Figure 3.7 MS data of methylene blue before the photocatalytic reaction

As can be seen from the Figure 3.7 the most intense line is located at $m/z=284$ is related to parent ion of methylene blue $[MB + H]^+$. The other intense line observed at $m/z= 270$ is related to Azure B known as well-known homologues of MB⁶⁵. New lines at $m/z= 131, 114, 98, 85$ and 73 are related to fragmentation of MB and/or organic contamination.

Structures related to parent ion and fragmentation of the parent ion known as Azure B is given in Figure 3.8.

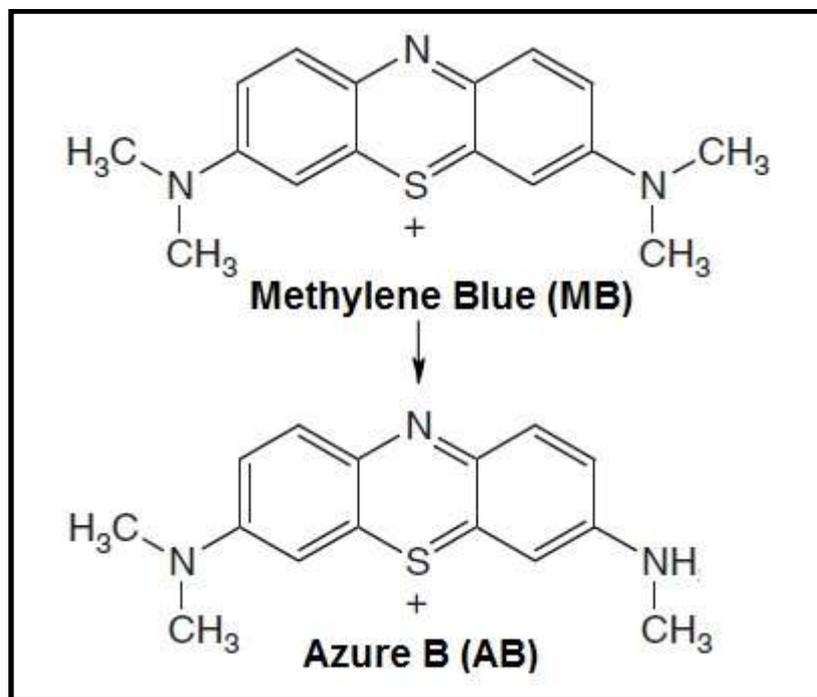


Figure 3.8 Structures related to lines located at $m/z = 284$ and 270 , respectively

After getting the MS data of methylene blue before the photochemical reaction, the sample obtained after total decolorization of methylene blue in the presence of TiO₂ nanoparticles as catalyst under UV light irradiation for 90 min. was analyzed by using LC-MS. The obtained data is given in Figure 3.9.

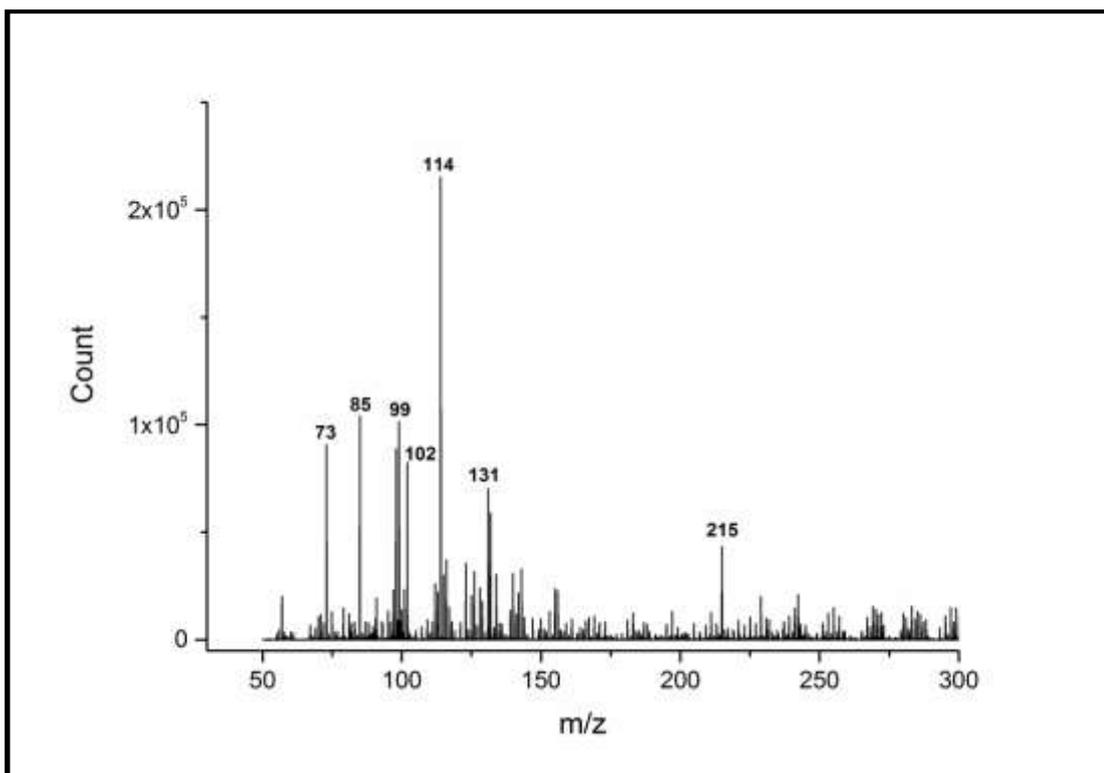


Figure 3.9 MS data of the photocatalytic degradation products of methylene blue in the presence of TiO₂ nanoparticles as catalyst under UV light irradiation

