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Green Synthesis of C-quantum Dots Modified ZnO Nanophotocatalyst: The Effect of Different Solvents Used in Production of C-quantum Dots Modified ZnO Nanophotocatalyst on Photocatalytic Performance

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ABSTRACT

Access the quality and sufficient amount of water is started to being problem with population increasing. One of the way to behalf the solution of this problem is usage waste water treatment in industry and agriculture. Wastewater treatment methods have disadvantages of being costly and producing secondary pollutants, photocatalysis, which is one of the advanced oxidation methods that is more advantageous and effective in removing pollutants, is promising. The newest member of nanomaterial, C-quantum dots (CQDs) has been increasingly get attention on lots of field including photocatalyst. Semiconductors are commonly used in photocatalysis however, they have electron pair recombination problem that results decreasing of efficiency. Doping semiconductors with different nanomaterials is one of the easiest ways to get over the problem. Recently CQDs has been started to used as dopping agent. Solvothermal method is among the easiest and environmentally friendly methods in nanomaterial synthesis. In this study, the effect of dimethylformamide, dimethylsulfoxide, ethylene glycol and water as solvothermal solvent on the photocatalytic efficiency of C-modified ZnO nanoparticles (CQDs@ZnO NPs) was investigated for the first time in the literature. Photocatalytic performance of CQDs@ZnO NPs was investigated on the photocatalytic degradation of methylene blue (MB). Angora mohair has been used as a CQDs source for the first time in the literature. Photocatalytic degradation performances of CQDs@ZnO NPs for MB at 300 min were 82.4%, 87.6% and 99% for ethylene glycol-water mixture, DMSO and DMF, respectively. The results proved that solvent type for solvothermal synthesis procedure has important role for photocatalytic performance of CQDs@ZnO NPs.

Keywords: Photocatalytic degradation, solvothermal synthesis, C-quantum dots, Angora mohair, ZnO NPs.

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Introduction

One of the biggest humanity concern is access to clean and sufficient water owing to global warming, climate change and population growth. According to United Nations Water Development Report 2020, 2.2 million people do not have access to clean water beside %55 of population sanitation. In respect of report waste water treatment is consider as an essencial solution to global warming because of waste water is source of methane gas due to undissociated organic waste that causes green gas effect [1]. Adsorption, membrane separation, coagulation and advanced oxidation processes such as photocatalysis are used as water treatment process. However adsorbtion, membrane separation and coagulation methods have disadvantages like high cost and occur secondary pollutant [2]. Photocatalysis, one of the advanced oxidation methods have a lot of promises thanks to being an effective way for degradation of pollutants [3]. Photocatalysis is the reaction by utilized light and semiconductor. The light is absorbed by substrate and the catalytic reaction that named photocatalysis takes place on the substrat's surface [4]. Zinc Oxide (ZnO) and Titanium dioxide (TiO_2) are the most commonly used photocatalysts. TiO_2 has superhydrophobic, non toxic, chemically stabil properties beside it is strong oxidizer therefore degradation of organic pollutants [5]. Furthermore ZnO is physically and chemically stable, nontoxic and harmless beside it has low cost, biocompatible, high redox potantial. Although ZnO and TiO_2 has the almost same band gap (3.37 eV and 3.2 eV), ZnO exhibit greater photocatalytic activity thanks to electron mobility of ZnO is much higher than TiO_2 [6,7] . One of photocatalysis dissadvantages is rapid recombination of photogenerated electrons and hole that lead to low quantum yield

When a semiconductor like ZnO is excited by light the photocatalysis process starts. Firstly electrons are moved from valance band to conductive band therefore the valence band is charged positively. The conduction band

electrons catches protons from oxygen that is presented on weather or water hence the oxygen is charged negatively and become superoxide ion. The superoxide ion is react with organic pollutants and makes the pollutant decomposed to CO_2 and H_2O. On the other hand, protons in the valence band react with H_2O in water or moisture and OH^- ions are formed as a product. The reactive OH^- ions are carried out reaction with organic pollutants and makes the pollutants have degraded to CO_2 and H_2O [8].

