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Bi Doped TiO_2 as a Photocatalyst for Enhanced Photocatalytic Activity

İlknur ALTIN[1*]

Abstract

This study is based on the preparation of TiO_2 and bismuth doped TiO_2 (Bi-TiO_2) nanoparticles by surfactant-assisted sol-gel approach. The physiochemical characteristics of prepared samples were examined by X-ray diffraction technique (XRD), Fiel emission scanning electron microscopy-energy dispersive analysis (FESEM-EDS), and UV-visible diffuse reflectance spectroscopy (UV-vis DRS). The XRD patterns revealed that the anatase crystal phase was only formed with high crystallinity. The band gap energies were measured to be of 3.11 eV for TiO_2-2 and 3.02 eV for Bi-TiO_2 by ultraviolet (UV)-visible diffuse reflectance spectroscopy, revealing that doping Bi improves the efficient interactive relation of the catalyst with visible light. Also, EDS results confirm that Bi particles are immobilized on the surface of TiO_2 successfully. The activities of the catalysts were tested by photocatalytic degradation of methylene blue (MB) under the visible light. Bi-TiO_2 photocatalyst could achieve the best MB degradation percentage of 70.2% after 180 min. of visible irradiation. Additionally, effect of some experimental parameters such as effect of humic acid (HA) and pH has been evaluated as much as reusability of catalyst. The characterization results confirmed the successful and desired preparation of the catalysts. The Bi-TiO_2 presented significant visible light response photocatalytic activity for the degradation of MB.

Keywords: Bi-TiO_2, photocatalysis, surfactant assisted sol-gel, visible light

1. INTRODUCTION

Many of organic dyes and their industrial effluents are toxic and carcinogenic, possing a threat for aquatic ecosystems and human health. Due to their hazard even at low concentration levels, it is necessary to improve cost effective technologies for the removal of these organic pollutants so as to minimize contamination risks and ensure the safety of environment [1-4]. These effluents are treated by many methods such as coagulation/flocculation, adsorption, ion-exchange and membrane filtration [5, 6]. However, these methods cause a secondary pollution by transferring the pollutants from the liquid phase to the solid phase and require further treatment methods [7, 8].

The photodegradation of the organic pollutants by catalysts is known as photocatalysis. Heterogeneous photocatalysis method has attracted much consideration for the degradation of dye pollutants due to its cost effective, soft reaction conditions and no secondary contamination [9, 10]. In

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photocatalysis, reactive oxygen species (ROS) such as ·OH, $O_2^{\cdot-}$ and H_2O_2 are formed on the surface of TiO_2 by absorbing UV radiation. These ROS species are responsible for the decomposition of organic compounds, including dye pollutants, present in waste water [11, 12].

Recently, TiO_2 based photocatalysis is the most popular candidate for waste water treatment, because it is non-toxic material, highly efficient and stable photocatalyst under UV light irradiation [13-15]. However, its photoactivity is relatively insufficient, because of the quick recombination of electron-hole (e^--h^+) pairs and large band gap energy (~3.2 eV), especially under the visible light. Many efforts are being made to develop economical and effective methods that work in sunlight or visible light for effective photocatalytic methods. Several methods have been proposed to enhance the photocatalytic efficiency of TiO_2 [16-21], such as modification with metal ions [16], non-metals [17], coupling with other semiconductors [18, 19] and dye sensitization [20, 21]. To increase catalytic activity of TiO_2, some researchers put their effort in doping TiO_2 with metals. Doping of TiO_2 photocatalyst can help in tuning the band gap energy, extend its photocatalytic reaction from the UV light range to visible light range and decrease the recombination of charge carries [16-21].

