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Research Article

Green Preparation of *Stachys Eudenia*-Derived Carbon Quantum Dots and Their Photocatalytic Applications

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ABSTRACT

In this present work, the composites were obtained from carbon quantum dots and TiO_f via green synthesis and the photoactivities of these composite structures were investigated under ultraviolet light. Carbon quantum dot was obtained from *Stachys euadenia* which is an endemic plant found only in southern Türkiye. Carbon quantum dot-TiO_2 nanocomposites were fabricated via facile hydrothermal approach which is an easy and effectual method to obtaining of environmentally friendly, low cost and well crystallized nanoparticles. The structural and morphological characteristics of these nanocomposites were investigated by X-ray diffraction, tunneling electron microscopy and scanning electron microscopy. Also, optical analyses of carbon quantum dots were carried out by absorbance and fluorescence spectroscopy. Photocatalytic activity of TiO_2 and carbon quantum dot-TiO_2 nanocomposites were investigated under ultraviolet light illumination with the decomposition of methylene blue dye. Carbon quantum dot-TiO_2 nanocomposites show a better activity than TiO_2.

Keywords: *Green synthesis, Carbon Quantum Dots, Photocatalysis*

Stachys Eudenia'dan Türetilmiş Karbon Kuantum Noktalarının Yeşil Sentezi ve Fotokatalitik Uygulamaları

ÖZ

Bu çalışmada, karbon kuantum noktaları ve TiO_2 kombinasyonu elde edilmiştir ve bu kompozit yapıların ultraviyole ışık altındaki fotoaktiviteleri rapor edilmiştir. Karbon kuantum noktası, sadece Türkiye'nin güneyinde bulunan endemik bir bitki olan *Stachys euadenia*'dan elde edilmiştir. Karbon kuantum nokta-TiO_2 nanokompozitleri, çevre dostu, düşük maliyetli ve iyi kristalleşmiş nanoparçacıkların elde edilmesinde basit ve etkili bir yöntem olan kolay hidrotermal yaklaşımla üretilmiştir. Bu nanokompozitlerin yapısal ve morfolojik özellikleri; X-ışını kırınımı, tünelleme elektron mikroskopisi ve taramalı elektron mikroskopisi analizleri ile karakterize edilmiştir. Ayrıca, karbon kuantum noktalarının optiksel analizleri soğuurma ve floresans spektroskopisi ile gerçekleştirilmiştir. TiO_2 ve karbon kuantum nokta-TiO_2 nanokompozitlerinin fotokatalitik aktivitesi ultraviyole ışık aydınlatması altında metilen mavisi boyasının bozulmasıyla incelenmiştir. Karbon kuantum nokta-TiO_2 nanokompozitleri, TiO_2'den daha iyi bir aktivite göstermiştir.

Anahtar Kelimeler: *Yeşil sentez, Karbon kuantum noktalar, fotokataliz*

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I. INTRODUCTION

Water pollution, which causes irreparable harm to human health and nature, is one of the major problems in the world today. The effluents of textile plants contain toxic and carcinogenic dyes that are dangerous for humans and the aquatic ecosystem. Many techniques likely ozonation, flocculation, adsorption on activated carbon, reverse osmosis, biosorption and nanofiltration are used to remove these dyes from wastewater [1]–[3] . Unlike these conventional methods, photocatalysis as a low-cost, environmentally friendly method for the water purification has recently attracted great attention. The term photocatalysis is a phenomenal process, in which materials that are exposed to light and change the reaction rate are used as photocatalysts. Since the first report work on the photocatalytic water splitting on titanium dioxide (TiO_2) by Fujishima and Honda in 1972 which was a groundbreaking study [4], great endeavors have been made to develop novel and efficient photocatalysts. In this context, many materials from semiconductors to carbonaceous materials and their composites have been employed as photocatalysts.

