INVESTIGATION OF THE PHOTOCATALYTIC ACTIVITY OF PALLADIUM NANOPARTICLES ADDED PEDOT

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IN

APPLIED CHEMISTRY

AT

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JANUARY 2017

Approval of the Graduate School of Natural and Applied Sciences, Atılım University.

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Prof. Dr. İbrahim AKMAN

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I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

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This is to certify that we have read the thesis "Investigation of the Photocatalytic Activity of Palladium Nanoparticles Added PEDOT" submitted by "Matira Miud Alaribi Ahmed" and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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ABSTRACT

INVESTIGATION OF THE PHOTOCATALYTIC ACTIVITY OF PALLADIUM NANOPARTICLES ADDED PEDOT

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Investigation and development of efficient and low-cost method for wastewater treatment to effectively eliminate the pollutants is so important for environmental remediation. Among the wastewater treatment methods, advanced oxidation processes (AOP's) consists of the usage of homogenous and heterogeneous photocatalysts, known as the most effective way. The development of photocatalytic materials used in AOP's is so important. The advancement of photocatalysts which sensitive to solar light would allow more effective utilization of solar light brings sustainable ways to various environmental problems. Recently conductive polymers noted as a new types of effective photocatalytic materials under solar light. Poly(3,4-ethylenedioxythiophene) (PEDOT) considered as one of the most important candidate among the conjugated polymers.

In this thesis, photocatalytic activity of the palladium added PEDOT (PdNPs/PEDOT) polymer was investigated. In this study, a facile production procedure was demonstrated to fabricate the PdNPs/PEDOT as a photocatalyst. The phtocatalytic activity of PdNPs/PEDOT nanocomposite material was checked into the decolorization of MB under UV and solar light exposure. The photocatalytic behavior of bare PEDOT, TiO_2 nanoparticles and PdNPs/TiO_2 nanostructure were also investigated in order to make comparison with PdNPs/PEDOT nanostructure.

The characterization of nanocomposite catalysts were done by scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution-transmission electron microscopy (HR-TEM) energy dispersive X-Ray (EDX) coupled with SEM and Raman Spectroscopy.

Keywords: Photocatalyst, Conjugated polymers, Palladium nanoparticles, PEDOT, Dye removal

ÖZ

PALADYUM NANOPARÇACIKLARIN EKLENMİŞ OLDUĞU PEDOT'UN FOTOKATALİTİK AKTİVİTESİNİN ARAŞTIRILMASI

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Çevre ıslahında, atık suların temizlenmesi işleminde etkili ve düşük maliyetli yöntemlerin araştırılması ve geliştirilmesi çok önemlidir. Atık suların temizlenmesinde homojen ve heterojen katalizörlerin kullanımını içeren geliştirilmiş oksidasyon prosesleri (AOP's) en etkili yöntem olarak bilinmektedir. Bu yöntemde kullanılacak fotokatalitik malzemelerin geliştirilmesi oldukça önemlidir. Görünür bölge ışığa duyarlı fotokatalizörlerin geliştirilmesi, çeşitli çevre sorunlarında gün ışığının daha etkin kullanımı ile ilgili uygulanabilir çözümler getirebilir. Son zamanlarda iletken polimerler gün ışığı altında çalışabilen etkili fotokatalizörler olarak bahsedilmektedir. İletken polimerler arasından Poly(3,4-etilendioksitiyofen) (PEDOT) en gelecek vaat eden aday olarak sayılmaktadır.

Bu tezde, paladyum nanoparçacık eklenmiş PEDOT (PdNPs/PEDOT) polimerinin fotokatalitik aktivitesi incelenmiştir. Bu çalışmada fotokatalizör olarak PdNPs/PEDOT hazırlanması için oldukça basit bir yöntem gösterilmiştir. PdNPs/PEDOT nanokompozit malzemenin fotokatalitik aktivitesi metilen mavisinin UV ve güneş ışığı altında boya giderimi ile araştırılmıştır. Ayrıca, PEDOT, TiO_2 nanoparçacıklarının ve PdNPs/TiO_2 nanoyapısının fotokatalitik aktivitesi, PdNPs/PEDOT'ın aktivitesi ile karşılaştırılmıştır.

Nanokompozit katalizörün karakterizasyonu taramalı elektron mikroskobu (SEM), geçirimli elektron mikroskobu (TEM), yüksek çözünürlüklü geçirimli elektron mikroskobu (HR-TEM), SEM ile birleştirilen enerji dağılım X-Ray (EDX) ve Raman spektroskopisi teknikleri ile yapılmıştır.

Anahtar Kelimeler: Fotokatalizör, Konjuge polimerler, Paladyum nanoparçacıklar PEDOT, Boya giderimi

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CHAPTER 1

INTRODUCTION

The developments in consumption, conversion and conservation of energy in addition finding solution for environmental problems are the serious challenges of the 21st century[1]. Due to their nanometric sizes, nanomaterials exhibit extreme properties such as optical, thermal, electrical, etc.. These subjects offer the reliable solution in energy conversion by surface and interface processes[2,3]. TiO_2 nanostructure is one of the examples of nanometric materials with high photocatalytic activity beside stability. Also, low synthesis costs and biocompatibility are the other properties of TiO_2 nanostructures that can be suggested. Nevertheless, restriction in TiO_2 nanoparticles applications can be considered because of their low quantum yield in the presence of fast charged carriers (e^-/h^+), recombination and the UV exposures requirement. Indeed, TiO_2 can only be excited in the presence of UV illuminations lower than 400 nm wavelengths and in mentioned domain only 3-4% of the solar light contains UV light[4,5,6]. In the recent years, a reasonable number of novel strategies including doping, heterojunctions, graphene-based composites and co-catalyst mediated techniques have been proposed to exhibit new photocatalytic materials as alternatives of TiO_2 for the most relative photocatalytic demands such as detoxification and disinfection, water splitting and organic material reactions[7,8,9].

To achieve high photocatalytic activity in visible region, it is necessary to accurate tuning in a few electronic parameters of photocatalytic agents such as atomic configuration, energy band-gap, band position, lifetime of electrons etc.[10]. Several approaches have applied to change these parameters[4].

In recent years, black hydrogenated TiO_2 nanocrystals are concentrated in photocatalytic reactions induced by solar light[11]. A promising case in TiO_2 activity enhancement has mentioned as plasmonic photocatalysts applications in the visible light region [12,13].

In addition, recent studies have been illustrated that the surface modification of TiO_2 (Cu, Ag or Au nanoparticles) extremely improved the photocatalytic activity at UV and visible light regime[14,15,16]. However, the high cost of the noble metal doped catalysts (i.e., Au, Ag) and low stability due to exist of repetitive cycles, remarkably restricted the large volume applications[17]. Hence, the conventional photocatalysts are not a good candidate for industrial scale applications.

In the past few years, new type of polymer nanostructures has expanded in the energy conversion and their applications[18]. Upon to mentioned field, there are novel reports related to experimental proofs of sensitive properties of photocatalytic reactions in visible light. Conjugated polymers such as poly (diacetylene)-based nanostructures and poly(diphenylbutadiyne) (PDPB) nanofiber morphologies used in waste water treatment have been presented[19].

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most promising conducting polymers because of its excellent thermal and chemical stability properties beside high conductivity and proper flexibility. Also other superior properties such as low end product costs, high transparency and elevated carrier mobility as well as biocompatibility PEDOT presents as an excellent candidate[20]. These unique characteristics render PEDOT potentially useful for a wide range of applications, including solar cells, organic light emitting devices, and biosensors[21,22,23].

Although oxide-based semiconductors have been in considered as the efficient photocatalysts in the past decade, the reports regarding photocatalytic activity of conjugated polymers are scarce[24].

1.1 Mechanism of Photocatalytic Process

The principles of photocatalysis mechanism have been identified and reported in literature[25,26]. The schematic illustration of photocatalytic mechanism of TiO_2 is given in Figure 1.1.

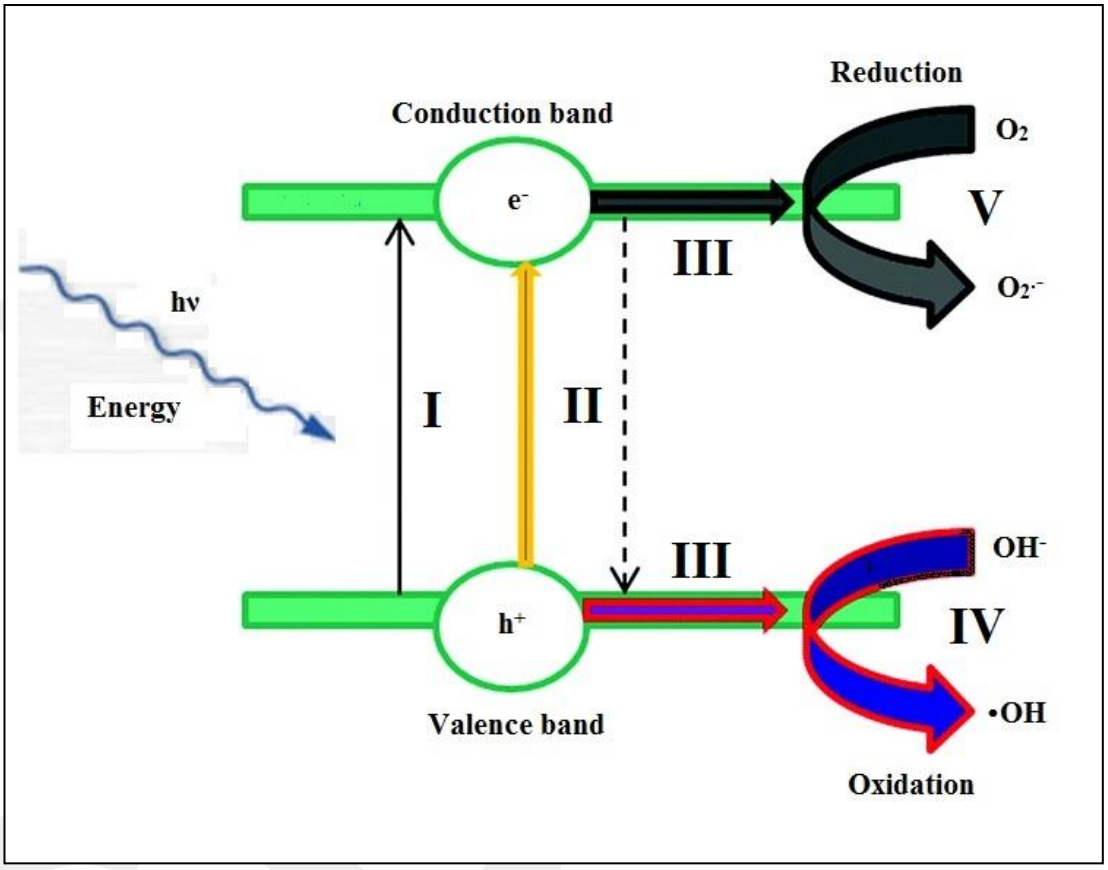

Figure 1.1 The Steps of the pohotocatalytic process[27]

According to Figure 1.1, in the first step photo-excitation which causes the formation of electron (e^-)–hole (h^+) pairs occurs. Than photo-induced charge recombination (II) and photo-induced charge transportation (III) take place respectively. Finally valence band hole induced oxidation (IV) and conduction band electron makes reduction (V)[27].

When energy of absorbed photon be in same or higher level than the band gap energy (Eg) of TiO_2, a valence electron can be excited from valence band root (VB) into empty conduction band (CB) resulting in the formation of a hole in VB (stage I). Both recombination (stage II) and transportation processes (stage III) actualize simultaneously. As illustrated in Figure 1.1, stage II process is happen faster than the stage III. The movement of electrons and holes participate in a redox reaction to find active sites on the surface of TiO_2 which are illustrated in stage VI and V steps. In other words, degradation of pollutants in mentioned photocatalytic process, holes occurred in VB can form hydroxyl radicals from water molecules which is adsorbed on the surface in all steps of reaction.

The importance of hydroxyl radicals can be defined because of their strong oxidizing potency in the case of organic pollutants without any particular requirement. Furthermore, organic pollutants are simultaneously oxidized by the holes to produce R^{+} [28,29].