Bismuth has d^{10} electronic configuration. Bi-doped TiO_2 shifts the spectral range of TiO_2 to the visible light region and minimizes electron-hole recombination, and therefore it is widely used for degradation of organic pollutants, antibacterial application and photocathode for fuel cell, etc. has been extensively studied. However, it is rarely used in photocatalytic oxidation reactions due to its more complex reaction mechanism [22]. According to Ma et al. [22], Bi doped TiO_2 catalyst displays visible light driven photoactive properties for oxidation of methanol to methyl formate, increasing the surface hydroxyls and decreased the band gap energy. Li et al. [23] showed that by doping Bi into TiO_2, TiO_2 created a new intermediate energy level below its conduction band edge, thus prolonging the absorption in the visible region and increased their photocatalytic efficiency. Xu et al. [24] prepared Bi-doped TiO_2 nanofibers with different Bi content by an electrospinning method. They reported that Bi^{3+} ions were successfully incorporated into TiO_2 and extended the absorption of TiO_2 into the visible light region. They evaluated the catalytic activity of the Bi-doped TiO_2 nanofibers against the degradation of Rhodamine B (RhB, 1×10^{-5} M) under visible light irradiation of a 500W Xe lamp with a 420 nm cut-off filter. They indicated that almost all of the dye was degraded after 90 minutes of photocatalytic processing. Sood et al. [25] succesfully synthesized Bi doped TiO_2 photocatalyst by a facile sol-gel process. They proved that the incorporation of Bi^{3+} into TiO_2 lattice expanding of TiO_2 spectral response into visible region. The authors achieved that more than 80% degradation of Alizarin red S dye (ARS) with the prepared Bi-doped catalysts under visible light (philips bulb 150 W)

To the best of my knowledge, this study is the first in which Bi-TiO_2 was prepared via a surfactant-assisted (CTAB) sol-gel procedure. The main importance of this study is that the photocatalytic removal of MB was achieved with Bi-loaded TiO_2 under reduced cost and ambient conditions by using a very low-energy lamp and higher efficiency was obtained compared to the control group. Surfactant plays an important role in reducing surface tension and keeping particles apart during gel treatment, promoting steric and/or electrostatic interactions and preventing agglomeration. Thus, surfactant assisted sol-gel method might be used to get better photocatalytic activity with TiO_2 based catalyst [26].

In this study, TiO_2 catalyst was prepared by both pure sol gel method (TiO_2-1) and the surfactant assisted sol gel method (TiO_2-2). To improve the photocatalytic activity of

TiO_2-2 for the removal of methylene blue under visible light irradiation, TiO_2-2 was modified with the combination of Bi doping (Bi-TiO_2) using surfactant supported sol gel procedure. The morphology of nanocomposites was characterized by field emission scanning electron microscopy (FE-SEM), energy dispersive spectroscopy (EDS), X-ray diffractometry (XRD), UV-vis spectroscopy. Finally, the photocatalytic performances of synthesized nanoparticles were evaluated for removal of the methylene blue (MB) by visible light exposure ($\lambda \geq 400$ nm, 300 $\mu W/cm^2$) under ambient conditions. This photocatalyst displayed good performance in photocatalytic removal of MB under visible light. Thus, this approach may be used an important way for the secondary treatment of industrial wastewater.

2. MATERIAL AND METHOD

2.1. Material

Titanium (IV) isopropoxide (99%), $Bi(NO_3)_3.5H_2O$, HCl (36.5%) and Cetyltrimethylammonium bromide (CTAB ≥ %99) and absolute ethanol were purchased from Sigma-Aldrich. Deionized water was used for solution preparation and dilution.

2.2. Synthesis of nanoparticles

The pure TiO_2 nanoparticles were synthesized in two different ways, including both sol-gel and surfactant assisted sol-gel method [27]. 8.4 mL titanium (IV) isopropoxide was added into 140 mL absolute ethanol (Solution A). After stirring for 2 h, a solution that contained 0.22 mL HCl (concentrated) and 0.50 mL deionized water (Solution B) was added to Solution A, and the resulting mixture was stirred for 24 h to get a wet gel.