Upon ultraviolet (UV) irradiation, signals related to main molecule were diminished and intermediate reaction products were detected. As can be seen from the Figure 3.9, the line located at $m/z=284$ which is related to parent ion of methylene blue and $m/z=270$, its main fragmentation Azure B, were disappeared. This is the indication of photocatalytic degradation of methylene blue into smaller molecules with TiO₂ nanoparticles. The comparison of the MS data related to before and after photocatalytic treatment of methylene blue is given in Figure 3.10.

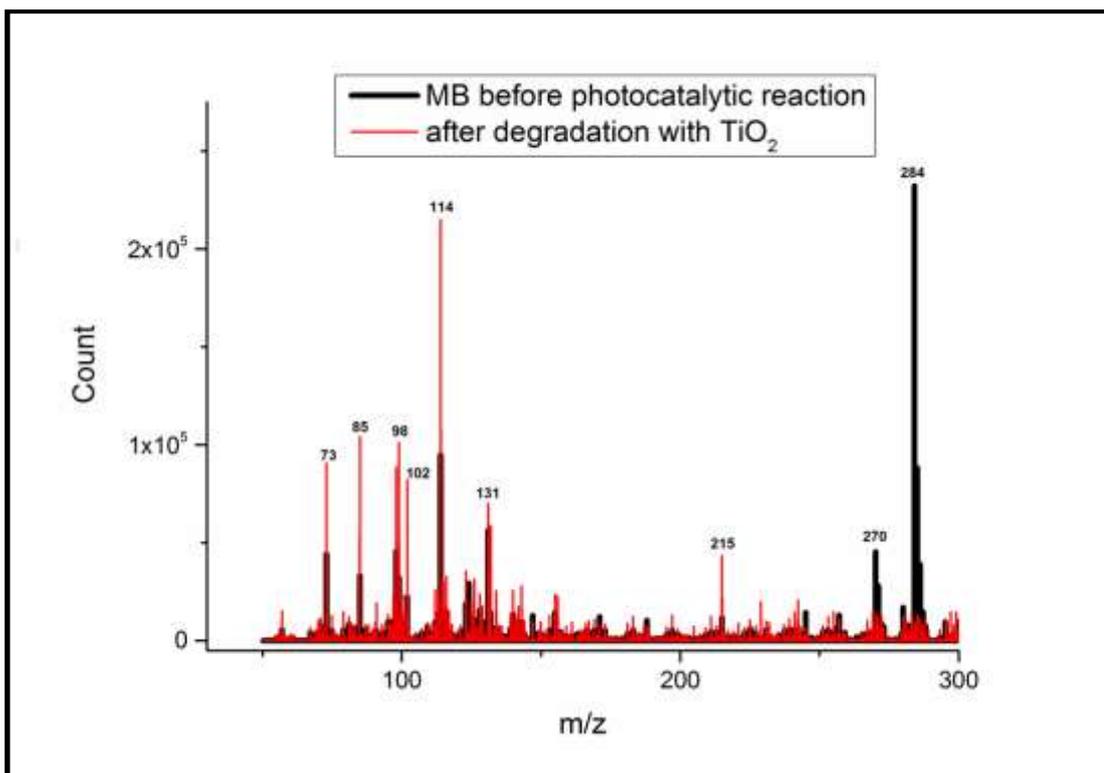


Figure 3.10 Comparison of the MS data of the methylene blue and photocatalytic degradation products of methylene blue in the presence of TiO_2 nanoparticles as catalyst under UV light irradiation

It can be said that from the Figure 3.10, after decomposition reaction, new line located at $m/z=215$ was formed. In particular, the lines located at $m/z=131, 114, 102, 99, 85$ and 73 are observed in both spectra. The increase in intensity of these lines obtained with the usage of TiO_2 nanoparticles as catalyst is the indication of degradation besides fragmentation. Many other hydroxylated intermediates have certainly been formed in a small amount but it was difficult to separate and detect them. The possible structure for the line located at $m/z=215$ were given in Figure 3.11.