Doping metal nanoparticles and carbon nanomaterials over the semiconductor's surface is one of the way to overcome the electron hole recombination drawbacks [8]. Recently many research proved that CQDs as the new class of nanoparticles is promising doping agent for semiconductor photocatalysts. CQDs are zero dimensional, water soluble, chemically stable, highly photo adsorbent nanomaterials. CQDs are cheap and non toxic thereby usage in catalysis, bioimaging and energy storage processes are desirable [9]. CQDs has been light absorber and electron reservoir therefore it has perfect electrical and optical properties. Many report has been published about CQDs being higly efficient photocatalytic material. The nano size of CQDs is resulted to difficulties to reusable therefore CQDs is doped to matrix like metal particles [10]. CQDs are synthesized by such as solvothermal, electrochemical oxidation, chemical oxidation, microwave excitation methods using a carbon source [11]. Electrochemical oxidaition method has disadvantages that being complex chemical reaction. The inability to synthesize homogeneous particles is the main problem of the chemical oxidation method. Microwave method is inexpensive and rapid. However it needs a lot of energy beside reaction conditions are uncontrollable. Solvothermal synthesis method is considered as one of the most effective methods in the production of CQDs doped materials. Solvothermal method has advantages like being enviroment friendly, taking place by one step reaction, having good dispersion and facile reaction condition comparing the other methods. The synthesis occur in solvent like water, ethanol, dimethylformamide, dimethylsulfoxide, stainless closed vessel named autoclove [12]. Solvent type has an important role in the carbonization rate of the carbon source and therefore in different performances in the methods in which it is used [13-15].

In this study, the effects of the use of aprotic solvents dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) and a protic solvent ethylene glycol-water mixture on the photocatalytic performance of CQDs@ZnO NPs were compared on the photocatalytic degradation of MB.

Another important parameter that affects the morphology, chemical content, and thus the in-use performance of CQDs is the type of carbon source used. Many studies have carried out about different organic carbon source usage for green synthesis of CQDs. For intance, instant coffee [9], citric acid [15] and urea anthracite [16] and aloe [17] have been used for carbon sources. In the present work, mohair was used as carbon source of CQDs for the first time in literature. Mohair is Angora goat's feather which has unique properties such as being resistant, dirt-proof, showing excellent insulation properties. Mohair has slippery and softness unlike the other goat's wool thanks to the oil layer on the surface that named as yolk [18]. Herein, C-quantum dots modified ZnO nanophotocatalyst was synthesized from mohair by using DMF, DMSO and water-glycol mixture as solvothermal solvent. This study was carried out to examine how the photocatalytic efficiency of carbon dots will change in different hydrothermal synthesis solvent medium.

Experimental

Materials and Apparatus

Angora mohair was obtained from Republic of Turkey Ministry of Agriculture and Forestry Çankırı Directorate of Provincial Agriculture and Forestry. Zinc chloride (ZnCl2) and ethylene glycol with 99% purity were obtained from Merck. NaOH pellets and N,N-dimethylformamide (%99) were purchased from Sigma-Aldrich. The degradation reactions of MB was carried out in a photochemical reactor had a UV irradiation source of 380 nm wavelength with a power of 400 W. The degradation rate of MB was calculated using the decrease in absorbance values measured by the UV-visible spectrophotometer (Perkin-Elmer Lambda 25 UV Visible Spectrophotometer). To study the morphology and size of nanomaterials, SEM images was taken by Gemini SEM500-71-08.