The resulting wet-gel was dried for 24 h at 80 ^oC. Finally, the final powder was calcined at 450 ^oC for 4 h. The as-prepared catalyst was defined as TiO_2-1.

The same TiO_2 catalyst was synthesized in the presence of Cetyltrimethylammonium bromide (CTAB). Initially, CTAB was added into absolute ethanol then titanium (IV) isopropoxide was added and the mixture was kept stirring for 2 h. The as-prepared catalyst was denoted as TiO_2-2. For the synthesis of Bismuth doped TiO_2 (Bi-TiO_2) catalyst in the presence of CTAB, absolute ethanol (10 mL) containing 0.1787 g $Bi(NO_3)_3.5H_2O$ (which is equal to 3% of TiO_2 mass) seperately added into the above solution under the same conditions. Given the photocatalytic results, bismuth was loaded on the best yielding TiO_2-2 catalyst.

2.3. Characterization of catalyst

The characteristic properties of the photocatalysts were examined by different techniques. X-ray diffraction (XRD) patterns were obtained by a PANanalytical Empyrean diffractometer with CuKα radiation in the 2θ range from 20^o to 80^o. Surface morphologies were analyzed by field emission scanning electron microscopy (FE-SEM, QUANTA 400F), UV-vis diffused reflectance spectra were recorded on a UV-VIS-NIR spectrophotometer (Shimadzu UV-3600 Plus).

2.4. Photocatalytic experiments

Methylene blue (MB) was prefered as a model dye contaminant to determine activity of the prepared catalyst in the photocatalytic duration. LED lamp ($\lambda \geq 400$ nm, 300 $\mu W/cm^2$) was used as the visible light source. For photocatalytic degradation, aqueous MB (50 mL, 10 mg/L) and 50 mg catalyst were added to the reaction cell and stirred first for 30 min, in the dark, to equilibrate adsorption process.

After the time, the reaction cell was then illuminated for 180 min of photocatalytic degradation. 5 mL of solution was taken from the reaction solution, centrifuged and analyzed using UV-VIS spectrofotometer (λ_{max} = 668 nm). The control tests were

performed out in the absence of light or without photocatalysts to investigate MB photolysis.

To simulate more realistic water, the influence of humic acid presence was evaluated on the degradation yield. The pH of the reaction solution was adjusted with 0.01 M NaOH or 0.01 M HCl solutions and the degradation efficiency was studied.

3. RESULTS AND DISCUSSION

3.1. Characterization

XRD pattern TiO_2-1 nanoparticles synthesized by sol-gel method and TiO_2-2 and Bi-TiO_2 synthesized by surfactant assisted sol-gel method is indicated in Figure 1. All materials exhibited reflections at 2θ=25.3°, 37.8°, 48.0°, 54.0°, 55.0°, 62.7°, 68.9°, 70.3° and 75.1° characteristic of the (101), (004), (200), (105), (211), (204), (116), (220) and (211) planes respectively of anatase TiO_2 (JCPDS card No. 21-1272) [25]. There was also no observable shift and additional peak in any of the titania reflections following Bi addition due to the relatively low amount of doped Bi.

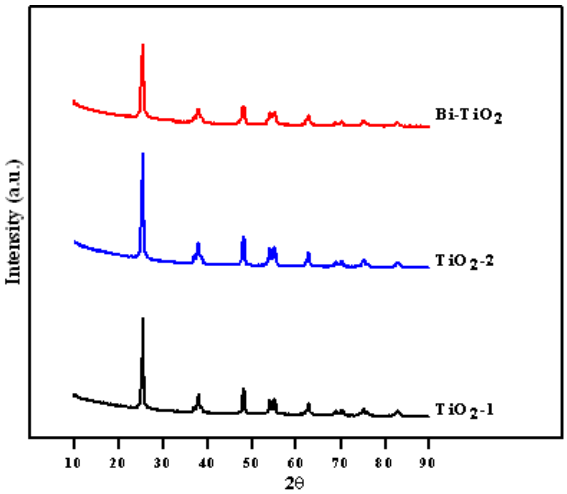

Figure 1 XRD patterns of TiO_2-1, TiO_2-2 and Bi-TiO_2 photocatalysts

The average crystallite sizes of the prepared samples were calculated by Debye Scherrer's formula:

$$D = K\lambda/\beta\cos\theta \quad (1)$$

D is the crystallite size, K=0.9 is a correction factor which accounts for the particle shape, λ is the wavelength of Cu target (0.15406 nm), β is the line width at half maximum height, and θ is the Bragg's angle [21]. Found that the average crystallite sizes of the TiO_2-1, TiO_2-2 and Bi-TiO_2 were 17.65, 16.06 and 13.09 nm, respectively.

The diffuse reflectance UV-vis spectra of the catalysts are shown in Figure 2. Figure 2 shows shift in the absorption peak of Bi-TiO_2 compared to TiO_2-2, absorption edges are found to be 411.1 nm and 398.7 nm respectively. The band gap energies can be calculated by the following equation

$$Eg=1240/\lambda_g \quad (2)$$

Where Eg is the band gap energy, and λ_g is the absorption edge of the catalyst [28]. Hence, the band gap was found out to be 3.11 eV for TiO_2-2, 3.02 eV for Bi-TiO_2. This shows that by doping Bi the efficient interactive relation of the catalyst with visible light is allowed. In addition, this reduction in band gap leads to the formation of additional energy levels induced by Bi-doping above the valence band (VB) of TiO_2, shifting its absorption into the visible region. Compared to TiO_2, Bi-TiO_2 shows a red shift in absorption wavelength favoring the successful incorporation of Bi into the TiO_2 lattice. Furthermore, compared to pristine TiO_2, the absorption in the visible region is enhanced for the Bi-TiO_2 photocatalyst.

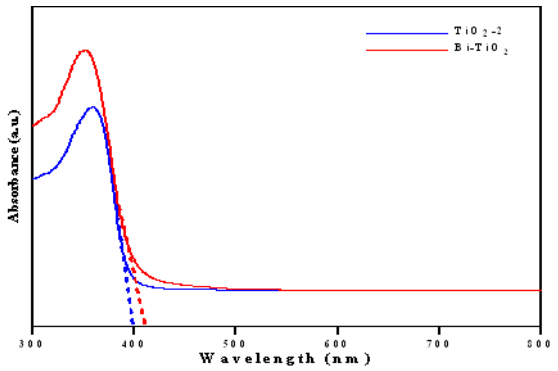

Figure 2 Optical band gap energies of TiO_2-2 and Bi-TiO_2

The morphology of the catalysts was studied by FESEM. The results are shown in the Figure 3 (a-d) shows FE-SEM images both Bi-TiO_2 and TiO_2-2 catalysts which indicates irregular oval shapped particles.

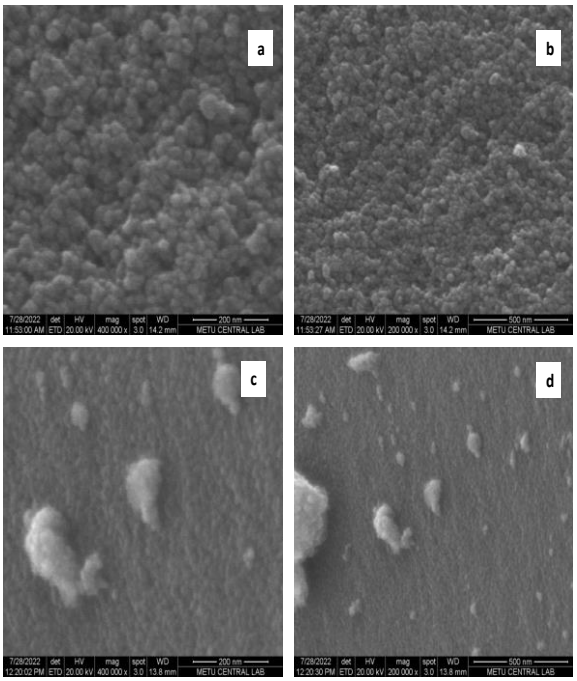

Figure 3 FE-SEM images of TiO_2-2 (a-b) and Bi-TiO_2 (c-d)