Among new photocatalysts, carbon quantum dots (CQDs) are a rising star in the carbon family due to their attractive properties such as abundance, low cost, low toxicity, chemical inertness, excellent aqueous solubility [5].CQDs have a great potential in photocatalytic applications due to their electron transfer and efficient light harvesting properties[6].CQDs were coincidentally discovered during the isolation of single-walled carbon nanotubes (SWCNTs) from the crude soot and this isolated component was defined a mixture of fluorescent nanoparticles by Xu et al. in 2004 [7]. Sun et al. denominated these fluorescent carbon nanoparticles as “carbon quantum dots” in a groundbreaking study where these nanoparticles were produced by laser ablation [8]. CQDs have great potentials in many application areas of nanotechnology since their discoveries. For instances, CQDs obtained from polymer/silica nanocomposites was used as bioimaging agents [9]. CQDs-gold nanoparticles were used as a biosensor for glucose in a study reported in 2019 [10]. N-doped carbon quantum dots combined with TiO_2 were applied as metal-free sensitizers in dye-sensitized solar cells [11]. Li et al. reported a CQD-TiO_2 combination which was used as an electron transfer layer in perovskite solar cells and achieved 19% efficiency [12]. Baslak et al. used the N containing CQDs obtained from kombucha fungus via green synthesis and applied them as electrode materials for supercapacitor structure [13] . In another report by Baslak et al., N doped CQDs fabricated from fermented kombucha tea were used an additive in perovskite solar cells and passivated the trap states decreasing the nonradiative charge recombination in the perovskite layer [14] . There are studies in the literature that CQDs are also used for drug delivery systems [15], [16]. Among the many nanotechnological applications of CQDs, photocatalytic studies also draw attention [16] . The basis of photocatalytic process is the photogeneration of electrons and holes. However, many semiconductor photocatalysts suffer from high recombination rate of electron and hole pairs. In addition, ultraviolet (UV) light is required to excite ground state electrons to the conduction band as a consequence of their wide band gaps. Carbon quantum dots can improve the photoactivity of photocatalysts due to their ability to transfer electrons quickly.

In order to produce CQDs, many routes have been developed including electrochemical oxidation[17], combustion [18],plasma induced [19], sonochemical [20] , hydrothermal [21],arc-discharge[22], microwave assisted [23]and laser ablation methods [8]. Among these methods, hydrothermal is a functional process for the synthesis of CQDs due to its affordability and suitability for green synthesis which is an environmentally friendly and low-cost method, has attracted a lot of attention recently.

Many natural resources were used to obtain the CQDs in the literature. For instances, Zhou et al. produced the high quality fluorescent CQDs using watermelon peel waste as a novel carbon source [24]. Tyagi et al. produced CQDs from lemon peel waste and developed composites of CQDs and TiO_2 nanofibers [25]. Ramezani et al. synthesized CQDs from quince via microwave irradiation and used these CQDs as fluorescence probe for arsenic detection[26].Also, when the photocatalytic activities of these nanofibers were examined, it was seen that the composites provided a better degradation. Li et al. prepared fluorescent carbon nanodots from ginger and these CQDs were used to hinder the growth of carcinoma cells [27].Alam et al. synthesized CQDs with down and up conversion photoluminescence properties via a green low-temperature hydrothermal method from cabbage and investigated the photostability and low cytotoxicity of CQDs [28]. In another interesting study, N and S co-doped carbon dots were prepared by hydrothermally where orange peel was used as the carbon resource by Karaman [29]. Anchoring these co-doped carbon dots to 3D graphene networks the electrocatalytic activity of the CDs were improved. Ramar et al. combined undoped CQDs and nitrogen doped CQDs from citrus grandis (pomelo fruit) via hydrothermal method and investigated photocatalytic degradation of methylene blue (MB) using these CQDs as photocatalysts [30]. In another interesting study, CQDs were synthesized from grass via hydrothermal method for removing pollutions using photocatalysis [31]. Tamarind was used in the synthesis of CQDs using one pot hydrothermal method by Asha Jhonsi and Thulasi [32].Tamarind carbon dots were characterized by some structural, morphological and optical analyses. Also, fluorescence quenching measurements were performed and it was explained that the fluorescent quenching mechanism was because of the delay of the electron-hole recombination. In another notable study, cobalt ferrite (CoFe2O4)-CQD magnetic nanocomposites were synthesized using turmeric in the production of CQDs [33].Besides, photocatalytic activities of the magnetic nanocomposites were appraised by the photodegradation of azo dyes under UV light. Li et al. prepared photoluminescent carbon nanodots (C-dots) using soya bean grounds via a facile and green technique [34]. These carbon nanodots were characterized by optical, structural and morphological analyses. Heng et al. prepared nitrogen doped CQDs using green oil palm frond [35].By combining nitrogen-doped CQDs with TiO_2, the photocatalytic activities of these composites were investigated by reducing MB under visible light radiation. In one of the most recent studies, Shafique et al. developed a facile synthesis method of CQD/TiO_2 nanocomposites and the degradation of methyl orange (MO) under direct and indirect sun illuminations [36].