1.2 Visible Light as a Greener Approach in Photocatalytic Process

Sunlight is considered as a natural energy reservoir. Beside of infinite energy deposit, sunlight serves nonpolluting, unlimited renewable green energy. Increment of population due to urbanization and industrialization influenced the world climate and environmental factors seriously. It can be seemed that twenty-first century is the effective challenge era to prevention solar radiation and its conversion as energy source[30,31,32]. The hypothesis between solar energy use and its sustainability is not a new idea. The observation that light alone could make a change in the structure of organic compounds return to early twentieth century in which chemists believe that the sunlight may considered as an unlimited and clean source[33,34,35]. In addition, the usage of UV light in photochemical reactions requires UV waves generator, which dramatically increases the cost of end product when compared with the direct usage of solar light. Vast adoption of non-pollutant photochemical methods in the industry driven by chemistry had been described previously.

Photochemical techniques development can be realized by using reactions promoted by visible light which is frequently accessible in the solar spectrum. Although the photochemistry of organic molecules under visible light is relatively developing but many inorganic and organometallic materials strongly absorbs the visible region of light. According researches solar energy has been addressed as huge energy source need for photochemistry reactions of transition metal complexes[36,37].

1.3 Heterogeneous Catalysts Used in Photocatalytic Process

Heterogeneous photocatalytic process has known as charmed techniques because of their promising potential in energy and environment issues. Among various methods in organic pollutants elimination, photocatalytic process can be selected as one of the effective mechanisms in this field. Because of its good results in non-specific conditions such as room temperature and sunlight as energy source without further utilities photocatalysis can be considered as good choice[38].

Over the past decade, comprehensive studies performed to find the most efficient technique utilizing solar energy. The explorations up to now have been resulted in metallic materials such as TiO_2-based[39,40] and non-TiO_2-based procedures in which Ga, In, Nb, Ta, W and Bi are base precursors in synthesis [41]. In spite of extraordinary advances in photocatalysis studies in the environment field, the search for cheap and sustainable novel photocatalytic methods applicable in visible light region are special investigation fields which attract researchers to utilize solar energy in the large-scale. Organic photocatalysts are widely preferred due to their wide sources, cheap production and strong light absorption capability in the visible region of electromagnetic spectrum[42].

Unsaturated bands (π bonds) of carbon-carbon in organic materials composition used in conjugated polymers grant semiconducting properties due to the overlap of their π bonds. The uncertainty in π electron location can cause absorption of the light to result charge vehicles used in photochemical processes. However, low-cost, facile and reliable reaction method for the production of organic semiconductor is always weakened by their low stability and catalytic activity.

1.4 Conjugated Polymers as Photocatalyst

Conjugated polymers include a few numbers of unsaturated bonds (π), present a new generation of heterogeneous photocatalysts with solar energy utilization. Three key explanations for photocatalytic process are in common use. Robust, non-toxic and visible light sensitive properties make them appealing candidates for scale up when integrating with their intrinsic soft features. Conjugated materials generally absorb visible light exposures due to their π-system. Because of these properties, π bond consisted materials find applications in organic electronics and organic photonics[43,44,45,46].

The leading research reported about conjugated photocatalysts (liner poly (p-phenylene)s) for H_2 evolution was investigated first time in 1985 by Yanagida and coworkers. Less investigation in the field of organic semiconductors in photocatalytic H_2 field due to their low stability and activity could not introduce as an attractive method in photocatalytic mechanisms [47].

Mentioned polymeric reagents in photocatalytic reactions only achieved a mild quantum yield (AQY=0.006 %) in photocatalytic activity under UV-light irradiation (λ>366 nm). However, this discovery stimulated the development of new generation photocatalytic reagents in which exhibit electronic band same as happen in conductive metals. These materials exhibit supreme tune ability with chemical composition. Photocatalytically active polymers are prominent members of photocatalyst reagents category with solar energy conversion properties.

Despite of all scientific studies in this field unfortunately very limited results have been achieved in photocatalytic studies since 2009. Graphitic carbon nitride (g-C_3N_4) polymer has been discovered firstly to exhibit activities for photocatalytic water splitting [48]. After mentioned research, the other research groups were showed their tendency toward synthesis of conjugated polymers in photocatalytic H_2 evolution[49,50] and in these classification photoredox catalytic methods have emerged as an important application of these polymers.

Since the emergence of new generated conjugated polymers in large-scale applications in 2009, researchers have commonly used the techniques to fabricate a type of photocatalytic agents be excited with visible region exposures. Excellent activity of organic photocatalyts applicable in photocatalytic processes even with visible light will be notable when compared to inorganic photocataysts.

The advantages of conjugated polymers (i.e. accessibility, chemical versatility and engineered characteristics) can be very interesting. Improvements in high yield organic conjugated photocatalytic chemicals can be considered in photocatalytic applications. In spite of a few studies in conjugated polymers in photocatalytic H_2 evolution field unfortunately any hot topics involve in this area with attendance to important points of photocatalysts are not accessed[51,52].

Recently, some of the polymers have been emerged to exhibit excellent activities in photocatalytic hydrogen (H_2) evolution from water[51,52]. It is interesting that organic semiconductor conjugates have enormous advantages compared to their inorganic counterparts. These advantages are including low investment cost for mass production of these materials, accessibility, sustainability and possible engineering on materials structure and properties which enable them to place as novel metal-free solar energy transducers in artificial photocatalytic classification.

Among the conjugated polymers, linear polymers were reported to have band gaps ranging from 2 to 5 eV depend on the different degrees of conjugation which make them applicable in visible light photocatalytic agents[53].

1.5 Dye Removal Studies by Using Solar Light

Industrial wastewaters exhausted from textile factories contain large amounts of toxic chemicals like azo dyes cause serious environmental risks[54]. Classical methods in removing of these chemicals from industrial wastewater have both advantages and disadvantages[55,56]. Nowadays, photocatalytic degradation way has been widely used as a technique in the organic pollutants removal especially in the case of toxic dyes which can be dangerous for human health[57,58].

Methylene blue (MB) is one of the dye molecules that decompose very hard. MB can be used as dye contamination in wastewater to evaluate the photocatalytic activity of catalysts both under UV[59,60] and visible light irradiation[61]. There is much information about photodegradation of MB in the literatures. Only a little study can be access in the field of visible light photodegradation.

In this field, mainly degradation of MB dye under light irradiation is focused such as the research of Asahi et al. in which TiOx (TiO_2−xNx) has been applied as catalytic reagent. The other study belongs to Li and his co-workers that are about Pt–TiO_2 application as photocatalyst[62,63] utilized by N-doped TiO_2 as catalyst for MB photodegradation under visible light. The team found out that the MB degradation ratio was only 35% after180 minutes visible light illumination.

Results showed that ultraviolet light only occupied 4% of the solar energy during photodegradation reaction. Hence, it can be considered as great successfulness to synthesize new visible light sensitive photocatalysts to use the large portion of solar energy (43%). Therefore, development of novel visible light sensitive photocatalysts will be desired[64,65].

1.6 Aim of the Study

In this study, palladium nanoparticles supported on PEDOT polymer, (PdNPs/PEDOT) were prepared. The characterization of the prepared catalyst was done by using ICP-OES, SEM, TEM and EDX. The catalytic activity of the prepared catalyst was checked in the removal of MB known as organic dye commonly founded in textile wastewater under UV and visible radiation at room temperature. In order to make a comparison, also the catalytic activities of titanium oxide nanoparticles (TiO_2), palladium nanoparticles added titanium oxide nanoparticles (PdNPs/ TiO_2) and PEDOT were revealed.

CHAPTER 2

MATERIALS AND METHODS

2.1. Materials

Chloroform ($CHCl_3$), 3,4 ethelenedioxythiophene (EDOT), titanium dioxide (TiO_2) nanoparticles, Palladium nitrate ($Pd(NO_3)_2.XH_2O$), anhydrous $FeCl_3$ and methylene blue (MB), Sodium Borohydride ($NaBH_4$) were purchased from Sigma-Aldrich. All reagents were used as received and they were in analytical grade. Deionized water used in experiments was obtained by using Milli-Q Water Purification System. Before experiments all glassware's and magnetic stir bars were cleaned by using water ethanol mixture.

2.2. Instrumentation

The amount of palladium loaded onto the PEDOT and the leaching of palladium into the solution after reaction were revealed by using Perkin Elmer DRC II model inductively coupled plasma mass spectroscopy (ICP-OES).

SEM images of the prepared catalyst were taken by using QUANTA 400F Field Emission Scanning Electron Microscope (FE-SEM). The suspension solutions of the prepared samples and dried forms were put onto the carbon tape-coated grids before the SEM measurements.

TEM images of the samples were taken by using JEOL JEM-2010F (FEG, 80-200 kV) the transmission electron microscopy (TEM).

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

Photocatalytic activity measurements were performed by using Labor-UV-reactor-System 2 (UV-RS-2) and ATLAS solar simulator.

Removal of methylene blues was observed by using Specord S 600 UV-Vis spectrometer.

2.3. Preparation of PEDOT

Chemical polymerization of EDOT were performed in order to prepare Poly (3, 4 ethelenedioxythiophene). The preparation procedure is given in Figure 2.1 given below. For this, initially 2.60 g anhydrous Iron (III) chloride ($FeCl_3$) and 10 ml of chloroform ($CHCl_3$) were mixed and stirred on magnetic stirrer for 5 min. In other beaker 0.568 g EDOT monomer and 10 ml of $CHCl_3$ were mixed and stirred on magnetic stirrer for 5 min. After that, initially prepared mixture was added drop by drop into the solution which contains EDOT monomer. Then the resulting mixture was stirred for 3 hours at room temperature for the achievement of polymerization.

At the end of this period 60 ml methanol was added into the mixture. In order to obtain precipitates of PEDOT final composition was stored in freezer for 24 h, and then formed were collected by filtration. After collecting the precipitate it washed with methanol in Soxhlet apparatus for 3 days. Finally obtained PEDOT was dried at room temperature.

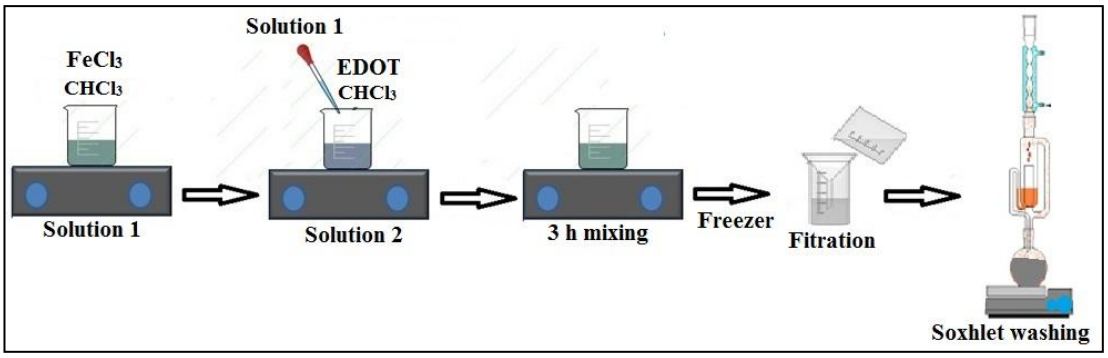

Figure 2.1 Preparation of PEDOT.

2.4. Preparation of PdNPs/PEDOT Nanocomposite Material

Addition PdNPs/PEDOT nanocomposite material was prepared by using wet chemical process known as liquid impregnation. In this procedure, 100 mg PEDOT support and 5 mg Palladium nitrate were put into 10 mL water and mixed on magnetic stirrer for 5 h. After that solid part of the mixture was isolated by applying centrifuge. Then the solid part washed several times with water. At the end all liquid part collected and kept for ICP-OES analyses. For the reduction of Pd^{2+} ions to obtain Pd nanoparticles, collected solid part was dispersed in 20 mL of water. After that 100 mg $NaBH_4$ were added to the solution and mixed for 1 h. After completion of the hydrogen evolution particles were collected and washed. Finally PdNPs/PEDOT nanocomposite material was dried in oven. The preparation procedure is shown in Figure 2.2 given below.