Synthesis of ZnO NPs

ZnO NPs were fabricated using the hydrothermal synthesis process according to the previous work of Şakir et al. [19] Brifely 2 g $ZnCl_2$ was dissolved in 25 ml ultra pure water and 5 g NaOH was dissolved in 25 mL ultra pure water NaOH solution was added dropwise to the $ZnCl_2$ solution stirred in the magnetic stirrer, and the resulting solution was then subjected to the hydrothermal synthesis procedure at 180 °C for 12 hours. ZnO NPs synthesized was centrifuged for separating to liquid phase from solid phase. The solid phase was washed with distilled water for twice and ehtyl alcohol for three times to remove contaminants. The resulting solid ZnO NPs was dried on oven at 60 °C [19].

Synthesis of CQDs@ZnO NPs

As pre-treatment, the mohair was washed with soap to clean and dried in the oven at 40 °C. 500 mg of ZnO NPs, 50 mL from one of the solvothermal solvents (DMF, DMSO, ethylene glycol/water (35/25)) was added into erlenmeyer and mixed for 30 min. Afterward 500 mg mohair is added to the solvent medium and mixed 30 min. The mixture was transferred to the autoclave of solvothermal reactor and put in an oven 180 °C for 12 hours. The reaction for DMSO was carried out at 220 °C. after the reaction was complete, the mixture was

centrifuged to separate CQDs@ZnO NPs from the liquid phase. CQDs@ZnO NPs was washed with distilled water for twice and ethyl alcohol for three times and dried at 60 ^{o}C.

Photocatalytic experiments

100 mg of each nanomaterial was placed in 100 mL of 10 ppm methylene blue solution and stirred for 15 hours in the dark for the solution to reach adsorption equilibrium. The mixture was exposed to 400 W UV light to carry out the photocatalytic reaction. The samples have taken every 30 minutes. The decrease in MB concentration versus phorocatalytic degradation time was calculated using the ratio of the decrease in the absorbance peak of MB at 664 nm wavelength in the UV-Vis spectrometer.

Results And Discussion

Characterization of Nanomaterials

To study the morphology and size of nanomaterials, SEM characterization studies were carried out (Figure 1). The avarage size of novel ZnO was 212 nm as shown in Figure 1A-C). When the synthesis of CQDs@ZnO NPs carried out via DMF, average ZnO size was around 80 nm and average CQDs size on the ZnO surface was 4 nm as shown in Figure 1D-F. While the synthesis reached out in DMSO solvent, average size of ZnO was 5.89 µm and CQDs size on the ZnO surface was 420 nm as shown in c) and g) by, lastly the avarage ZnO and CQDs size by ethylene glycol- water mixture were 200 nm and 35 nm, respectively.

Near IR analysis show that fingerprint of materials, difference between doped ZnO in the graph prove that doping has made changing on ZnO structure (Figure 2). According to the FTIR graph, entire NPs exhibit Zn-O characteristic stretch bonds peaks at around 400 cm-1. ZnO NPs shows double peak on around 2900 cm-1 which represent C-H stretch bonds, peak around 1500 cm-1 that attributed C-O and also peak around 1000 cm-1 that represent C-C bond. CQDs@ZnO Nps in DMF shows peak on 1020 cm-1,1262 cm-1,1655 cm-1 and 2900 cm-1 that means C-N, CH2, C-O-C and C-N bonds in addition 2966 cm-1 peak represent N-H bonds. C@ZnO NPs (DMSO) exhibit peaks on 1662 cm-1 and 2930 that are C-H, C=H bonds. CQDs@ZnO NPs (Ethylene Glycol+Water) exhibits peaks on about 1000 cm^{-1}, 1412 cm^{-1}, 1638 cm^{-1}, 2930 cm^{-1} and 3749 cm^{-1} which attributed C-C, C-N, N-H, C-H and O- H respectively (Figure 2). To sum up of all the FTIR results prove that functional groups on NPs depend on the solvent type. Therefore photocatalytic efficiency is depend on solvent type, either.