In this present study, we synthesized CQDs and CQD-TiO_2 composites from *stachys euadenia* which is an endemic plant via a facile hydrothermal treatment. Structural and morphological properties of the nanoparticles were investigated with X-ray diffraction (XRD), scanning electron microscopy (SEM) and tunneling electron microscopy (TEM) analyses. Besides, absorbance and fluorescence spectra of CQDs were obtained. Comparing the photocatalytic activities of CQDs and CQD-TiO_2 composites, it was seen that the composites degraded MB solution better under UV irradiation.

II. MATERIAL AND METHOD

A. MATERIAL

S. euadenia P.H. Davis is a locally endemic plant species belonging to the Lamiaceae family and found in Southern Anatolia Region of Turkey [37].The green leaves of *S.euadenia* was used in the experiment. TiO_2 nanopowder and MB solution were purchased from Sigma-Aldrich.

B. METHOD

A. 1. Solution Preparation

Dry *Stachys euadenia* leaves were grinded with grinder. 0.5 g was weighed from the ground leaves. 0.5 g leaf was taken into 60 ml pure water. It was made homogeneous in a 400-rpm magnetic mixer at 60 °C at 1 hour. 1 ml Ethylenediamine (EDA) was added to the homogeneous solution.

A. 2. Hydrothermal Synthesis

The solution was placed to the stainless-steel autoclave. The temperature of the oven was set 140 °C. The autoclave was placed in the oven which reaches to 140 °C and kept in the oven for 4 hours. After 24 hours, the autoclave was taken out the oven and opened.

A. 3. CQD Purification

The solution removed from the autoclave was applied a coarse centrifugation within 3 minutes at 4000 rpm. Ultracentrifuge was applied to the separated liquid sample at 15,000 rpm for 10 minutes. In order to make it purer and finer, large particles were removed by ultracentrifugation, and it was passed through a syringe filter. The purified sample was dried in a glass petri dish at room temperature for 48 hours.

A. 4. CQD-TiO_2 Synthesis

0.2 g of TiO_2 was added to a solution of 10 ml of distilled water and 3 ml of ethanol. The obtained solution was mixed in a magnetic stirrer. It was stirred at 400 rpm at 25°C for 1 hour. When a homogeneous solution was formed, 7 ml of CQD solution at a concentration of 4 mg/ml was added into it. It was stirred at room temperature for another 1 hour. After 1 hour, the thoroughly dissolved sample was taken into the Teflon of the stainless-steel autoclave and the hydrothermal process was performed at 140°C for 4 hours. Purification and drying processes were applied. The production scheme of the whole study is shown in Figure 1.