Figure 4 and Figure 5 shows the EDS spectra of the TiO_2-2 and Bi-TiO_2, respectively. The EDS spectra could also support that Bi was succesfully immobilized in the TiO_2 catalyst because of the presence bismuth, oxygen, and titanium signals. Also, the EDS data confirmed that catalysts are pure and not having any impurities.

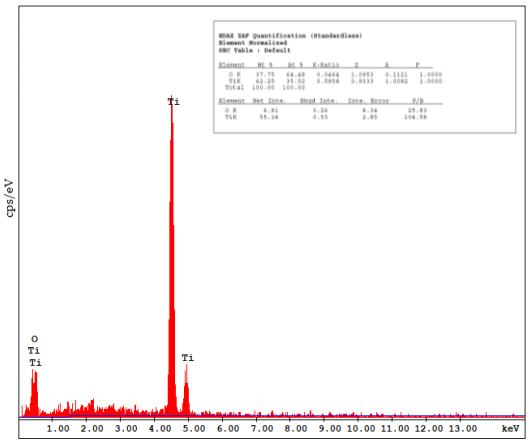

Figure 4 EDS spectra of TiO_2-2

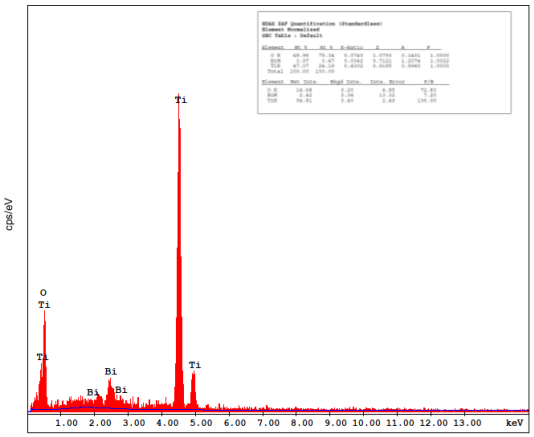

Figure 5 EDS spectra of Bi-TiO_2

3.2. Photocatalytic activity

The photocatalytic degradation percentage of MB in the presence of the prepared catalysts is given in Figure 6. Initially, the efficiency of MB degradation, in the absence of photocatalyst, only is around 1% after 180 min visible light irradiation. It can be seen that the degradation of MB with Bi-TiO_2 (70.2%) is higher than that reached with TiO_2-1 (24.3%) or TiO_2-2 (32.0%) after 180 min irradiation under the visible light. The high catalytic of Bi-TiO_2 is attributed to presence of Bi which provides a synergetic effect on MB photodegradation and results in better catalytic efficiency. Procedures for improving the photocatalytic degradation of MB due to the resistance of MB to degradation; (i) the use of CTAB as a surfactant in the process is to control aggregation, allow the surfactant to act as a surface-directing agent, lower the surface tension and increase the solubility of the reaction mixture, and act as an excellent medium for nucleation and crystal growth. Thus, the quantum efficiency may be increased, (ii) recombination of electron hole types can be inhibited by formation the heterojunction composition of Bi and TiO_2 together [26,27].