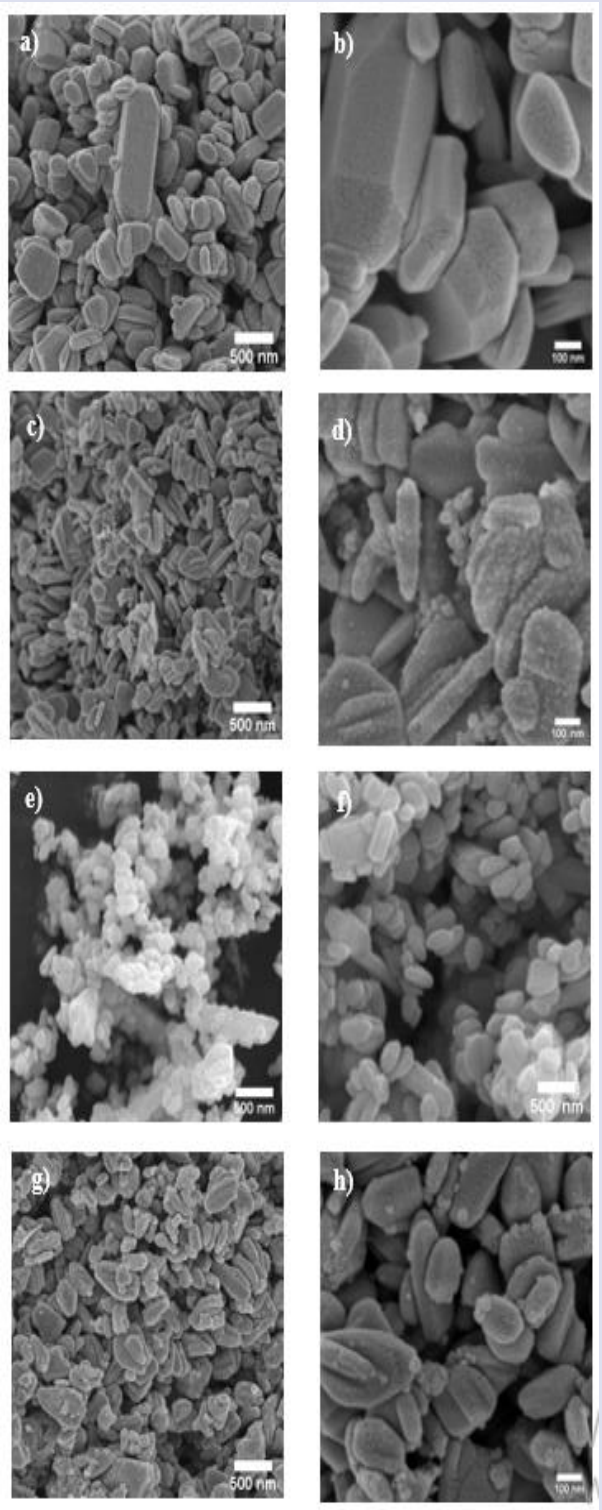

Figure 1. SEM images of nanomaterials, a-b) ZnO NPS (50K-10K), c-d) CQDs@ZnO NPs in DMF (50K-10K), e-f) C@ZnO NPs in DMSO (25K-15K), g-h) CDs@ZnO NPs (50K-10K).