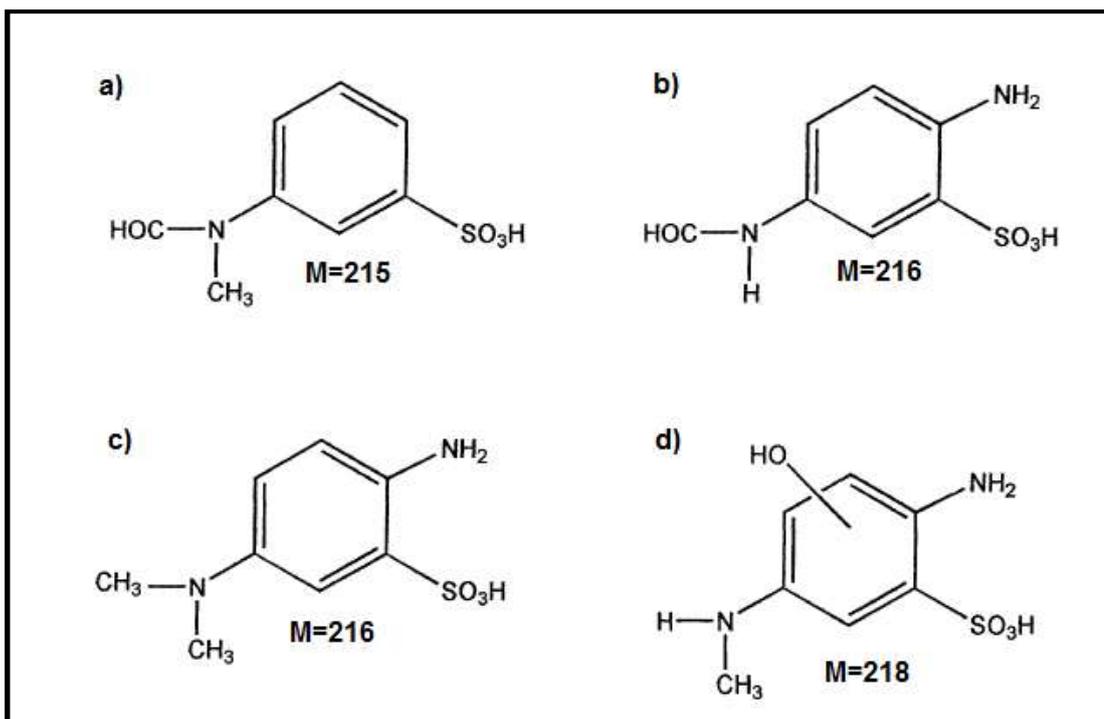


Figure 3.11 Possible structures related to line located around $m/z = 215$.

Finally the degradation product of the photocatalytic reaction assisted with PdNPs/PEDOT was revealed by using LC-MS and the result is given in Figure 3.12.

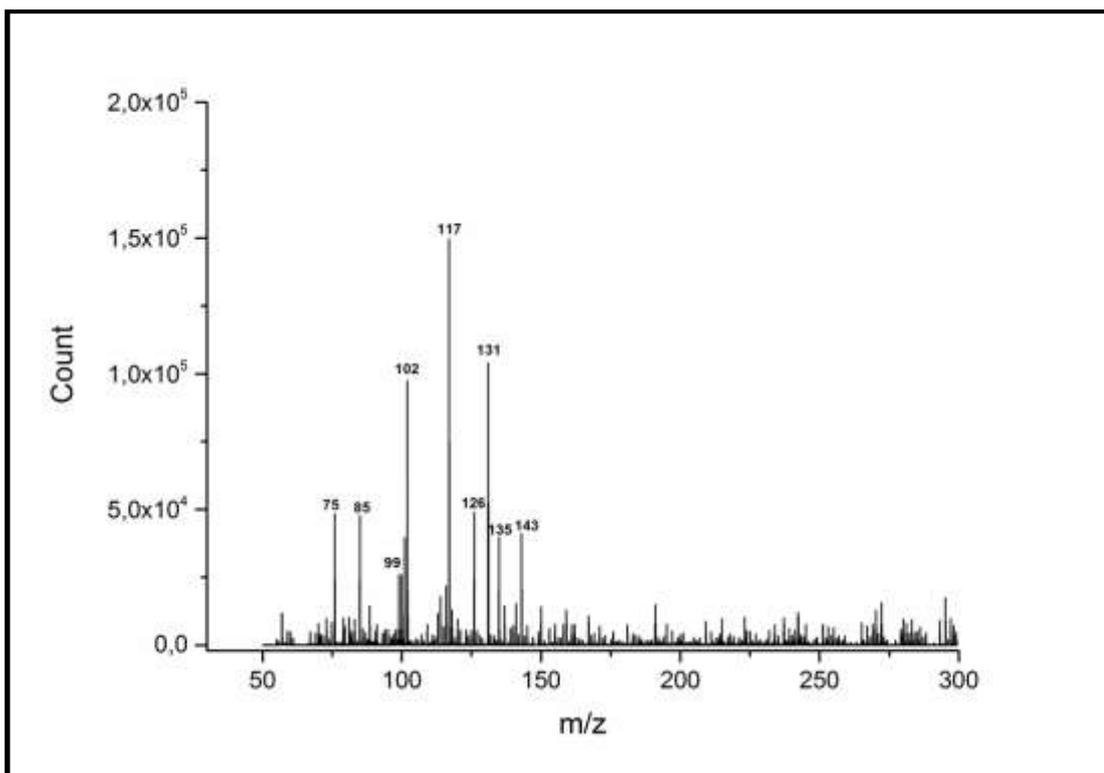


Figure 3.12 MS data of the photocatalytic degradation products of methylene blue in the presence of PdNPs/PEDOT as catalyst under UV light irradiation for 10 min.