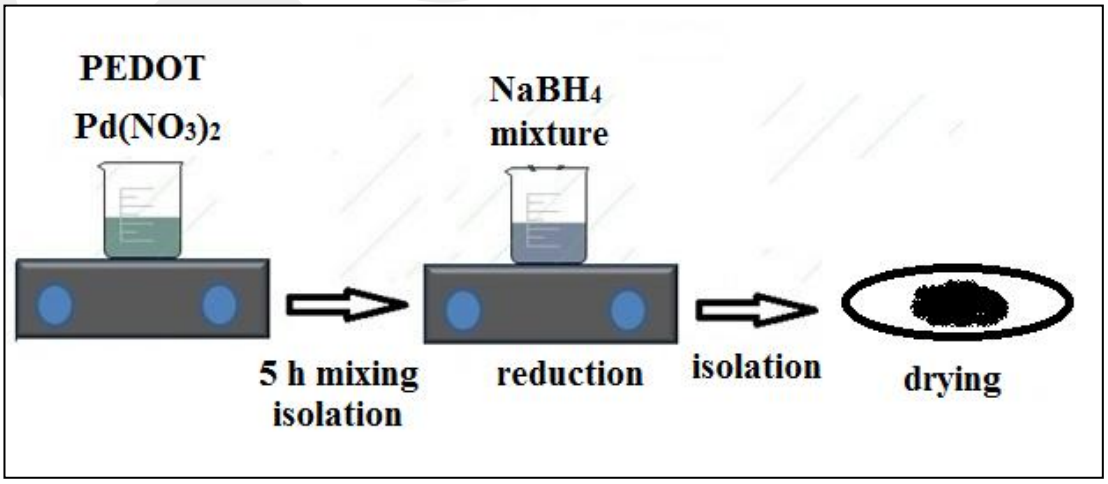

Figure 2.2 Preparation of PdNPs/PEDOT nanocomposite material

2.5.Preparation of PdNPs/TiO_2 Nanostructure

Liquid impregnation technique was used to load the PdNPs on to the TiO_2 nanoparticles. For this, initially 100 mg TiO_2 nanoparticles and 5 mg Palladium nitrate were put into 10 mL water and mixed on magnetic stirrer for 5 h. After that solid part was isolated and washed several times with water. The liquid part collected and stored for ICP-OES analysis. Then the particles were re-dispersed in 20 mL water for reduction. To get PdNPs over TiO_2 nanoparticles 100 mg sodium borohydride was added and mixed for 1 h. Finally particles were washed with water and isolated to dry in oven. The preparation procedure is shown in Figure 2.3 given below.

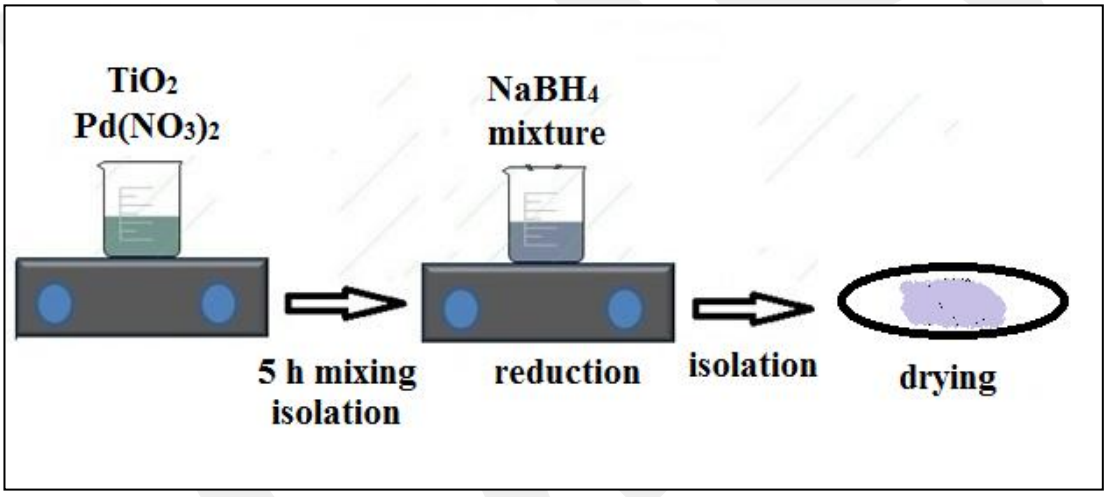

Figure 2.3 Preparation of PdNPs/ TiO_2 nanostructure

2.6. Determination of Catalytic Performance of the Prepared Materials

In order to determine the catalytic performance of the prepared materials initially adsorption–desorption profile of the TiO_2, PdNPs/TiO_2, PEDOT and PdNPs/ PEDOT nanostructures was investigated. For this 0.01 g of each nanocomposite photocatalyst prepared was added to 10 mL of ethylene blue (MB) aqueous solution and stirred in the dark until the concentration of the MB solution became constant. Then the mixture was exposured with a UV and solar light separately at constant magnetic stirring to obtain good mixing of photocatalyst and MB solution. The UV and the solar systems used for catalytic activity measurements are given in Figure 2.4 and Figure 2.5 respectively.

Figure 2.4 UV light exposure system used in this study

Figure 2.5 Solar simulator used in this study

In order to find the catalytic activity of the prepared catalysts under UV and solar light exposure, decolorization of MB was checked at every 10 min by taking 2 mL of sample with a syringe. Removal of the MB dye was revealed by using a UV-Vis spectrophotometer. To calculate the amount of MB removed, the absorbance maximum at 660 nm was followed. The system used for the UV-Vis measurements was given in Figure 2.6.

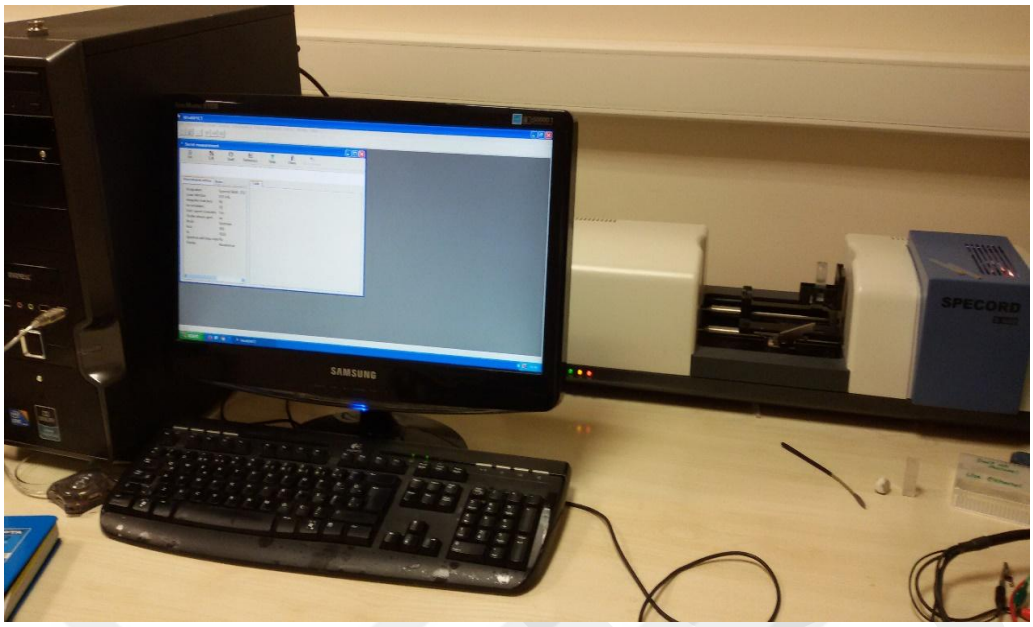

Figure 2.6 UV-Vis spectrometer**.**

The photocatalytic degradation rate of MB was founded 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)

CHAPTER 3

RESULTS AND DISCUSSION

Due to their toxicity, non-biodegradability and potential carcinogenicity, disposal of wastewaters which contain large amounts of dyes from the textile industries has become a great problem for the environment. So the development of low-cost, non-toxic and efficient photocatalysts for remediation of the wastewater by using advanced oxidation process (AOP) to get rid of these wastes. In order to meet this need, photocatalysis is considered to be a unique technique for the removal of organic pollutants from water. For the purpose of giving full play to solar energy, numerous investigations have been done to developed materials which are active under solar light.

Nowadays in order to clean the wastewaters poured out by the industries, semiconductor based photocatalysis, known as a "green" technology, has been widely used. There are lots of publications related to degradation of organic pollutants by using semiconductor based photocatalysts under ultraviolet (UV) light exposure. However, solar light coming from sun contains only a small amount of UV light (5%) when compared with visible light (45%). For this reason, development of high-efficiency visible light driven photocatalysts for removal of wastes from environment has become one of the most important research area in photocatalysis.

Conjugated polymers considered as the new class of heterogeneous photocatalysts which can work under solar light exposure. They are robust, non-toxic and highly active under visible light. This type of materials can absorb visible light because of their delocalized π-system. Due to these properties, usage of new class of photocatalyst that shows similar electronic behaviour like conductive metals with a high possibilty of chemical composition and structure, becomes wide.

In this study, our aim was to prepare a polymer based material with high photocatalytic activity under both UV and solar light exposure. In order to prepare these nanostructured materials a facile polymerization method was demonstrated. After preparation of materials, detailed characterizations of materials were done. Finally, the photocatalytic activities of the prepared materials were tested.

3.1. Preparation and Characterization of PEDOT

Poly(3,4-ethylenedioxythiophene) (PEDOT) considered as one of the most important conjugated polymers due to their high conductivity, perfect thermal and chemical stability, moderest cost and high transparency. These unique characteristics make PEDOT potentially useful for a wide range of applications.

In this study, PEDOT were prepared by applying modified polymerization method explained in experimental part to use in the photocatalytic dye removal study. The morphological property of the prepared PEDOT structure was investigated with SEM. Figure 3.1 shows the SEM image of the prepared PEDOT.

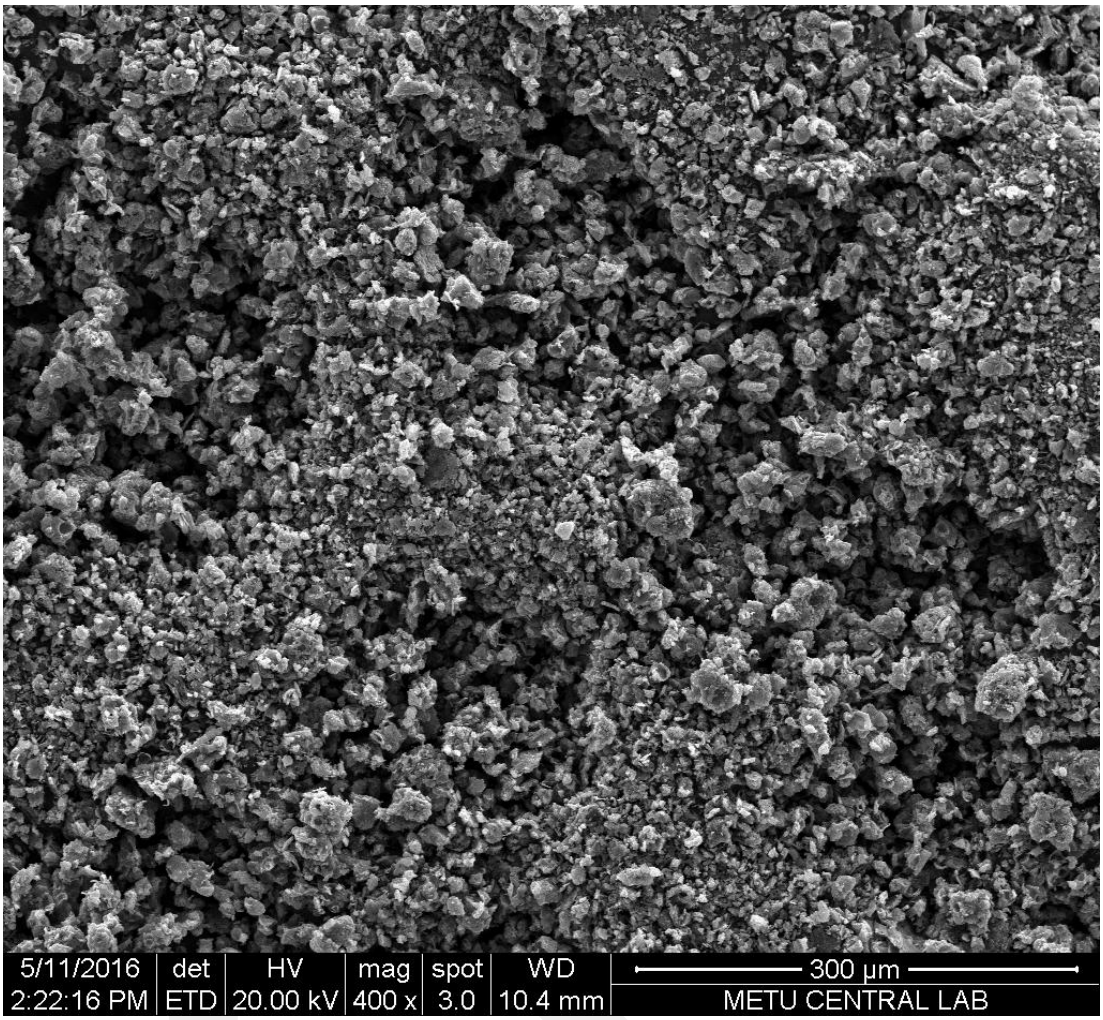

Figure 3.1 SEM image of PEDOT.