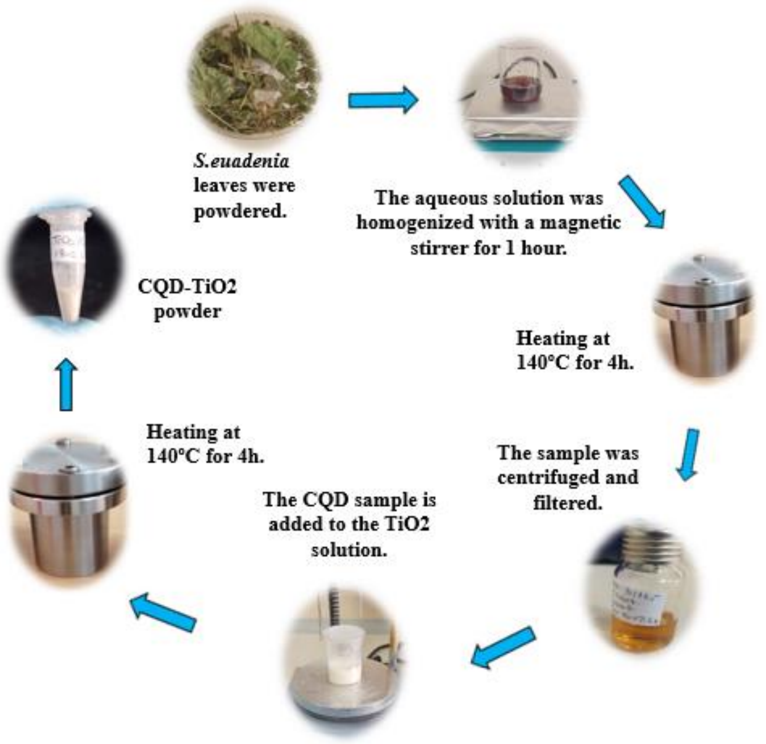

Figure 1. *Synthesis of CQD-TiO_2*

III. RESULTS AND DISCUSSION

A. Structural Analysis

Figure 2a, b and c represent the XRD patterns of pure TiO_2, CQD and CQD-TiO_2 composites. As seen in Figure 2a, the diffraction peaks of pure TiO_2 confirm the mixed phases of both anatase and rutile. While the diffraction peaks observed at 25.6, 38.1, 48.3, 54.2, 55.4, 62.8 and 75.3 correspond to anatase phase, 27.7, 36.3, 41.5, 56.8, 69.1 and 70.5 correspond to rutile phase of TiO_2. In Figure 2b, there is a broad peak at the vicinity of $2\theta=21°$ which is associated with the amorphous nature of CQDs. Figure 2c shows the diffraction peaks of the composite structure.

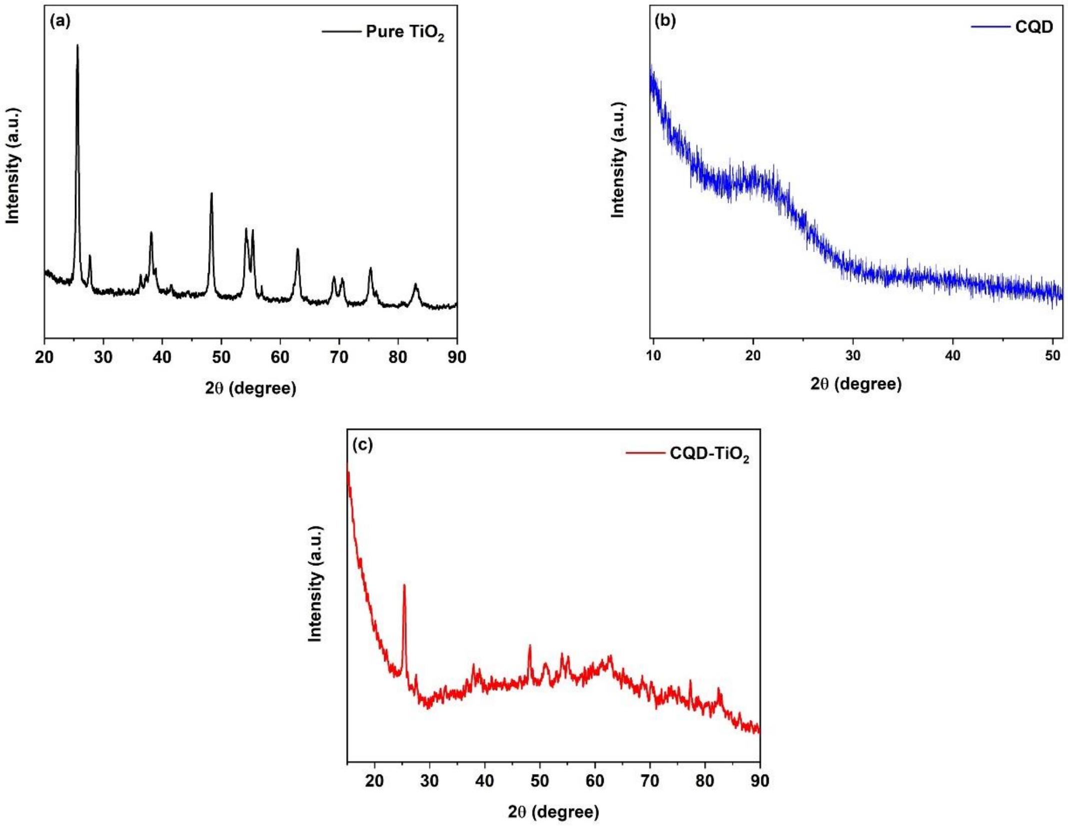

Figure 2. *XRD patterns of (a) pure TiO_2 (b) CQD and (c) CQD-TiO_2 powders*

B. Optical Analysis

Figure 3 shows absorbance and fluorescence spectroscopy of CQD from derived Stachys Euadenia. The absorption curve of the obtained carbon dots in the UV-visible region appears as a very wide peak, which is assigned to the π-π* transition bands in this region. Wide absorption bands can also be explained by the fact that they have complex band structures and random energy levels. When excited at 360 nm, CQDs show a broad emission peak that is blue-green and falls in the range of about 400-550 nm [38], [39].