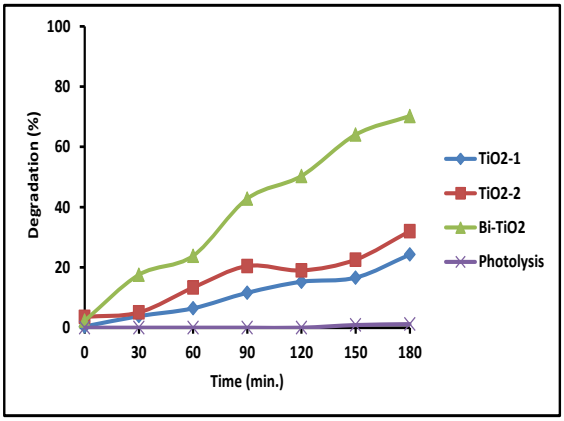

Figure 6 Photocatalytic degradation of MB under visible light irradiation [C_0=10 mg/L; Catalyst amount= 1g/L; pH 6.12]

As shown in Figure 7, the adsorption removal efficiencies of MB over the TiO_2-1, TiO_2-2 and Bi-TiO_2 (experiments in the without light) were 15.2%, 22.1% and 24.5% respectively. Although there was no significant difference between the adsorption removal of the catalysts, Bi-TiO_2 exhibited better adsorption activity.

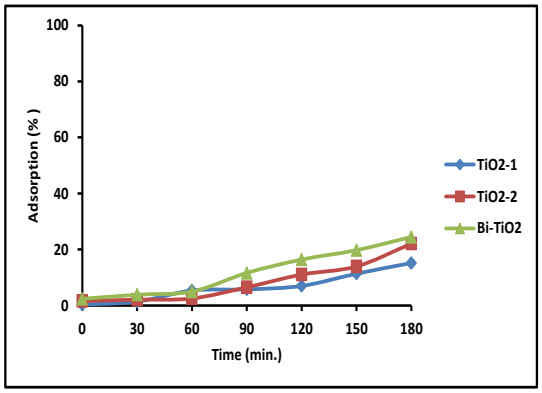

Figure 7 Adsorption removal of MB in the absence of light [C_0=10 mg/ L; Catalyst amount= 1g/L; pH 6.12]

The effect of experimental conditions on the degradation of MB such as the presence of humic acid (HA) and pH was examined on the best photocatalyst (Bi-TiO_2). Also, the reusability tests of the Bi-TiO_2 were investigated for the degradation of MB.

As seen from Figure 8, it is clear that the removal of MB was significantly reduced at acidic pH (3.04). The removal results of MB at neutral pH 6.12 did not show a significant difference from the removal results at pH 8.02 or pH 12.06. It is seen as an advantage since no additional pH arrangement is required in the removal processes of MB [29].

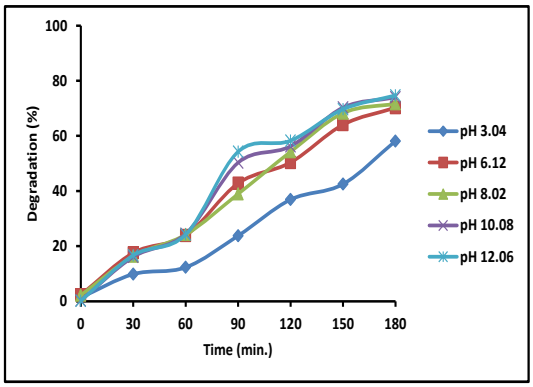

Figure 8 The effect of pH on photocatalytic removal [C_0=10 mg/ L; Bi-TiO_2= 1g/L]

HA, an important natural organic component (NOM), is typically surface water and can adversely affect the physical and chemical properties of water [30]. Humic acid (HA) solution was used in this study to simulate the reaction solution in real water. Chemical degradation reactions can be negatively affected due to the interactions of HA with ROS (Reactive Oxygen Species), which are responsible for the degradation of MB and are expected to be generated during photocatalysis removal processes.