As can be seen from the SEM image, micron sized particles with high surface area were obtained at the end of the production process.

The elemental composition of PEDOT was revealed by energy dispersive X-ray (EDX) analysis. EDX patterns of PEDOT nanoparticles shown in Figure 3.2 confirmed the presence of the elements employed in the preparation of PEDOT.

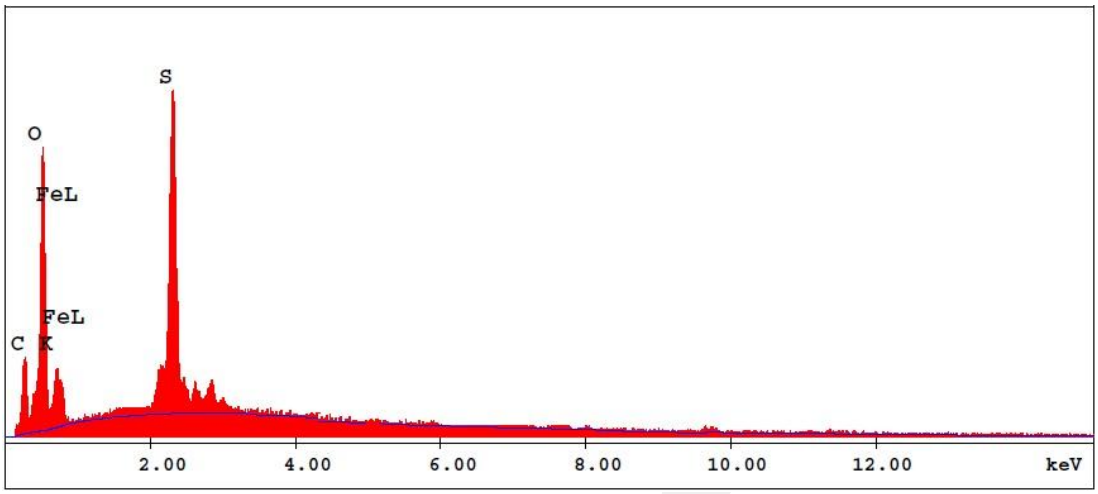

Figure 3.2 EDX pattern of PEDOT.

3.2. Preparation and Characterization of PdNPs/PEDOT and PdNPs/TiO_2 Nanocomposite Materials

Addition of Pd nanoparticles onto the PEDOT and TiO_2 nanoparticles were performed by using liquid impregnation method, according to the procedure given in experimental part. The characterizations of resulting particles were done by using SEM and EDX.

The structure and morphology of the prepared TiO_2 nanoparticles and PdNPs/PEDOT nanocomposite materials were investigated with SEM, TEM and EDX.

The morphologies of the TiO_2 nanoparticles and PdNPs/PEDOT nanocomposite materials are shown in Figure 3.3 and 3.4, respectively.

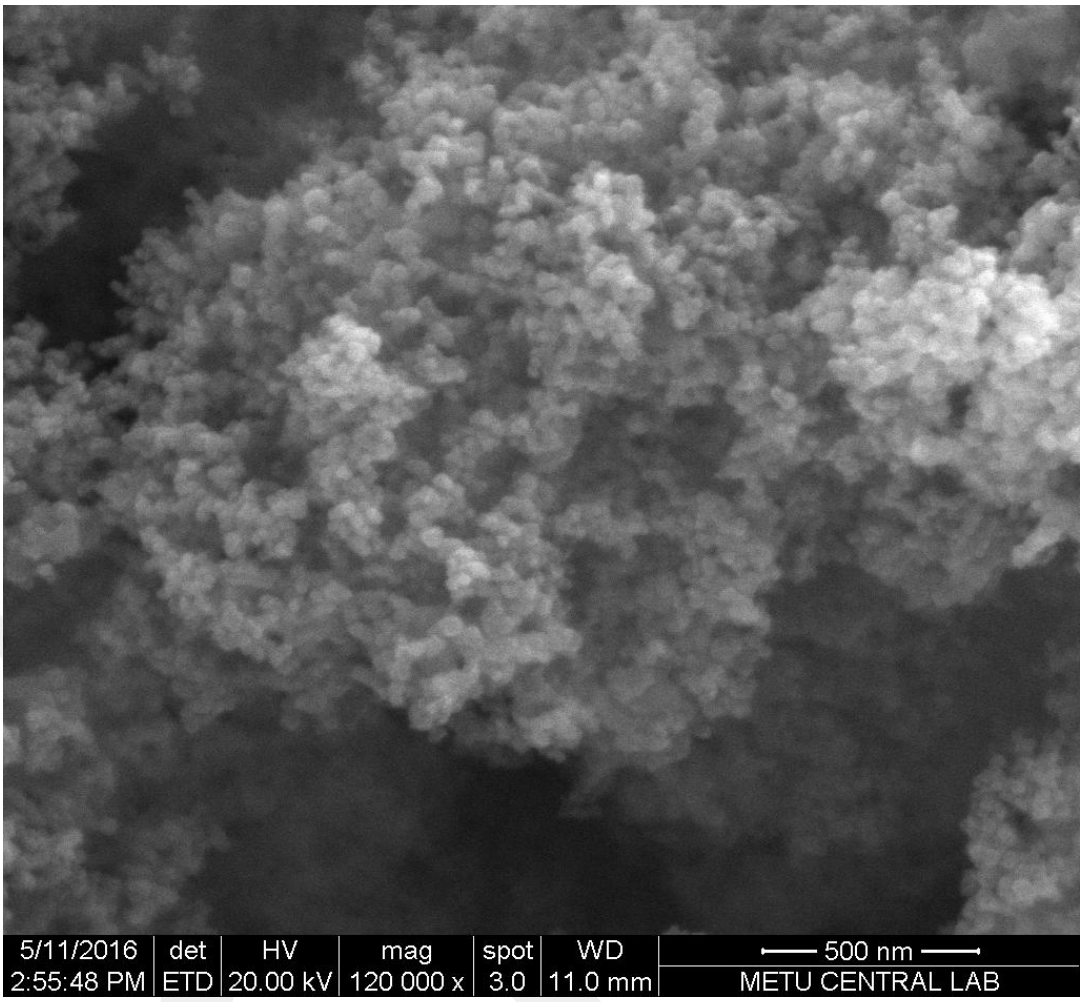

Figure 3.3 SEM image of TiO_2 nanoparticles.

Figure 3.3 shows the SEM images of TiO_2 nanoparticles used as reference, demonstrating that the size of TiO_2 nanoparticles lies between 20-25 nm. The morphologies of the as-prepared PdNPs/PEDOT nanoparticles were investigated with TEM and obtained image is shown in Figure 3.4.

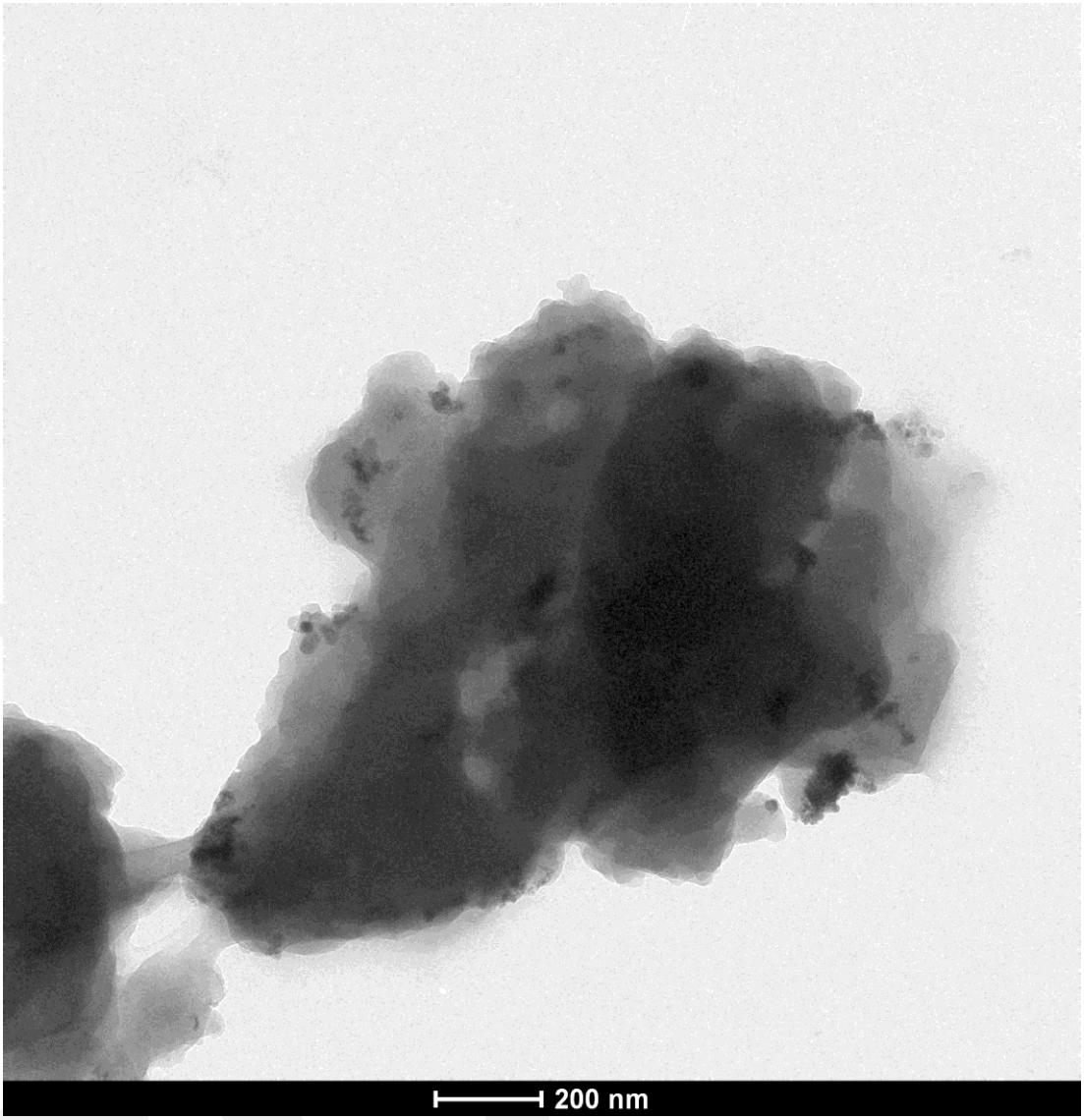

Figure 3.4 TEM image of PdNPs/ PEDOT nanostructure

The size of the palladium nanoparticles was founded around 10 nm from the figure given above. Elemental composition of prepared PdNPs/PEDOT nanocomposite materials was also checked by using EDX coupled with SEM. The results are given in Figure 3.5.