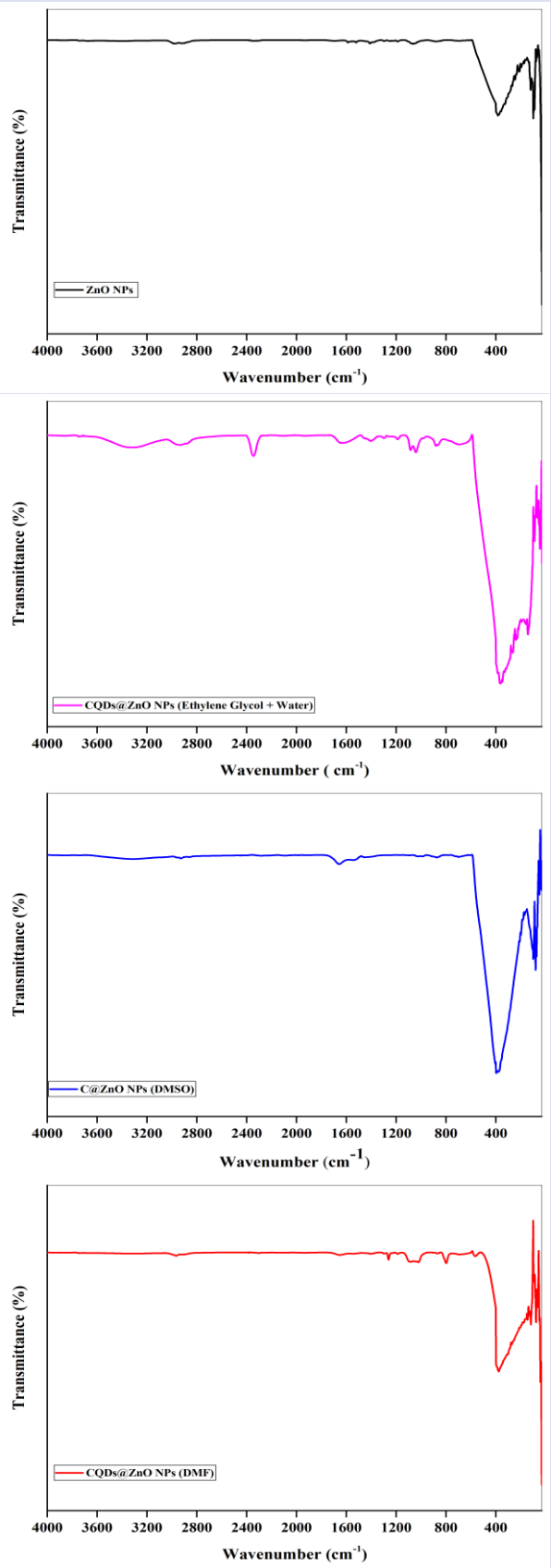

Figure 2. FTIR spectrums of ZnO NPs, CQDs@ZNO NPs in DMF, C@ZnO NPs in DMSO, CQDs@ZnO NPs in EthyleneGlycol+Water.

Acording to the Figure 3, XRD analysis result, the material shows ZnO NPs characteristic peaks which are located at 2θ, 31.9o, 34.5o, 36.4o,47.6o, 56.7o, 62.9o, 66.5o, 68.0o and 69.2o corresponded to the (100), (002), (101), (110), (103), (200), (112) and (201). The XRD analysis demonstrate that different solvent usage on the synthesis was not made changing on main structure of ZnO NPs. The results can be interpreted that density of CQDs on ZnO was lower than %4 percent and CQDs distributed uniformly [20].

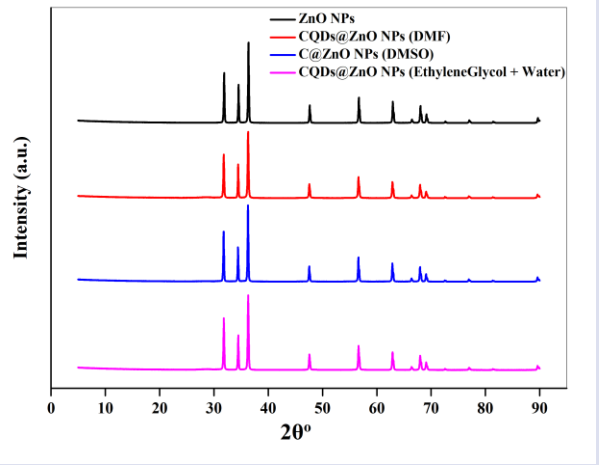

Figure 3. XRD spectrums of ZnO NPs, CQDs@ZNO NPs in DMF, C@ZnO NPs in DMSO, CQDs@ZnO NPs in EthyleneGlycol+Water.