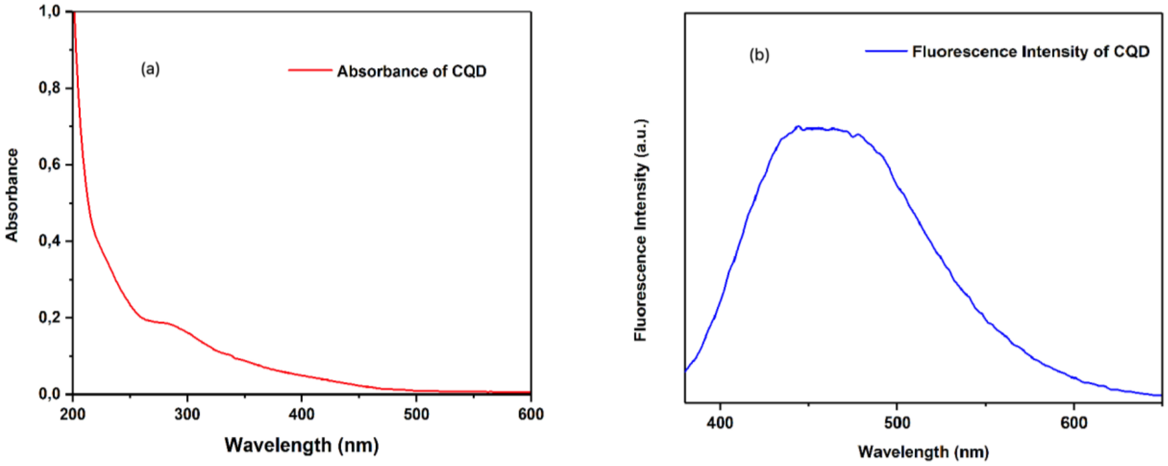

Figure 3. *(a) Absorbance and (b) fluorescence intensity of CQD derived from Stachys Euadenia.*

C. Morphological analysis

The morphologies of the pure TiO_2 and CQD-TiO_2 nanocomposites were investigated by using SEM and TEM given in Figure 4 and Figure 5, respectively. SEM images were obtained at 40000 magnifications. Compared to TiO_2, particulate structure of the composite will increase the porosity. A porous structure provides a higher surface area which is a sign of the adsorption property of the materials.