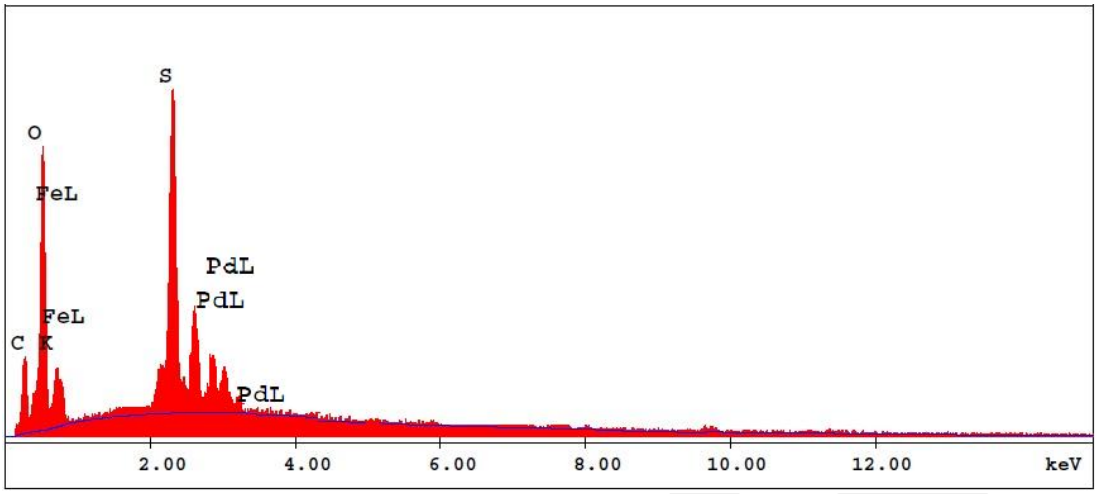

Figure 3.5 EDX patterns of PdNPs/PEDOT nanocomposite material

EDX patterns PdNPs/PEDOT nanocomposite materials indicating that structure contains all framework elements. Percent palladium loadings of TiO_2 and PEDOT were revealed with ICP-OES. According to obtained results, palladium amount loaded on TiO_2 and PEDOT were founded as 1.24% (w/w) and 1.35% (w/w), respectively.

3.3. Investigation of the Photocatalytic Activity of the Prepared Catalysts

In order to find and compare the photocatalytic activity of the PEDOT, PdNPs/PEDOT, TiO_2 nanoparticles and PdNPs/TiO_2 nanocomposite materials, dye removal of the MB, well known organic azo-dye, known as typical pollutant in the textile industry, was measured under both UV and solar light exposures. MB known as highly toxic material with a complex structure. For this reason the removal of MB with physical or biological methods is so difficult. To show the activity and power of the prepared catalysts, MB was chosen as a simulant of textile wastewater.

In a typical photocatalytic experiment, aqueous solution of MB was placed in a beaker and 0.01 g of photocatalysts was added. Before starting to irradiate the MB and catalyst mixture with UV and solar light respectively, the mixture was stirred magnetically in darkness to establish adsorption-desorption equilibrium.

For a catalytic test under UV light, mixture was transferred into the photocatalytic reactor. For solar light exposure, mixture was kept in the beaker. After that, stirring was applied during the UV and solar light illumination to prevent settling of the photocatalyst. During the experiments, 2 mL sample solution was taken out by using centrifuge in every 10 minutes interval to completely remove catalyst particles. Removal of MB was followed by using UV-Vis spectrophotometer by measuring the absorbance (A) at 660 nm. Absorbance value was used to find the rate of degradation (D) of MB according to equation 1 given in Experimental part. These steps were repeated through the all study.

Before starting the main experiments, control experiments were also performed by UV and solar light irradiations of MB solution without catalyst under optimum experimental conditions and no change were observed in absorbance of MB solution.

3.3.1. Dark Profiles of the Prepared Catalysts

Revealing the dark profile (adsorption/desorption behavior) of the prepared catalysts is an important step in the degradation of pollutants with photocatalytic process. So, the MB solution and photocatalyst mixture was stirred magnetically in the dark to figure out the adsorption/desorption equilibrium before starting to UV and light irradiation respectively.

Initially adsorption-desorption equilibrium of TiO_2 nanoparticles and PdNPs/TiO_2 nanostructures were founded. The results are given in Figure 3.6, Table 3.1 and Table 3.2 respectively.

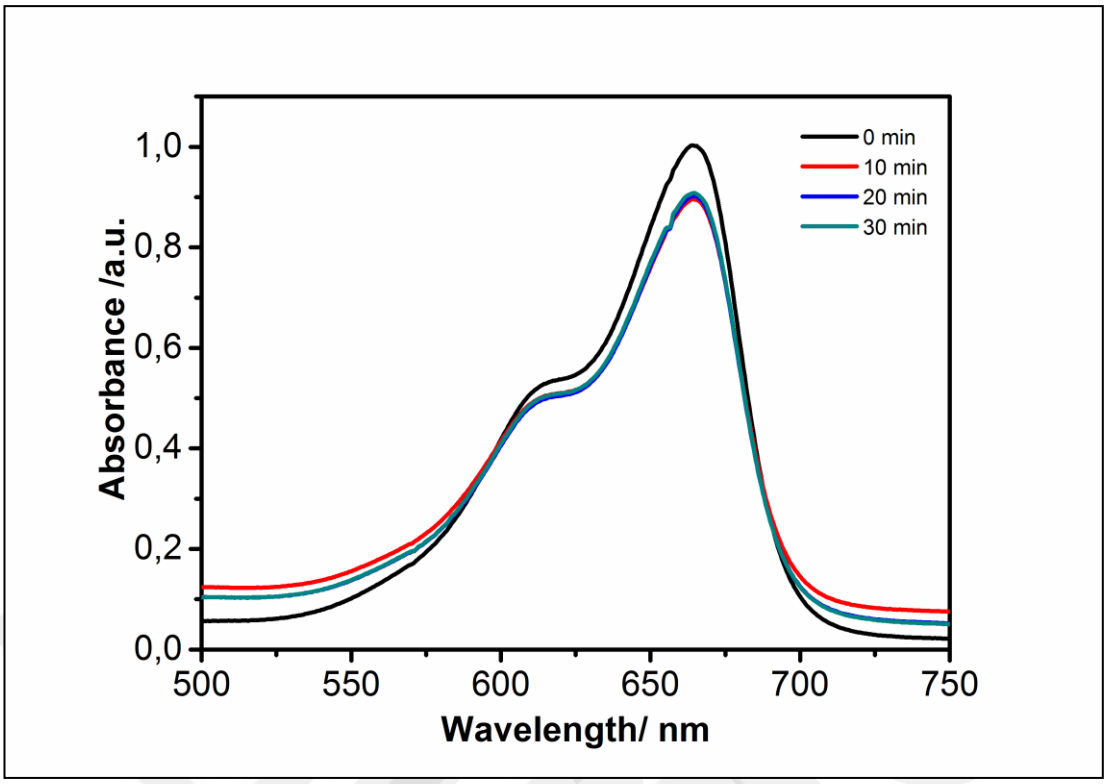

Figure 3.6 UV-Vis spectra of the MB solution processed with 10 mg of TiO_2 nanoparticles under dark.

Figure 3.6 shows a series of absorption maxima of the MB solution with 10 mg of TiO_2 nanoparticle as photocatalyst obtained under dark for different durations. The absorption maxima of MB located at about 660 nm decreases about 10 % in 60 min. According to obtained UV-Vis Spectra, adsorption/desorption equilibrium was obtained after 10 min (Table 3.1).

Table 3.1 Percent MB removal results related to adsorption-desorption behavior of TiO_2 nanoparticles under dark conditions.

Time (min)	%Adsorption
10	10.3
20	9.9
30	9.8
60	10.1

After that the adsorption/desorption equilibrium of PdNPs/TiO_2 nanocatalyst were figured out. The results are given in Table 3.2.

Table 3.2 Percent MB removal results related to adsorption-desorption behavior of PdNPs/TiO_2 nanoparticles under dark conditions.

Time (min)	%Adsorption
10	9.6
20	9.5
30	9.5
60	9.6

According to obtained results, adsorption/desorption equilibrium was obtained after 10 min (Table 3.2). The decrease in adsorption value of TiO_2 nanoparticles is related to addition of Pd nanoparticles over the TiO_2 nanoparticles.

As a next step, the dark behavior of PEDOT and PdNPs/PEDOT catalysts were investigated. The results related to PEDOT are given in Figure 3.7 and Table 3.3.

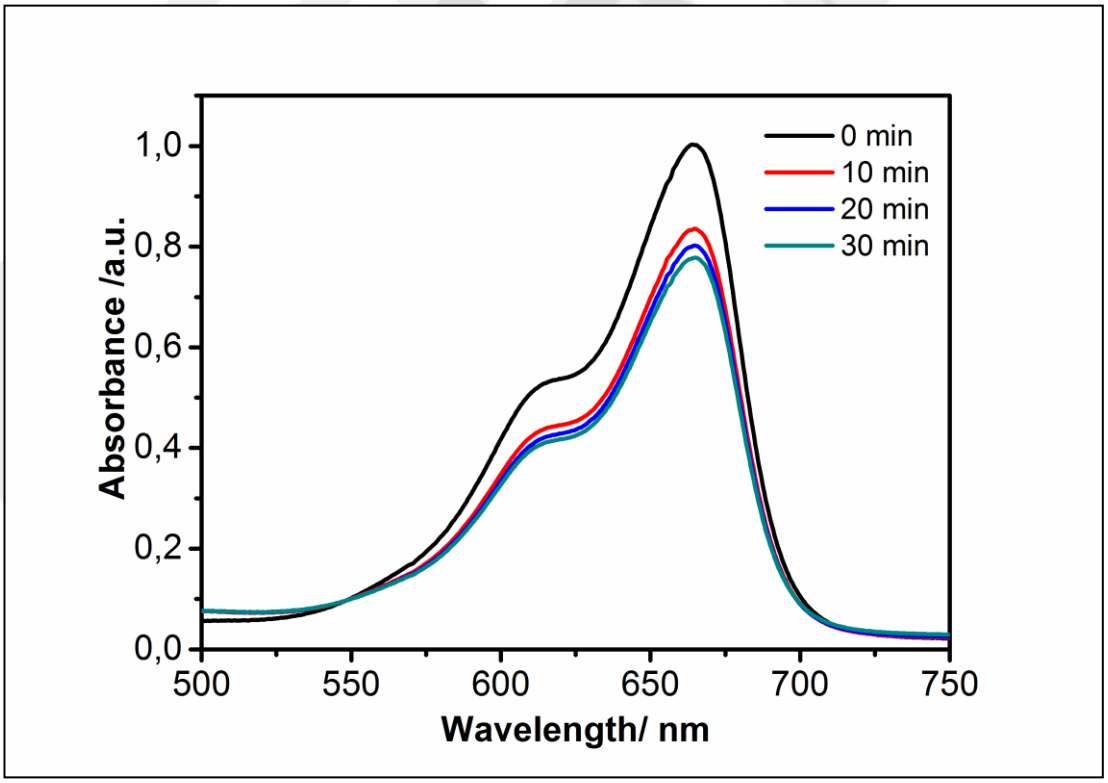

Figure 3.7 UV-Vis spectra of the MB solution processed with 10 mg of PEDOT under dark.

Table 3.3 Percent MB removal results related to adsorption-desorption behavior of PEDOT under dark conditions.

Time (min)	%Adsorption
10	16.7
20	20.8
30	20.7
60	20.6

The adsorption of MB onto the PEDOT under dark is given in Figure 3.7. The characteristic absorption of MB located at about 660 nm decreases about 21% in 30 min (Table 3.3). The adsorption/desorption equilibrium was reached after 30 min. When we compare the results between TiO_2 and PEDOT, higher adsorption of MB can be addressed to high surface area of PEDOT.

Finally the adsorption/desorption profile of PdNPs/PEDOT nanocomposite material was investigated. The results are given Table 3.4.

Table 3.4 Percent MB removal results related to adsorption-desorption behavior of PdNPs/PEDOT nanocomposite material under dark conditions.

Time (min)	%Adsorption
10	17.2
20	18.3
30	18.1
60	18.0

The characteristic absorption of MB located at about 660 nm decreases about 18% in 30 min. The adsorption/desorption equilibrium was reached after 30 min. Decrease in the adsorption rate can be explained by the addition of Pd nanoparticles which decreases the specific surface area of the PEDOT.

3.3.2. Measurements of the Photocatalytic Activity of the Prepared Catalyst under UV Light Illumination

Commercially available Degussa P25 TiO_2 nanoparticles were used as the reference photocatalyst for comparisons with the activity of prepared PdNPs/TiO_2, PEDOT and PdNPs/PEDOT catalysts. For this, initially decolorization of MB under UV and solar light illumination by using 10 mg TiO_2 nanoparticles (Degussa P25) was performed. The results related to UV light illumination is given in Figure 3.8.