The comparison of the MS data of degradation product of methylene blue obtained with the usage of PdNPs/PEDOT as catalyst under UV light irradiation with the data of methylene blue before degradation is given in Figure 3.13.

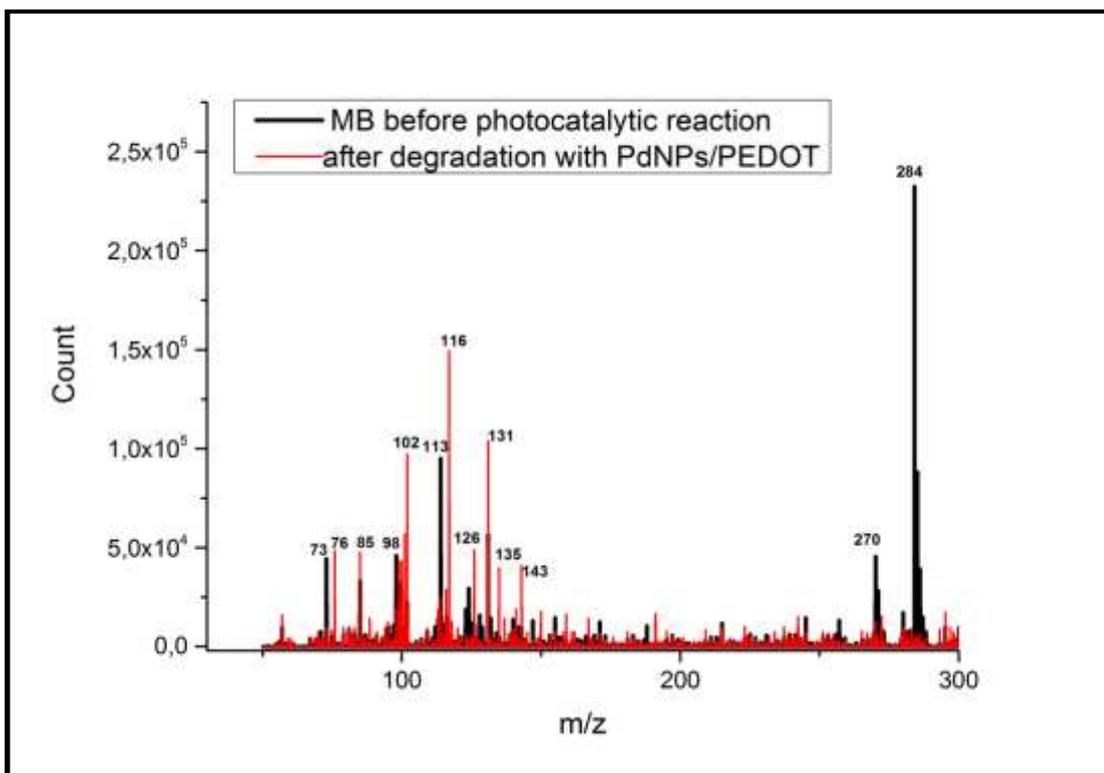


Figure 3.13 Comparison of the MS data of the methylene blue before photocatalytic reaction with photocatalytic degradation products of methylene blue in the presence of PdNPs/PEDOT as catalyst under UV light irradiation

According to Figure 3.13, main lines at $m/z=284$ and 270 related to parent ion of methylene blue and its fragment were disappeared after treatment with PdNPs/PEDOT under UV light irradiation and new lines related to degradation products of methylene blue in small quantities were formed at $m/z=143$ and 135 . Besides, the intensity of lines located at $m/z=131$, 102 , and 85 related to other fragments of methylene blue were increased. Also some locations of the lines were changed from $m/z=123$, 113 , 98 and 73 to $m/z=126$, 116 , and 76 , respectively. These changes can be considered as the proof of photocatalytic degradation of methylene blue with the usage of PdNPs/PEDOT as catalyst. As can be seen from the MS data, there is a decrease in the total amount of methylene blue which can be attributed the decomposition of it into CO_2 and other inorganic ions like nitrate and sulfate besides degradation products and fragments.

The LC-MS results of photocatalytic degradation of methylene blue with PdNPs/PEDOT catalyst was also compared with the one obtained with TiO₂ nanoparticles and result is given in Figure 3.12.