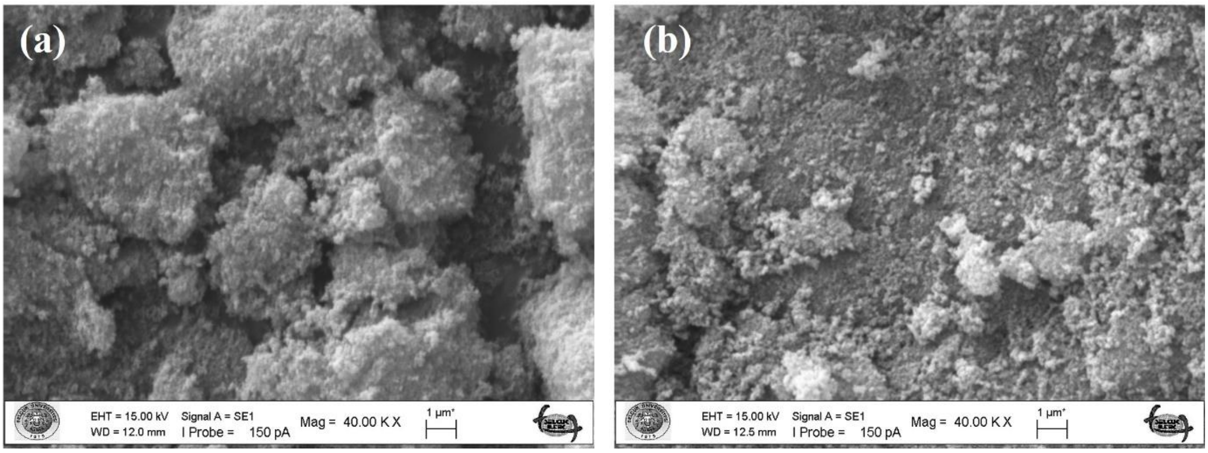

Figure 4. *SEM pictures of a) the pure TiO_2 and b) CQD-TiO_2 nanopowders*

Figure 5 shows the TEM image of CQD derived from Stachys Euadenia. As can be clearly seen from the figure, the particle shapes do not show a complete sphericity and it is seen that they have an average size of about 5-20 nm, also particle distribution is identified as homogeneous.

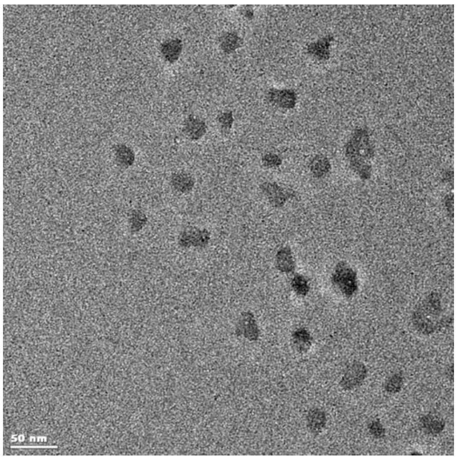

Figure 5. *TEM image of CQD from Stachys Euadenia*

D. Photocatalytic Activity

The appraisal of photocatalytic activity of the pure TiO_2 and CQD-TiO_2 nanoparticles was demonstrated by monitoring the MB solution under UV light irradiation. MB solution with a concentration of 12 ppm was prepared with 50 ml of deionized water. After adding 10 mg of photocatalyst to the dye solution, it was kept in the constant stirring for 30 minutes in the dark to establish adsorption-desorption equilibrium. The dye solution was exposed to UV light for a total of 130 minutes in the photocatalytic reactor and absorbance measurements were performed by taking samples at 10-minute intervals. These absorbance spectra were showed in Figure 6 for both photocatalysts. Main peak was observed in the vicinity of 664 nm. As it seen in Figure 6, CQD-TiO_2 composites showed better degradation than the pure TiO_2 nanoparticles. This increase in the degradation is also depicted in the degradation rate graph over time in Figure 7. Degradation rate can be acquired using the expression $(C_0 - C_t)/C_0 \times 100$. Where C_0 and C_t are obtained from the absorbance spectrum and correspond the initial and any time concentrations, respectively. When TiO_2 is stimulated by UV light, electrons located in the valence band are excited and move to the conduction band. In the meantime, they leave holes behind. While the electrons interact with the water in the dye solution to form hydroxyl radicals, the holes interact with the water to form superoxide radicals. However, the recombination rate of photogenerated electrons and holes is high in TiO_2. CQDs enable electrons to reach the surface quickly and decrease the recombination of charge carriers due to their extraordinary conductivity properties. This induces an increase in the degradation of the dye. Photocatalytic degradation kinetics is generally modeled by the Langmuir-Hinshelwood equation [40] which is given in equation 1:

$$-\ln\left(\frac{C_t}{C_0}\right) = k_{app}t \tag{1}$$

Here, k_{app} is apparent kinetic rate constant and calculated using $ln(C_t/C_0)$ according to the irradiance time which is given in Figure 8. Kinetic rate constants were found 0.00515 min^{-1} and 0.07722 min^{-1} for the pure TiO_2 nanoparticles and CQD-TiO_2 composites, respectively. So that, k_{app} value of the composites is 28.7% higher than pure TiO_2 nanoparticles.