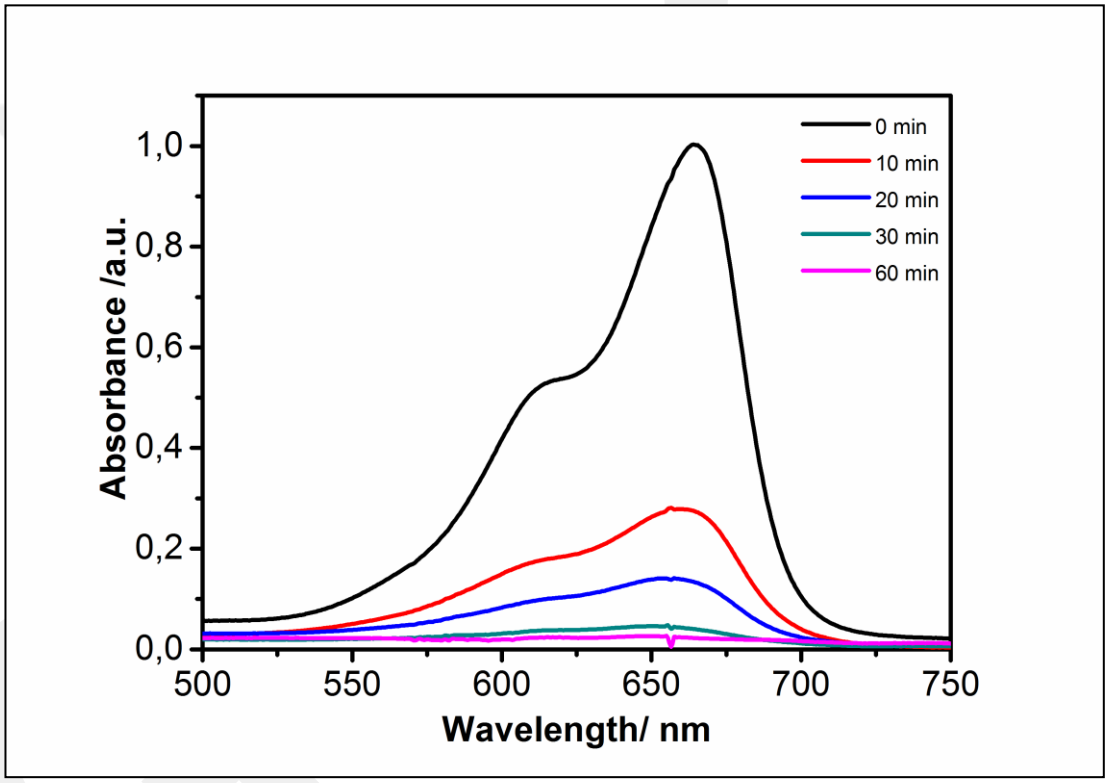

Figure 3.8 UV-Vis spectra of the MB solution processed with 10 mg of TiO_2 nanoparticles under UV light illumination.

The complete removal of the MB was obtained at the end of the 60 min UV light exposure. The percent MB removal of TiO_2 nanoparticle at different time is given in Table 3.5.

Table 3.5 Percent MB removal results of TiO_2 nanoparticle under UV light exposure for different durations.

Time (min)	%Removal
10	66.0
20	82.0
30	93.0
60	99.5

As a second, the MB removal efficiency of Pd nanoparticles added TiO_2 nanoparticles (PdNPs/TiO_2) was investigated under UV light exposure. For this, 10 mg PdNPs/TiO_2 nanoparticles was put into the reactor and exposured to UV light. The results are given in the Figure 3.9 and Table 3.6, respectively.

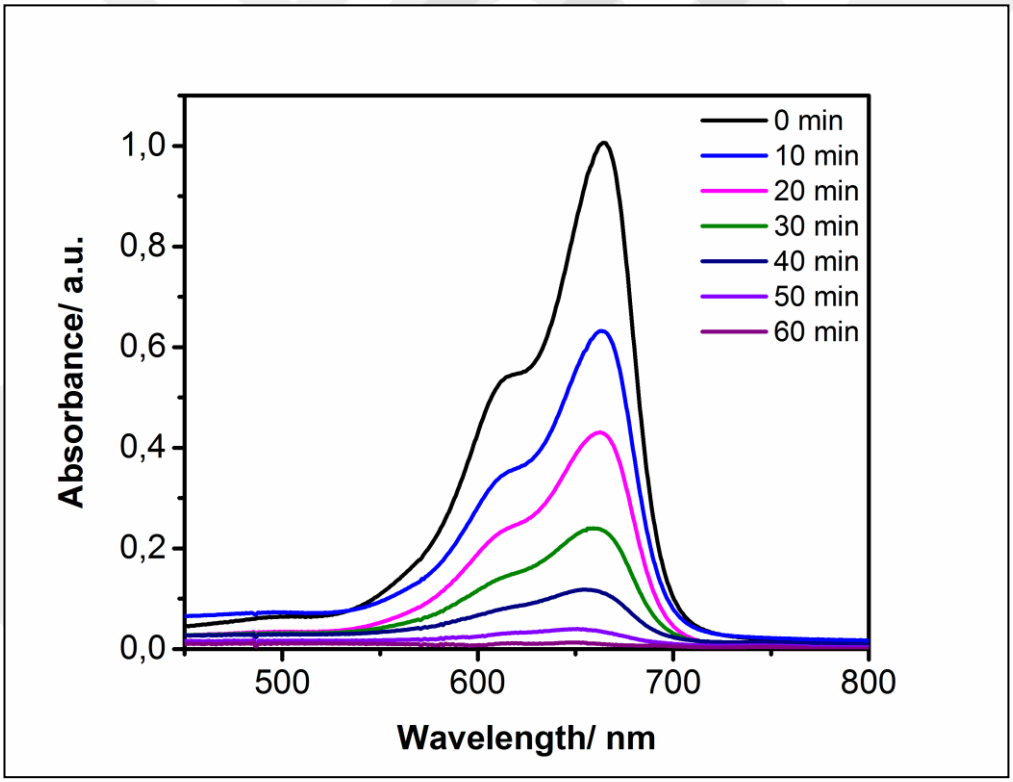

Figure 3.9 UV-Vis spectra of the MB solution processed with 10 mg of PdNPs/TiO_2 under UV light illumination.

Table 3.6 Percent MB removal results of PdNPs/TiO_2 under UV light exposure for different durations.

Time (min)	%Removal
10	38.0
20	57.4
30	77.0
60	97.1

After that, decolorization efficiency of PEDOT polymer was checked. Results are given in Figure 3.10 and Table 3.7.

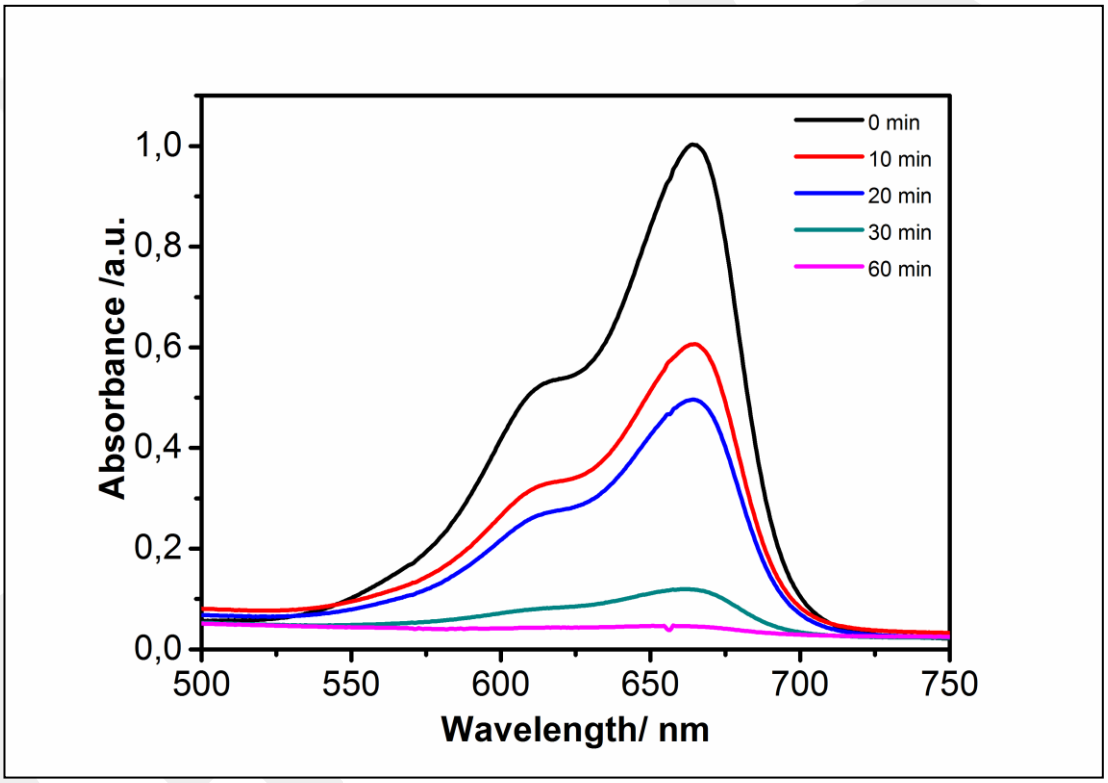

Figure 3.10 UV-Vis spectra of the MB solution processed with 10 mg of PEDOT under UV light illumination.

Table 3.7 Percent MB removal results of PEDOT under UV light exposure for different durations.

Time (min)	%Removal
10	39.4
20	50.4
30	88.1
60	95.0

Finally the activity of the PdNPs/PEDOT in the removal of MB was measured by using same conditions. The results are given in Figure 3.11 and Table 3.8 respectively.

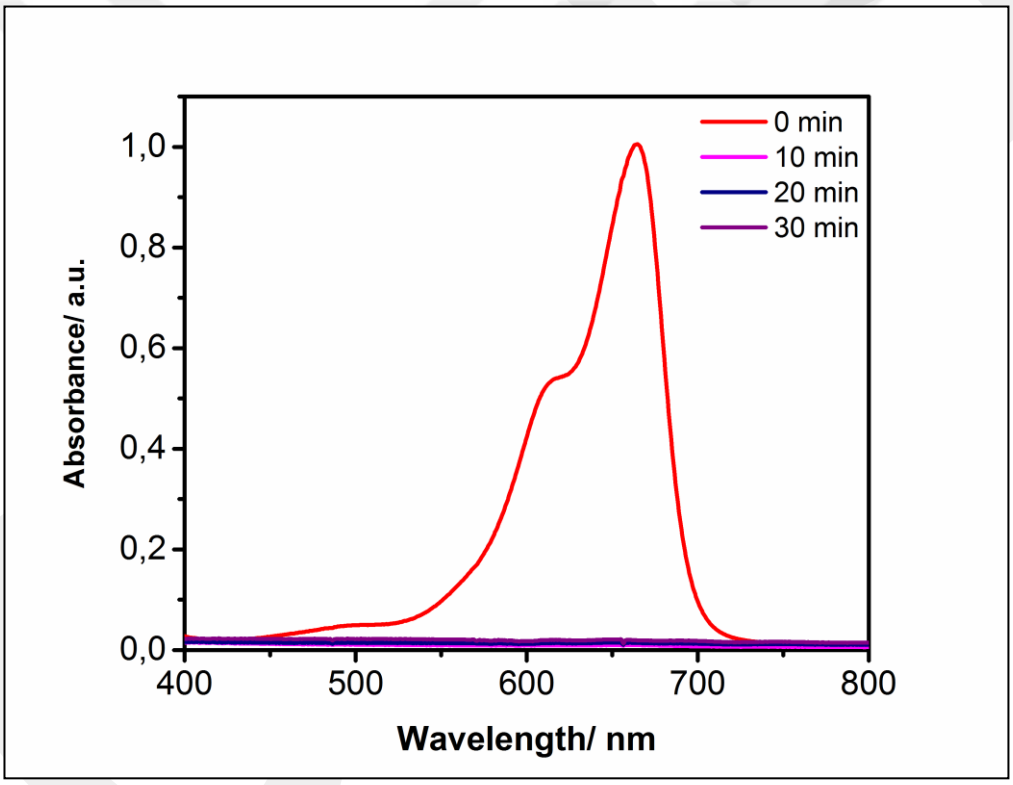

Figure 3.11 UV-Vis spectra of the MB solution processed with 10 mg of PdNPs/PEDOT under UV light illumination.

Table 3.8 Percent MB removal results of PdNPs/PEDOT under UV light exposure for different durations.

Time (min)	%Removal
10	99.1
20	99.5
30	99.6
60	99.6

The comparison of the removal capacity of the all prepared catalyst under UV light illumination is given in Figure 3.12.