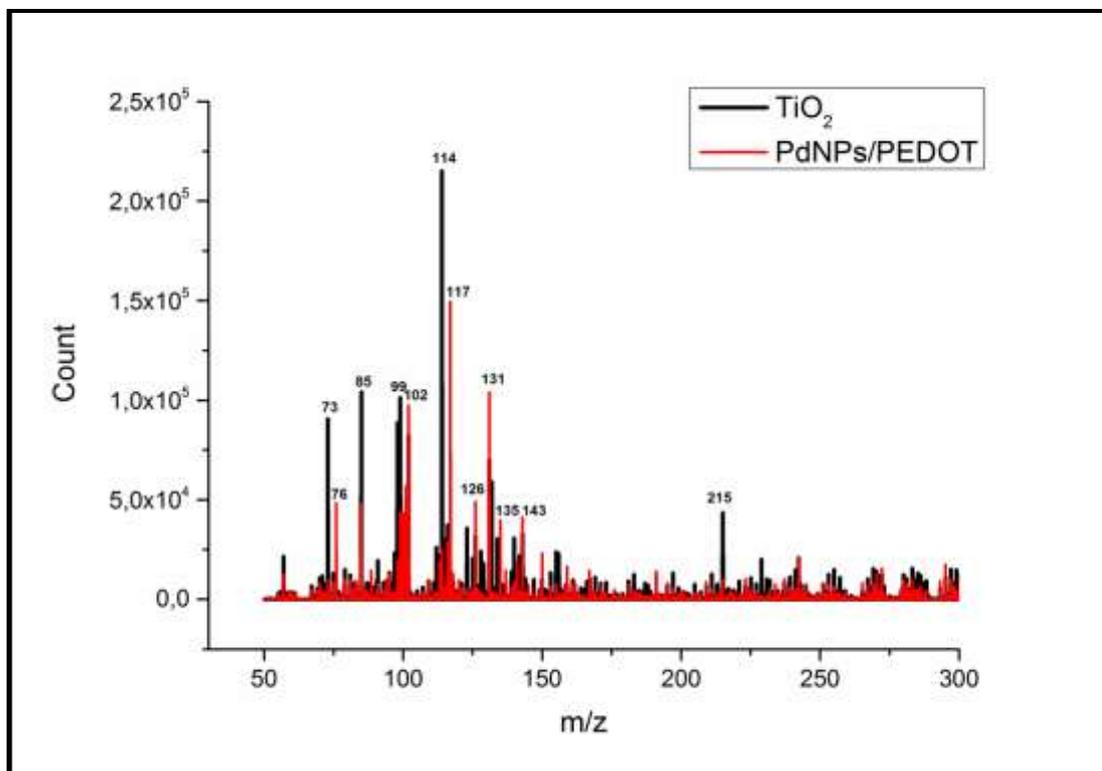


Figure 3.14 Comparison of the MS data of the photocatalytic degradation products of methylene blue in the presence of TiO₂ nanoparticles with PdNPs/PEDOT as catalyst under UV light irradiation.

As can be seen from the figure given above, except the lines located at $m/z=215$, usage of TiO₂ nanoparticles and PdNPs/PEDOT as catalyst in the photochemical degradation of methylene blue under UV light produces same products and fragments. So it can be concluded that PdNPs/PEDOT use similar degradation pathway with the heterogeneous photocatalysts like TiO₂ nanoparticles³.

When the MS data is compared, the total amount of degradation products obtained with the usage of PdNPs/PEDOT under 10 min. UV light illumination was less than the products obtained with the TiO₂ nanoparticles under 60 min. UV light illumination.

So it can be concluded that PdNPs/PEDOT is more active than TiO_2 nanoparticles in photocatalytic degradation of methylene blue under UV light exposure.

The MS results also consistent with the results obtained in decolorization studies. After long UV light irradiation species founded after decolorization were not observed and the methylene blue was considered as completely mineralized. The degradation under long time UV light exposure leads to production of CO_2 with the conversion of organic carbon. Besides nitrogen and sulfur heteroatoms founded in structure were converted into inorganic ions, such as nitrate and ammonium, and sulfate ions, respectively.

In order to find the intermediates formed during the photocatalytical degradation of MB with PdNPs/PEDOT catalyst, sample is illuminated only 5 minutes. The comparison of the data is given in Figure 3.15.