In the manner of the Raman spectrum (Figure 4), all NPs shows ZnO characteristic peaks which are 308 cm^{-1}, 495 cm^{-1}, 607 cm^{-1} and 758 cm^{-1}, respectively. CQDs doped to ZnO did not cause a change in ZnO structure as can be seen in Raman Analysis.

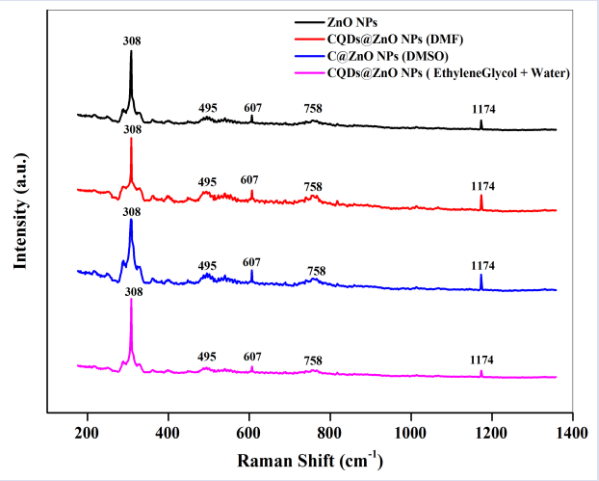

Figure 4. Raman spectrums of ZnO NPs, CQDs@ZNO NPs in DMF, C@ZnO NPs in DMSO, CQDs@ZnO NPs in Ethylene Glycol+Water.

Photocatalytic Efficiency of Different Doped Nanomaterials

The effect of dimethylformamide, dimethylsulfoxide, ethylene glycol and water as solvothermal solvent on the photocatalytic efficiency of C quantum dots-modified ZnO nanoparticles (CQDs@ZnO NPs) was investigated by adding 100 mg of CQDs@ZnO NPs in 100 mL of 10 mg·L-1 of MB solution and then these mixtures subjected to 400

W UV irridation for 300 min. The decrease in MB concentration was measured by using the ratio of the decrease in the absorbance peak of MB at 664 nm wavelength in the UV-Vis spectrometer (Figure 5). The reaction rate constant was calculated according to Langmuire Hinshelwood kinetics models. In the equation; Co represents initial MB dye concentration and C is MB dye concentration at irradiation time 't', in addition k is reaction rate constant [21].

$$\ln\left(\frac{Co}{C}\right) = -kt$$

The methylene blue degradation by CQDs@ZnO NPs that synthesis via ethylene glycol-water mixture, DMSO and DMF were calculated as 82.4%, 87.6% and 99%, respectively.