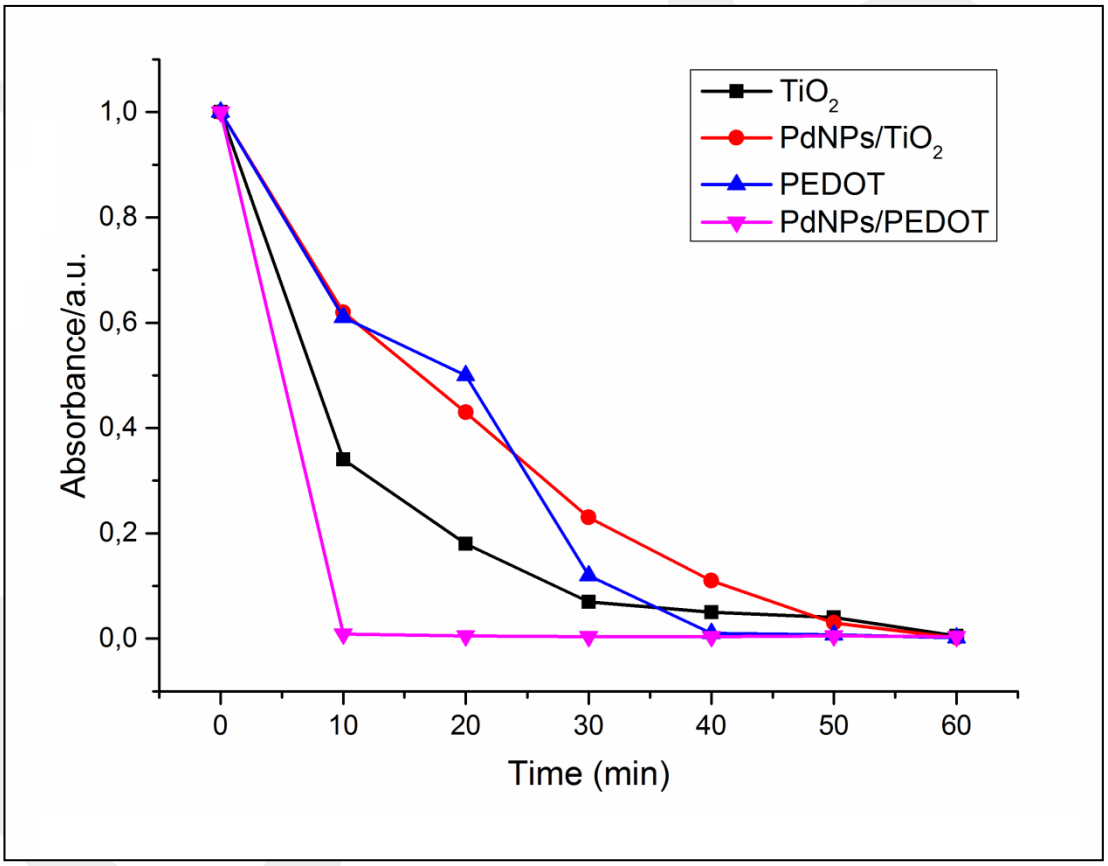

Figure 3.12 Comparative photocatalytic activities of TiO_2, PdNPs/TiO_2, PEDOT and PdNPs/PEDOT on MB degradation under UV light.

As can be seen from the results, complete removal of MB was obtained after 60 min with TiO_2 nanoparticle, PdNPs/TiO_2 nanostructure and PEDOT polymer used as photocatalysts under UV light illumination. For the PdNPs/PEDOT the complete removal of MB was achived after 10 min UV light illumination.

It can be seen that from Table 3.5-8 within 20 min 82%, 57% and 50 % of the MB were degraded by UV light in the presence of TiO_2 nanoparticle, PdNPs/TiO_2 nanostructure and PEDOT polymer, respectively. In the case of PdNPs/PEDOT, 99.5% of the initial MB was removed. From the percent removals for different durations, it can be concluded that the initial rate of the removal process is higher when PdNPs/PEDOT nanostructure is used as a photocatalyst under UV. This suggests that the presence of Pd nanoparticles over PEDOT polymer and the synergetic interaction of Pd nanoparticles with PEDOT play a very important role in the photocatalytic activity of the prepared composite material.

A conclusion may be given that combining PdNPs with PEDOT polymer can remarkably increase the photocatalytic activity of PdNPs/PEDOT nanocomposite material. The decrease in the activity of PdNPs/TiO_2 nanostructure can be attributed the decrease of the surface area thus the number of active sites of the TiO_2 nanoparticle.

3.3.3. Measurements of the Photocatalytic Activity of the Prepared Catalyst under Solar Light Illumination

After completing the activity measurement study under UV light illumination, the catalytic activity of the prepared catalysts in the MB removal under solar light exposure was revealed. For this, solar simulator was used. In a typical experiment, 10 mg catalyst was dispersed in to the MB solution and then exposure to solar light by using solar simulator. Initially the activity of TiO_2 nanoparticles under solar light illumination was investigated. The results are given in Figure 3.13.

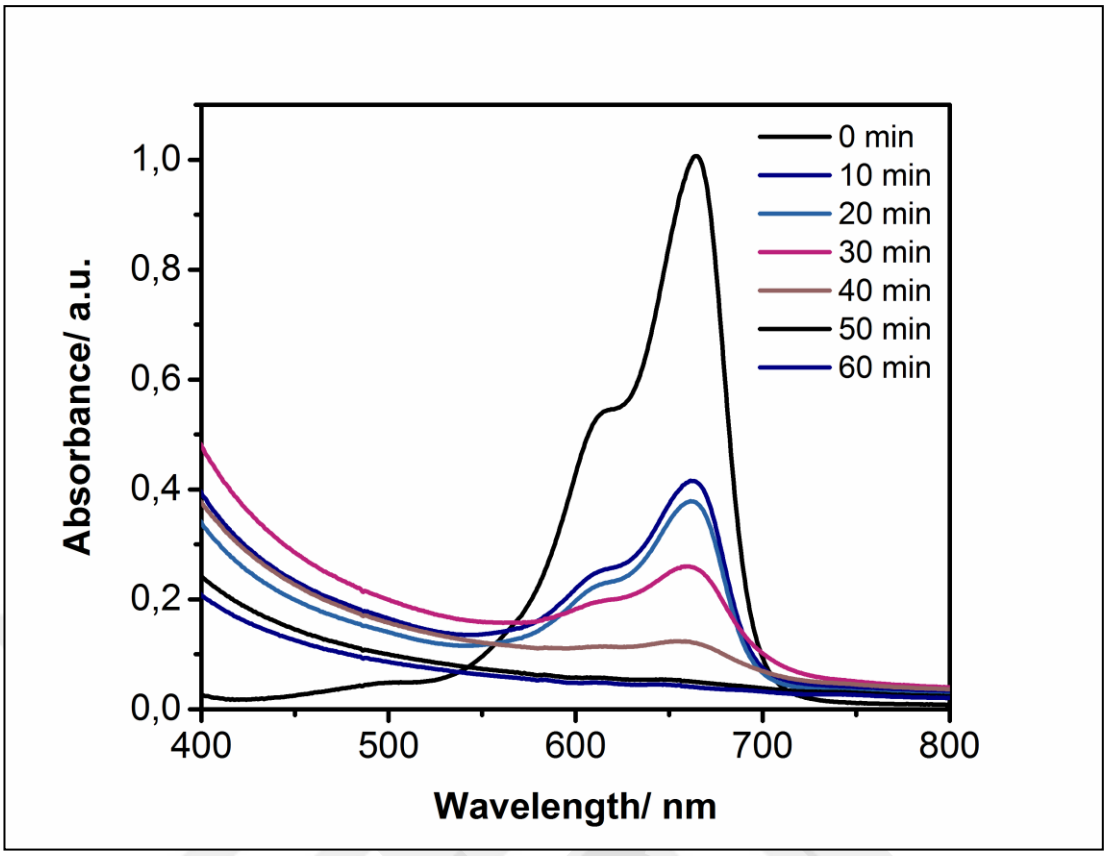

Figure 3.13 UV-Vis spectra of the MB solution processed with 10 mg of TiO_2 nanoparticles under solar light illumination.

Percent removal of MB by using 10 mg of TiO_2 nanoparticles under solar light illumination is given in Table 3.9.

Table 3.9 Percent MB removal results of TiO_2 nanoparticles under solar light exposure for different durations.

Time (min)	%Removal
10	48.9
20	52.7
30	64.6
40	78.1
50	85.1
60	86.1

After that activity of PdNPs/TiO_2 under solar light illumination was investigated. The results are given in Figure 3.14.

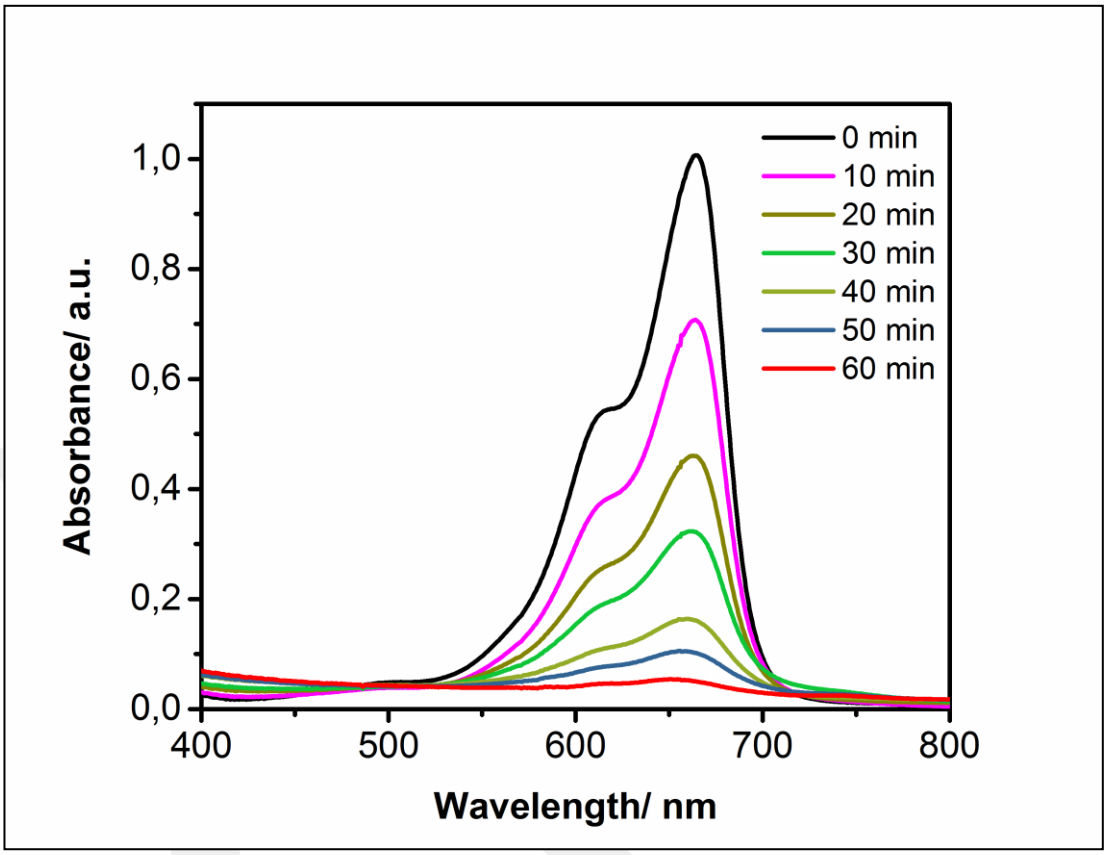

Figure 3.14 UV-Vis spectra of the MB solution processed with 10 mg of PdNPs/TiO_2 under solar light illumination.

Percent removal of MB by using 10 mg of PdNPs/ TiO_2 under Solar light illumination is given in Table 3.10.

Table 3.10 Percent MB removal results of PdNPs/TiO_2 under solar light exposure for different durations.

Time (min)	%Removal
10	29.8
20	54.4
30	68.1
40	84.1
50	87.9
60	89.0

Finally, MB removal capacity of PEDOT and PdNPs/PEDOT was revealed under solar light illumination. The absorption spectra and percent dye removal capacities of the catalysts are given in Figure 3.15-16 and Table 3.11-12, respectively.