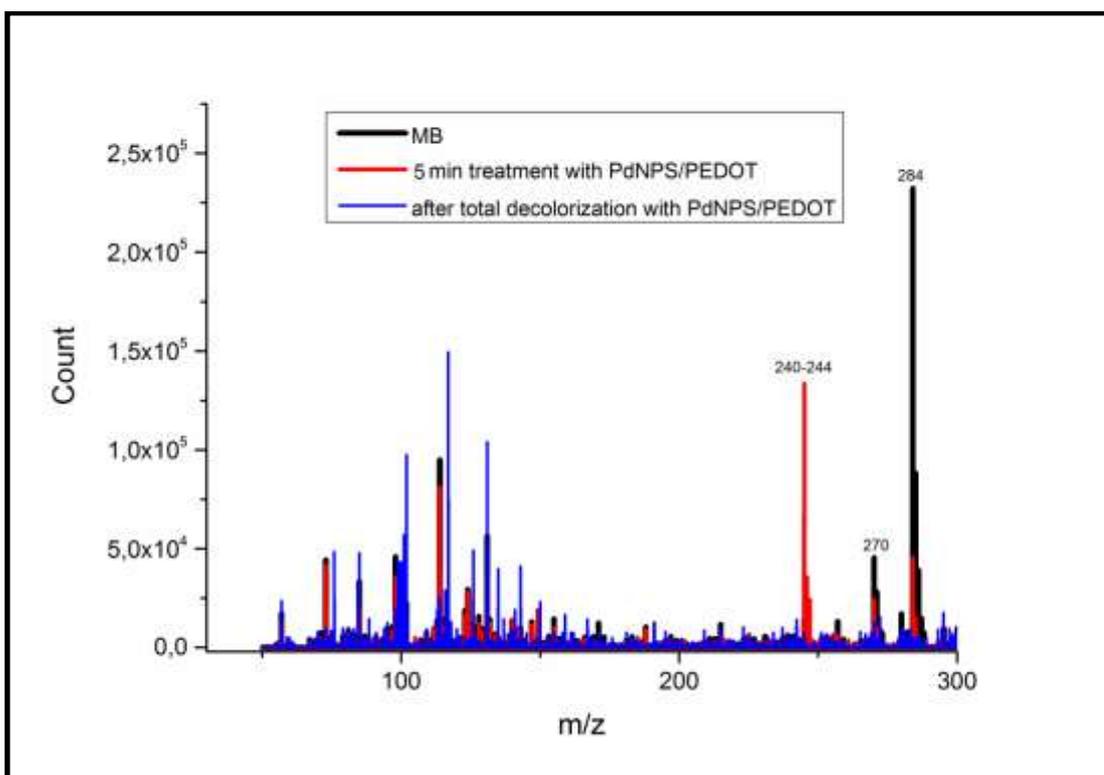


Figure 3.15 Comparison of the MS data of the methylene blue, photocatalytic degradation products of methylene blue in the presence of PdNPs/PEDOT as catalyst under UV light irradiation for 5 and 10 min, respectively.

After 5 min. illumination with UV light, the intensity of lines located at $m/z = 284$ and 270 decreases and the line related to intermediate which is located around $m/z = 240$ was appeared with a fragments similar to methylene blue.

According to the information given above, the suggested degradation pathway for the photocatalytic removal of methylene blue^{64,65} with PdNPs/PEDOT catalyst under UV light is given in Figure 3.16.

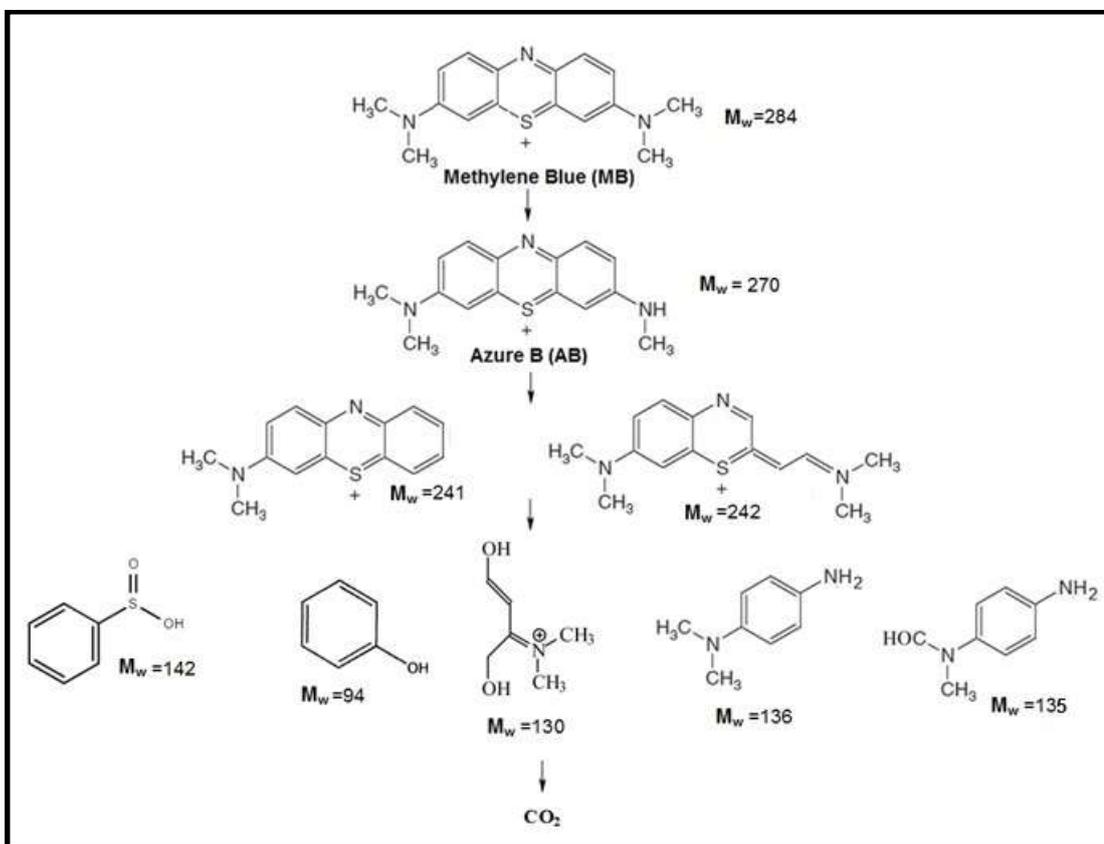


Figure 3.16 Suggested photocatalytic degradation pathway of methylene blue with PdNPs/PEDOT catalyst under UV light

CHAPTER 4

CONCLUSION

In this study, in order to prepare PdNPs/PEDOT photocatalyst, initially PEDOT polymer was prepared with polymerization of EDOT and then Pd nanoparticles were added onto PEDOT by using liquid impregnation method. Then characterization of the catalyst used in this study was performed by using SEM, TEM, EDX and ICP-OES.