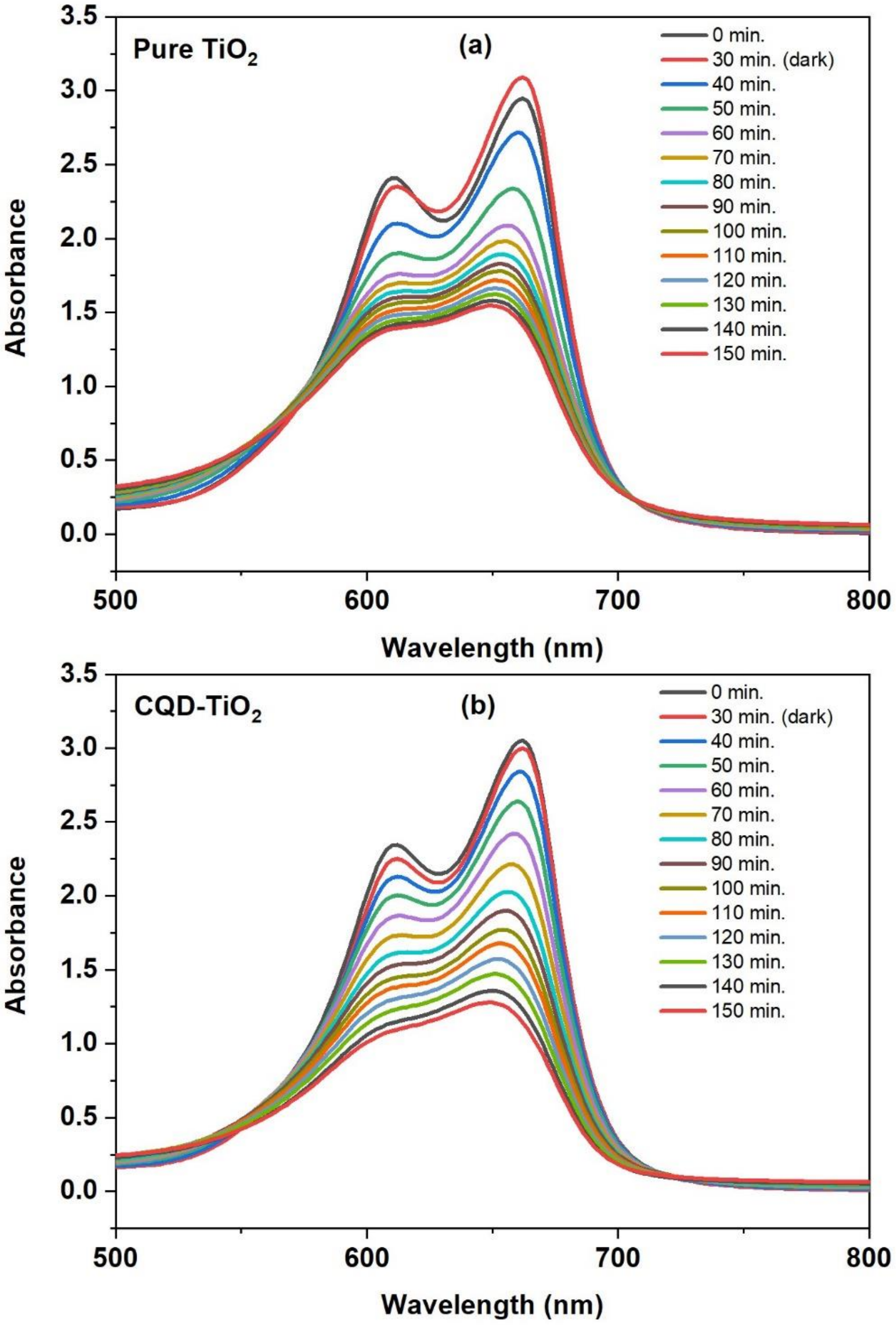

Figure 6. *Absorption spectra of UV light degradation of MB solutions containing (a) pure* TiO_2 *and (b) CQD-*TiO_2 *nanopowders*