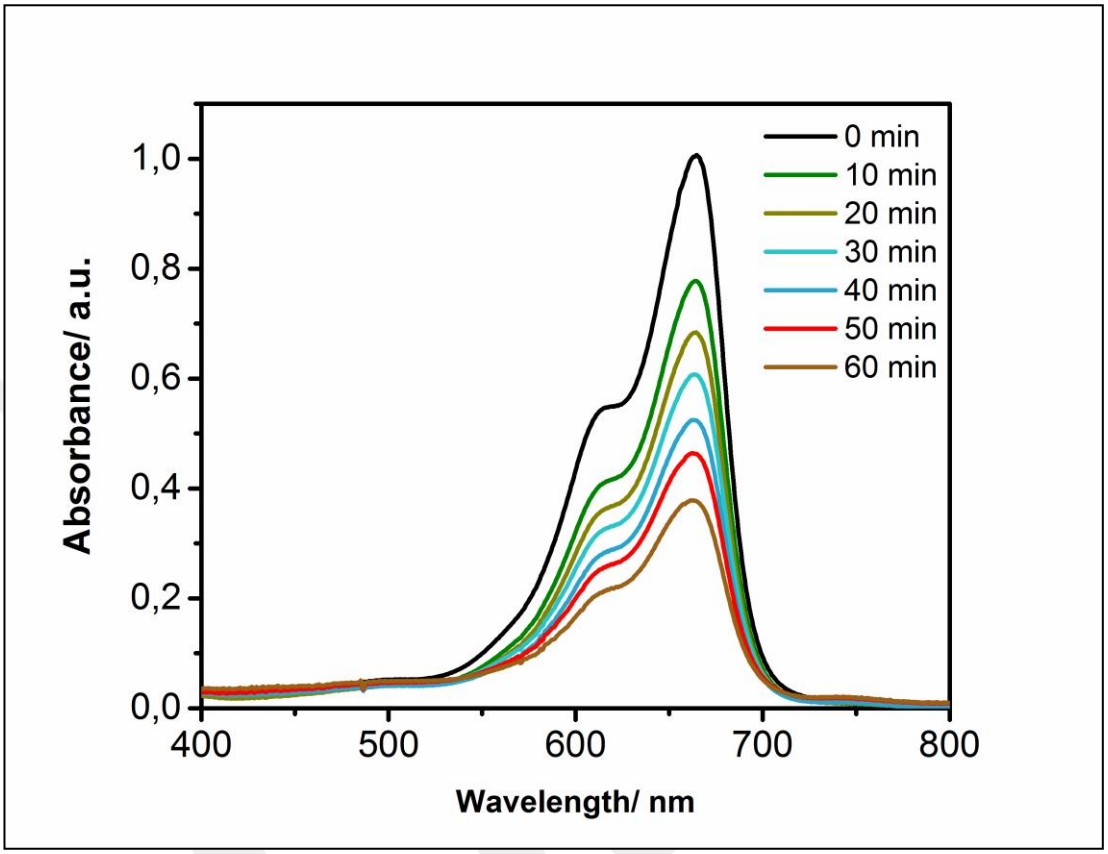

Figure 3.15 UV-Vis spectra of the MB solution processed with 10 mg of PEDOT under solar light illumination.

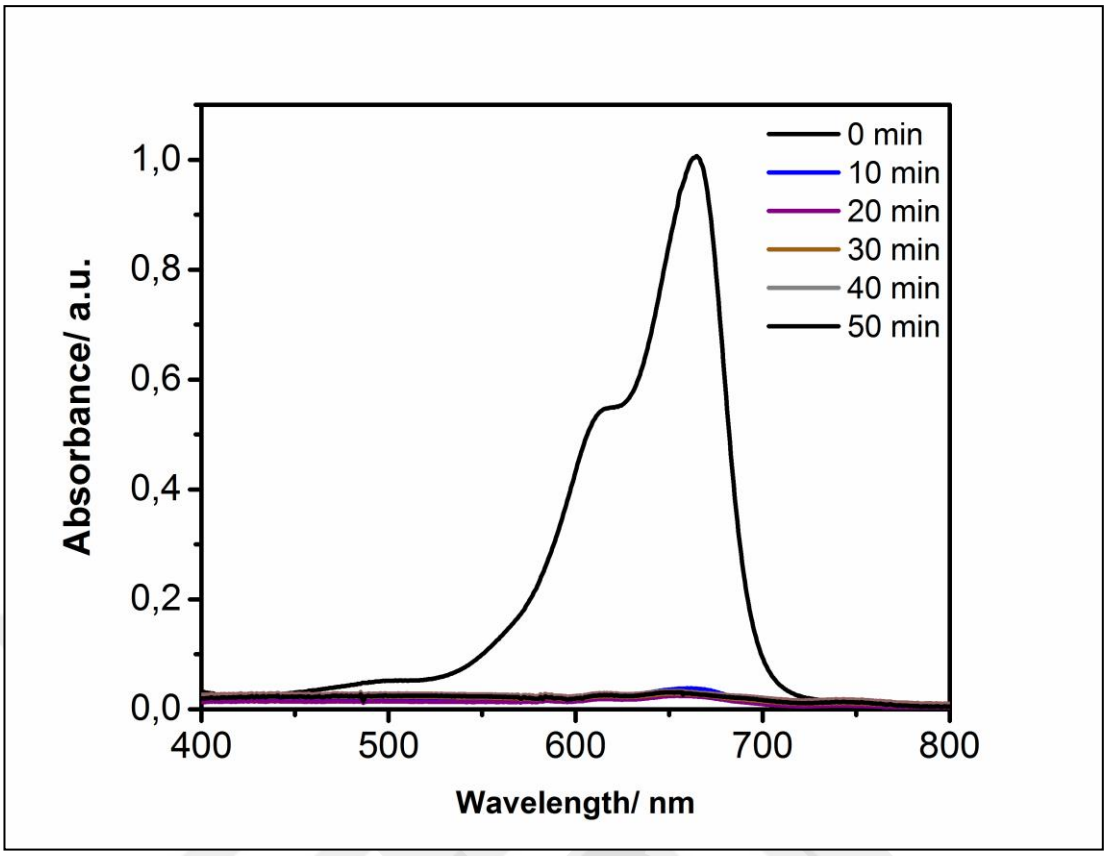

Figure 3.16 UV-Vis spectra of the MB solution processed with 10 mg of PdNPs/PEDOT under solar light illumination.

Table 3.11 Percent MB removal results of PEDOT under solar light exposure for different durations.

Time (min)	%Removal
10	22.8
20	32.2
30	39.8
40	48.1
50	54.1
60	62.7

Table 3.12 Percent MB removal results of PdNPs/PEDOT under solar light exposure for different durations.

Time (min)	%Removal
10	96.2
20	99.5
30	99.5
40	99.6
50	99.6

The comparison of the removal capacity of the all prepared catalyst under solar light exposure is given in Figure 3.17.

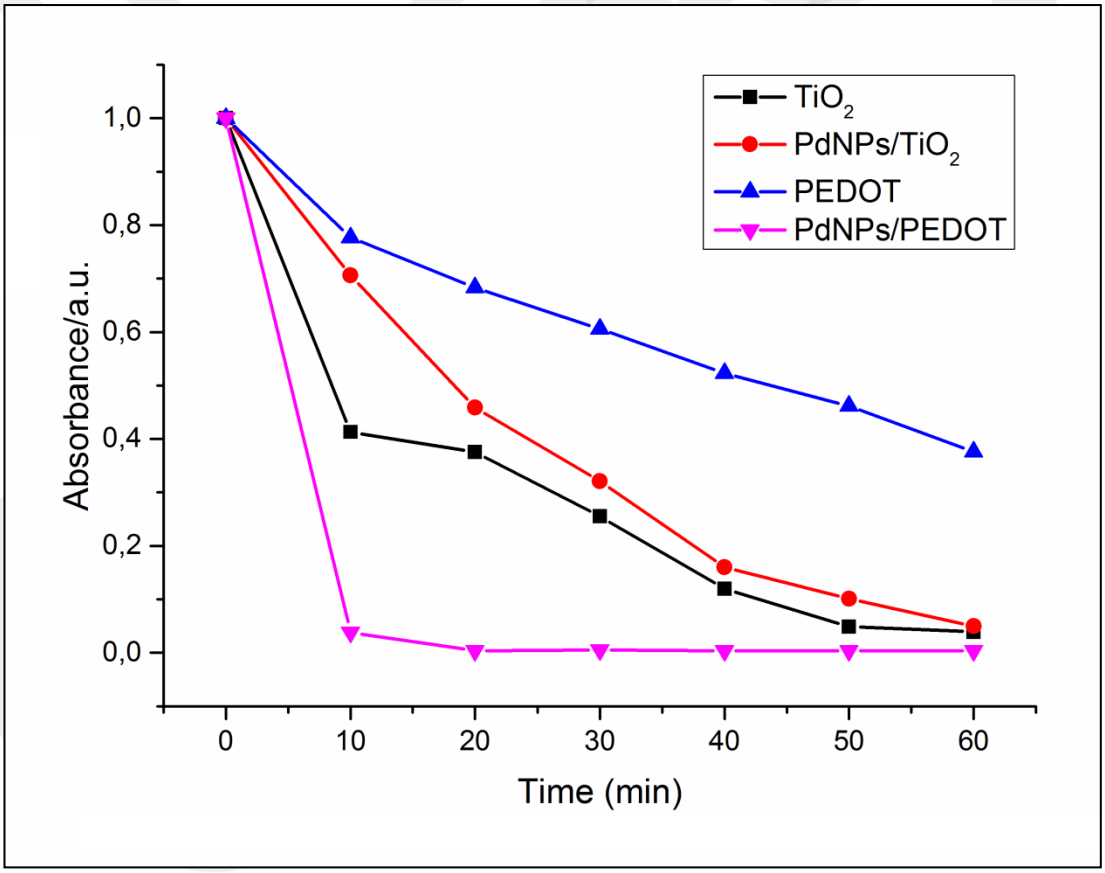

Figure 3.17 Comparative photocatalytic activities of TiO_2, PdNPs/TiO_2, PEDOT and PdNPs/PEDOT on MB degradation under solar light.

According to the results given above, when we compare the photocatalytic activities of commercial TiO_2 (P25, known to be one of the best active photocatalysts under UV light) and Pd nanoparticles modified TiO_2 with that of PEDOT and Pd nanoparticle added PEDOT on photodegradation of MB under solar light, PdNPs/PEDOT composite material exhibit the highest catalytic activity.

Figure 3.17 shows the summary of the results taken with the four different catalyst in the photocatalytic degradation of MB. Accordingly, complete degradation of MB has been obtained for TiO_2, PdNPs/TiO_2 and PdNPs/PEDOT, after irradiation for 90 min (Figure 3.13), 120 min (Figure 3.14) and 10 min (Figure 3.16) respectively. However, only 60% degradation has been achieved for PEDOT polymer under identical reaction conditions (Figure 3.15). In fact, the PdNPs/PEDOT catalyst displayed a significant MB photodegradation achieving nearly 100% degradation after 10 min irradiation under solar light (Figure 3.16). Interestingly, PdNPs/PEDOT also showed an efficient photocatalytic activity under UV light for MBand the photocatalytic activity was much higher than that of TiO_2 and PdNPs/ TiO_2 (Figure 3.13), which is known as one of the best photocatalyst under UV light. Hence PdNPs/PEDOT, the example of conjugated polymer nanostructures, because of their excellent photocatalytic activity and stability, can be considered as a new type of photocatalyst active not only under UV irradiation but also under solar light for environmental remediation.

CHAPTER 4

CONCLUSION

Organic conjugated photocatalysts show more advantages, including being light-weight, low-cost, sustainable, accessible, and processible, in comparison with their inorganic counterparts. The development of new organic conjugated photocatalysts (including hypercrosslinked polymers as a typical example) and further improvements in the activities are therefore highly envisaged.

In conclusion, palladium nanoparticles added PEDOT nanocomposite materials successfully prepared through an in situ polymerization of PEDOT and liquid impregnation method respectively. The PdNPs/PEDOT composite materials used as a photocatalytic material which showed enhanced photocatalytic activity in degradation of MB solution under both UV and solar light irradiation. The prepared catalyst degraded the MB solution completely in 20 min. The enhanced photocatalytic activity of the PdNPs/PEDOT nanocomposite material under UV and solar light exposure is attributed to the synergistic effect between PEDOT, and Pd nanoparticles. Obtained results demonstrate that PdNPs/PEDOT nanostructures show exceptional high photocatalytic activities under both UV and solar light.

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