After that total decolorization and degradation of methylene blue (MB) has been investigated in aqueous heterogeneous suspensions by using TiO₂ nanoparticles and PdNPs/PEDOT as photocatalyst under UV light exposure with UV-Vis spectrometer and LC-MS. The decrease in absorption intensity of the dye solution was monitored at 668 nm with time upon irradiation in the presence of the catalyst. Degradation products were analyzed by using LC-MS technique. The efficiency of PdNPs/PEDOT was founded higher than TiO₂ nanoparticles in the photocatalytic degradation of MB. Decolorization of methylene blue was obtained at the end of 10 min. by using PdNPs/PEDOT catalyst. Besides degradation products of the reaction was revealed. These results suggest that PdNPs/PEDOT photocatalysis can be used for treatment of dye molecules founded in textile waste waters.

REFERENCES

1. H. Zollinger, *Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments*, second revised ed., VCH, 1991.
2. C. Ràfols, D. Barceló, *J. Chromatogr. A* 777 (1997) 177.
3. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Hermann, *Appl. Catal. B: Environ.* 31 (2001) 145.
4. A. Bianco-Prevot, C. Baiocchi, M.C. Brussino, E. Pramauro, P. Savarino, V. Augugliaro, G. Marci, L. Palmisano, *Environ. Sci. Technol.* 35 (2001) 971.
5. B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, *Chemosphere* 46 (2002) 1173.
6. M. Saquib, M. Muneer, *Dyes Pigm.* 56 (2003) 37.
7. V. Meshko, L. Markovska, M. Mincheva, A.E. Rodrigues, *Wat. Res.* 35 (2001) 3357.
8. C. Galindo, P. Jacques, A. Kalt, *Chemosphere* 45 (2001) 997.
9. P. Cooper, *J. Soc. Dyers. Colour.* 109 (1993) 97.
10. I. Arslan, I.A. Balcioglou, *Dyes Pigm.* 43 (1999) 95.
11. U. Pagga, K. Taeger, *Wat. Res.* 28 (1994) 1051.

12. F. Strickland, S. Perkins, *Text. Chem. Color.* 5 (1995) 11.
13. Y.M. Slokar, A.M. Le Marechal, *Dyes Pigm.* 37 (1998) 335.
14. M.M. Alnuaimi, M.A. Rauf, S.S. Ashraf, *Dyes Pigm.* 72 (2007) 367.
15. J.H. Sun, S.P. Sun, G.L. Wang, L.P. Qiao, *Dyes Pigm.* 74 (2007) 647.
16. M. Muruganandham, M. Swaminathan, *Dyes Pigm.* 68 (2006) 133.
17. F. Sayilkan, M. Asilturk, P. Tatar, N. Kiraz, S. Sener, E. Arpac, H. Sayilkan, *Mater. Res. Bull.* 43 (2008) 127.
18. S. J. Park, J. P. Lee, J. S. Jang, H. Rhu, H. Yu, B. Y. You, C. S. Kim, K. J. Kim, Y. J. Cho, S. Baik and W. Lee, *Nanotechnol.* 24 (2013) 295.
19. Y. Zhi, Y. G. Li, Q. H. Zhang and H. Z. Wang, *Langmuir* 26 (2010) 15546.
20. I. Arslan, T. Akmehmet, T. Tuhkamen, *Environ. Technol.* 20 (1999) 921.
21. S.F. Kang, C.H. Liao, S.T. Po, *Chemosphere* 41 (2000) 1287.
22. W.S. Kuo, P.H. Ho, *Chemosphere* 45 (2001) 77.
23. A.F. Caliman, C. Cojocaru, A. Antoniadis, I. Poulis, *J. Hazard. Mater.* 144 (2007) 265.
24. K. Konstantinou, T.A. Albanis, *Appl. Catal. B: Environ.* 42 (2003) 319.
25. Y. Wang, *Wat. Res.* 34 (2000) 990.
26. M. Styliidi, D.I. Kondarides, X.E. Verykios, *Appl. Catal. B: Environ.* 40 (2003) 271.