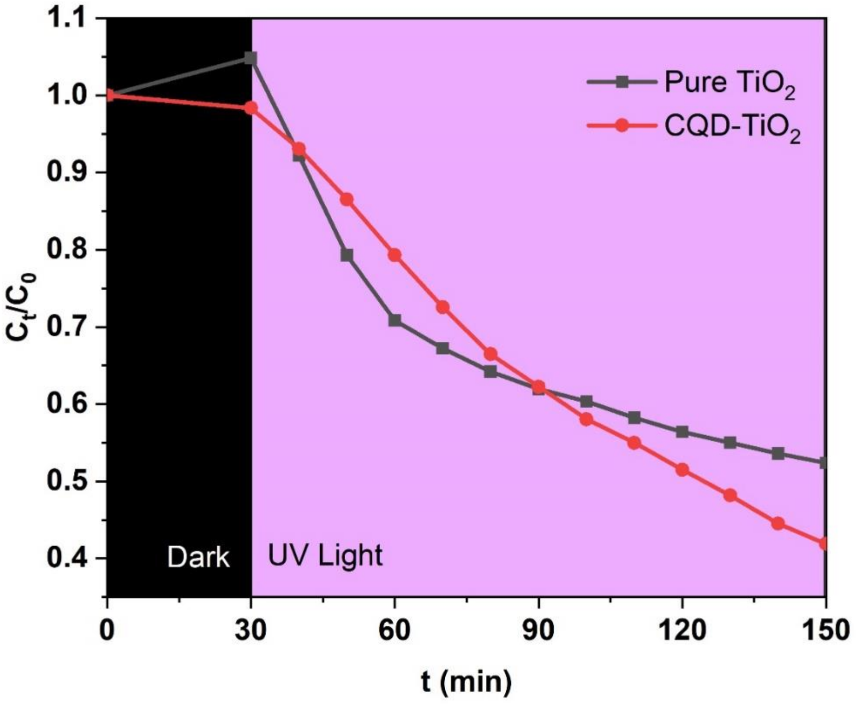

Figure 7. Concentration ratio of the pure TiO_2 and CQD-TiO_2 nanopowders

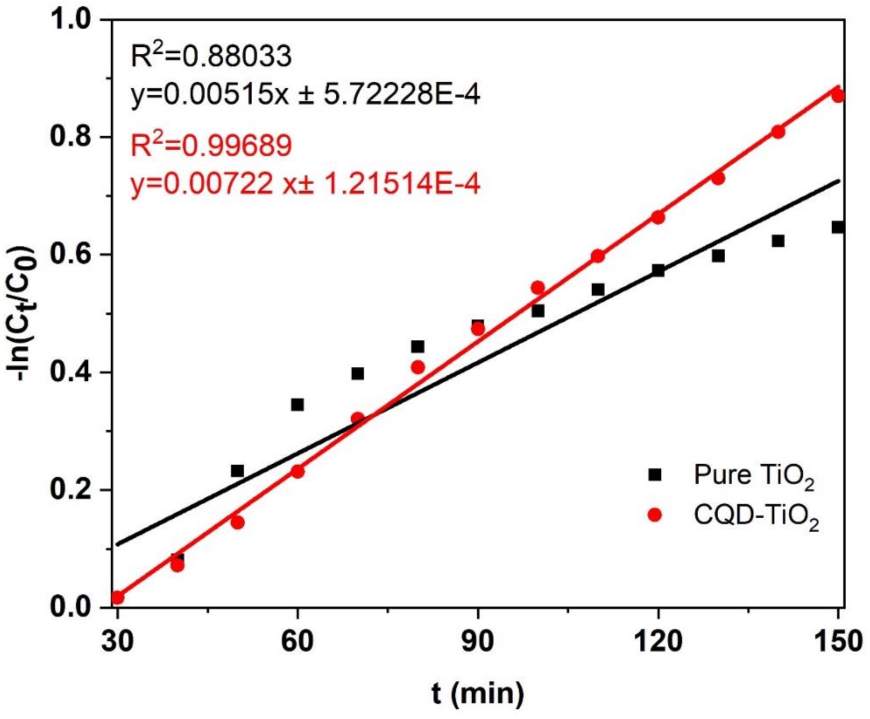

Figure 8. The pseudo first-order kinetic model of photocatalytic performance of the pure TiO_2 and CQD-TiO_2 nanopowders under UV light irradiation.

IV. CONCLUSION

In this study, pure and CQD-TiO_2 nanoparticles were synthesized by a facile and green hydrothermal method. The XRD results of TiO_2 show that rutile and anatase mixed phases due to inner temperature of autoclave during the hydrothermal process. SEM image of CQD-TiO_2 depict a more porous structure than the pure TiO_2. The photocatalytic activities of the nanocomposites were appraised by the photodegradation of MB under UV light irradiation. CQD-TiO_2 nanocomposites exhibited a better performance than the pure one due to fast electron transfer ability of CQDs.

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