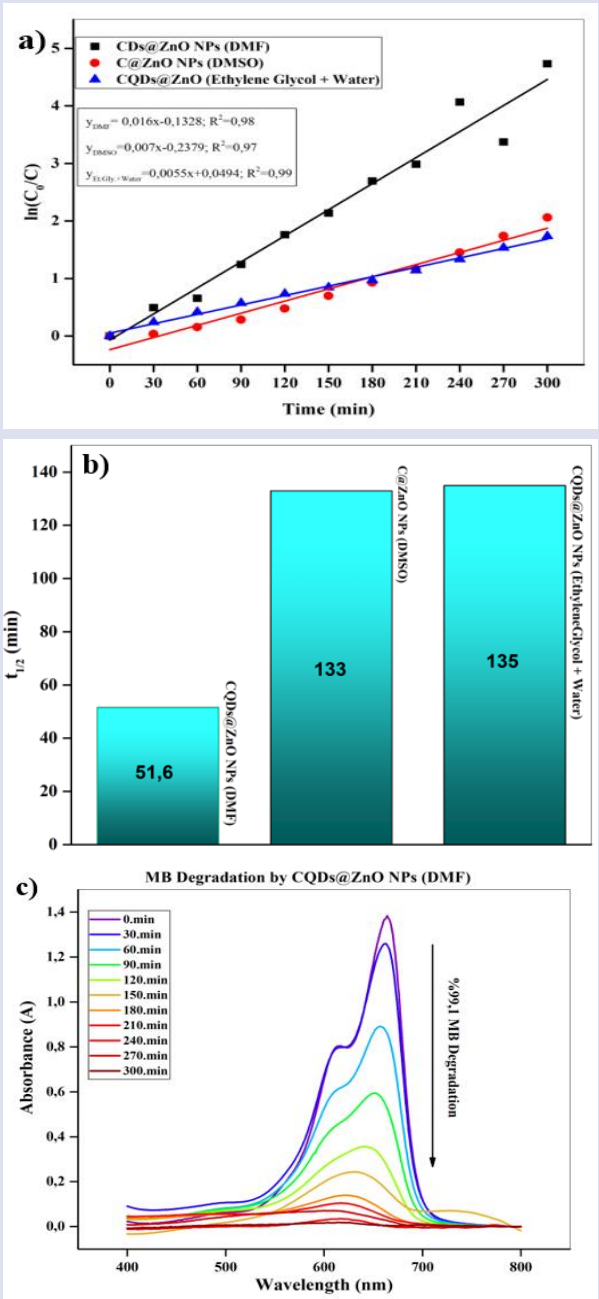

Figure 5. a) ln(C0/C) Graph of different NPs, b) Time taken for MB concentration to half by different NPs, c) UV-Vis result of MB degradation by CQDs@ZnO NPs (DMF).

The results shows that the most efficient material is CQDs@ZnO NPs that synthesized by DMF. This situation can be explained by the particle sizes of the nanomaterials synthesized with 3 different solvents. The ZnO nanoparticles in the CQDs@ZnO NPs produced using the DMF solvent had a smaller particle size, that is, a larger surface area. Higher surface area means that there are more regions where the photocatalytic reaction takes place and therefore higher photocatalytic performance. The half life of MB concentration were calculated as 51.62 min, 133 min and 135 min by CQDs@ZnO NPs that synthesis via ethylene DMF, DMSO and glycol-water mixture, respectively (Figure 5). The graph show that the methylene blue concentration is rapidly decreased when CQDs@ZnO synthesis by DMF solvent comparing to other nanomaterial. Beside reaction kinetic constants were calculated 0.0134 min^{-1}, 0.0052 min^{-1} and 0.0051 min^{-1} with the same row.

Reusability of CDs@ZnO NPs Photocatalyst

Besides being effective, the reusability of photocatalysts is important in terms of eliminating repetitive material production, cheapness of the process, minimizing the post-process waste problem and sustainability. For reusability studies, 100 mg of photocatalysis which synthesized with DMF was used. When first cycle was complated, the mixture was centrifugated, after that the liquid phase was removed. The remained CQDs@ZnO NPs was washed with distilled water and ethyl alcohol. Afterward the washed CQDs@ZnO NPs was added into 100 mL of 10 ppm MB solution and the procedure was cycled. MB has been almost entirely degraded by the CDs@ZnOinDMF when 100 mg of the photocatalysis's reusabilitiy is studied four times subjected by 400 W UV lamp for 300 minutes. The results obtained proved that the carbon photocatalyst could be used at least 3 times without any change in its performance (Figure 6). MB concentration were dropped 98.31%, 98.70%, 98.64% and 14.69% when CQDs@ZnO NPs used four times respectively. Reaction kinetic constants were calculated as 0.0134 min^{-1}, 0.016 min^{-1}, 0.0177 min^{-1} and 0.0085 min^{-1}. Half lifes of MB for each cycle were calculated as 31.62 min, 43.46 min, 33.07 min and 81.92 min.