27. K. Kabra, R. Chaudhary, R.L. Sawhney, *Ind. Eng. Chem. Res.* 43 (2004) 7683.
28. D.S. Bhatkhande, V.G. Pangarkar, Beenackers, *J. Chem. Technol. Biotechnol.* 77 (2001) 102.
29. W. Yajun, W. Qisheng, Z. Xueying, Fengmei, W., Muhammad, S.R., H. Jun, *Nanoscale* 5 (2013) 8326.
30. O. Carp, C.L. Huisman, A. Reller, *Prog. Solid. State. Chem.* 32 (2004) 177.
31. A. Kudo, Y. Miseki, *Chem. Soc. Rev.* 38 (2009) 253.
32. G. Palmisano, V. Augugliaro, M. Pagliaro, L. Palmisano, *Chem. Commun.* (2007) 3425.
33. R. Vinu, G. Madras, *Journal of the Indian Institute of Science* 90 (2010) 189.
34. K. Rajeshwar, M.E. Osugi, W. Chanmanee, C.R. Chenthamarakshan, M.V.B. Zaroni, P. Kajitvichyanukul, R. Krishnan-Ayer, *J. Photochem. Photobiol. C: Photochem. Rev.* 9 (2008) 171.
35. M.A. Rauf, S.S. Ashraf, *Chem. Eng. J.* 151 (2009) 10.
36. I.K. Konstantinou, T.A. Albanis, *Appl Catal B: Environ.* 49 (2004) 1.
37. U.G. Akpan, B.H. Hameed, *J. Hazard. Mater.* 170 (2009) 520.
38. F. Han, V.S.R. Kambala, M. Srinivasan, D. Rajarathnam, R. Naidu *Appl Catal A: Gen.* 359 (2009) 25.
39. J.W. Tang, Z.G. Zou, , J. Yin, , J.H. Ye, , *Chem. Phys. Lett.* 382 (2003) 175.

40. W.W. Zhang, J.Y. Zhang, Z.Y. Chen, T.M. Wang, *Catal. Commun.* 10, (2009) 1781.
41. C.H. Chen, Y.H. Liang, W.D. Zhang, *J. Alloys Compd.* 501, (2010) 168.
42. H.R. Zhang, K.Q. Tan, H.W. Zheng, Y.Z. Gu, W.F. Zhang, *Mater. Chem. Phys.* 125, (2011) 156.
43. G. Chiavari, *J. Chromatogr. A* 206 (1981) 55.
44. T. C. Schmidt, *J. Chromatogr. A* 81 (1998) 161.
45. C. S. Eskillson, *J. Chromatogr. A* 955 (2002) 215.
46. L. Zhu, H. K. Lee, *J. Chromatogr. A* 963 (2002) 231.
47. A. Plum, *Chromatographia* 57 (2003) 243.
48. J. Franc, *J. Chromatogr. A* 170 (1979) 89.
49. M. R. Hoffmann, S. T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69.
50. B. Muktha, G. Madras, T.N. Guru Row, U. Scherf, S. Patil, *J. Phys. Chem. B* 111 (2007) 7994.
51. F. Xia, E. Ou, L. Wang, J. Wang, *Dyes Pigm.* 76 (2008) 76.
52. D. Carriazo, M. Addamo, G. Marci, C. Martin, *Appl. Catal. A: Gen.* 356 (2009) 172.
53. P. Mahata, G. Madras, S. Natarajan, *Catal. Lett.* 115 (2007) 27.

54. D. Saha, S. Mahapatra, T.N. Guru Row, G. Madras, *Ind. Eng. Chem. Res.* 48 (2009) 7489.
55. B. Muktha, G. Madras, T.N. Guru Row, *J Photochem Photobiol A: Chem.* 187 (2007) 177.
56. M. L. Marin, L. S. Juanes, A. Arques, A. M. Amat, M. A. Miranda, *Chem. Rev.*, 112 (2012) 1710.
57. S. Y. Ding, J. Gao, Q. Wang, Y. Zhang, W. G. Song, C. Y. Su, W. Wang, *J. Am. Chem. Soc.* 133 (2011) 19816.
58. G. Zhang, V. Lami, F. Rominger, Y. Vaynzof, M. Mastalerz, *Angew. Chem. Int. Ed.* 55 (2016) 3977.
59. H. M. Heitzer, B. M. Savoie, T. J. Marks, M. A. Ratner, *Angew. Chem. Int. Ed.* 53 (2014) 7456.
60. C. Gu, N. Huang, Y. Chen, H. Zhang, S. Zhang, F. Li, Y. Ma, D. Jiang, *Angew. Chem. Int. Ed.* 55 (2016) 3049.
61. R. S. Sprick, J. X. Jiang, B. Bonillo, S. Ren, T. Ratvijitvech, P. Guiglion, M. A. Zwijnenburg, D. J. Adams, A. I. Cooper, *J. Am. Chem. Soc.* 137 (2015) 3265.
62. R. S. Sprick, B. Bonillo, R. Clowes, P. Guiglion, N. J. Brownbill, B. J. Slater, F. Blanc, M. A. Zwijnenburg, D. J. Adams, A. I. Cooper, *Angew. Chem. Int. Ed.* 55 (2016) 1792.
63. S. Yanagida, A. Kabumoto, K. Mizumoto, C. Pac, K. Yoshino, *J. Chem. Soc. Chem. Commun.* (1985) 474.

64. H.W.P. Carvalho, A.P.L. Batista, P. Hammera, T. C. Ramalhoc, J. Hazard. Mater. 184 (2010) 273.

65. M. A. Rauf, M. A. Meetani, A. Khaleel, A. Ahmed, Chem. Eng. J. 157 (2010) 373.