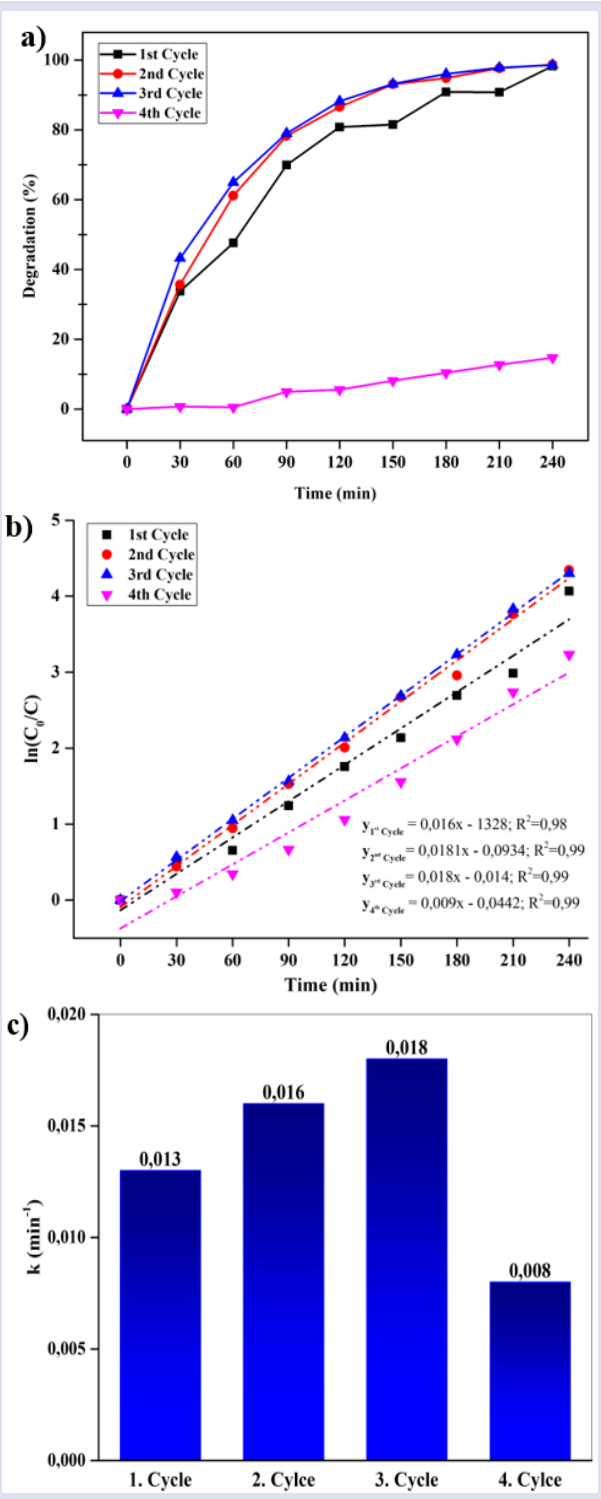

Figure 6. a) Reusability studies degradation percentage of MB concentration b) ln(C0/C) result of reusability studies. C)Reaction kinetic constants of each reusing reaction.

Conclusion

To conclude, angora mohair was used as carbon source for green synthesis of CQDs on ZnO NPs for the first time in the literature. Thus, one of a special Turkey's precies mohair has acquired an scientifical usage field. CQDs@ZnO NPs were synthesized in three different solvothermal solvent environments and proved that the solvent type significantly affects the morphology, size and photocatalytic properties of ZnO NPs. When DMF is used as solvent, the particles exhibit smaller size as shown as SEM images therefore the photocatalytic efficiency increase. Doping the semiconducters with CQDs is a promising way to improve photocatalytic efficiency of semiconductors.

Acknowledgements

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Conflicts of interest

The authors declare that there are no conflicts of interest.

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