Considering that HA concentration usually ranges from 2 mg/L to 10 mg/L in surface natural water, 5 mg/L or 8 mg/L HA was added to the reaction solution and its effect on the removal of MB was studied. As shown in Figure 9, the presence of HA in the reaction solution slightly affected the photocatalytic degradation of MB. In detail, 5 mg/L HA and 8 mg/L HA were added to the reaction solution and the degradation rate decreased from 70.2% to 67.3% and 64.3%, respectively. This slight decrease in activity may be due to: (i) competitive adsorption of HA with MB on the catalyst surface which delays the photocatalytic oxidation process interfering with the ROS and, (ii) reduced light penetration in suspension. Based on the above experimental results involving HA, the

degradation of photocatalytic MB is expected to be slower in real water samples [27,31,32].

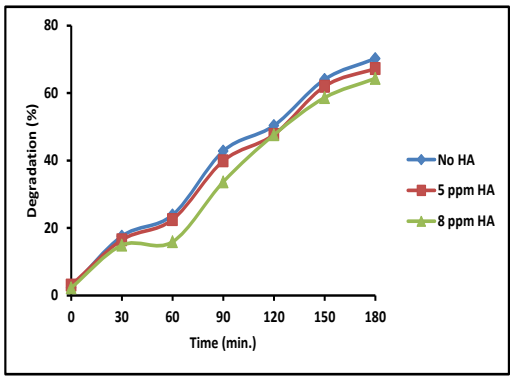

Figure 9 Photocatalytic removal of MB in the presence of different concentrations of HA [C_0=10 mg/ L; Bi-TiO_2 = 1g/L; pH 6.12]

The reusability tests of the Bi-TiO_2 were investigated for the MB. After the first 180 min. treatment the catalyst was simply washed with water and reused in a new treatment at the same pollutant concentration. Since the amount of catalyst decreased slightly before each use, fresh Bi-TiO_2 was added as much as the decreasing amount.

The degradation percentages obtained after 5 times usage for MB are shown in Figure 10. As shown in Figure 10, Bi-TiO_2 activity decreased nearly 20% for MB removal after 5 cycles. It was clear that Bi-TiO_2 was still effective but dye removal rates were lower. The degradation rate may have decreased due to the irreversible adsorption of the dye on the catalyst surface [29].

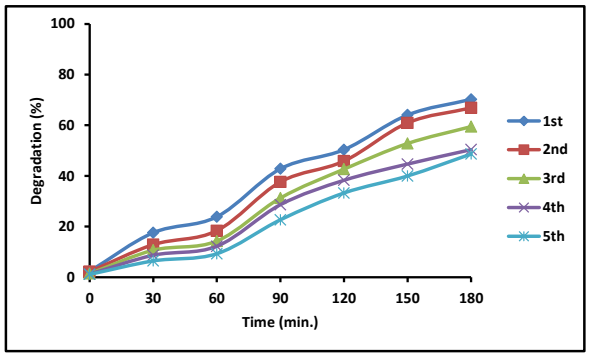

Figure 10 The recycling tests of Bi-TiO_2 [C_0=10 mg/ L; Bi-TiO_2 = 1g/L; pH 6.12]

4. CONCLUSION

In summary, in this study, bismuth doped TiO_2 (Bi-TiO_2) photocatalyst succesfully prepared using a surfactant assisted sol-gel method. It was found that Bi-TiO_2 catalyst had anatase crystal structure with non-impurity. According to the results of photocatalytic studies, Bi-TiO_2 catalyst presented on improved catalytic activity in degradation for MB and showed extention in the spectral response range shifted to the visible region. MB degradation in the presence of Bi-TiO_2 after 180 min visible light irradiation was reached 70.2%. No significant reduction in the MB catalytic activity was observed during five cycles in the reusability test, showing that the Bi-TiO_2 catalyst remains stable and performance in time and can be applied in scale-up processes. Also, the presence of HA in the reaction solution slightly affected the photocatalytic degradation of MB. This study could be a hopeful base for applicability of visible or solar light water remediation process especially those containing dye pollutants.

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The Declaration of Conflict of Interest/ Common Interest
No conflict of interest or common interest has been declared by the author.

The Declaration of Ethics Committee Approval
This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics
The author of the paper declare that she complies with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that she does not make any falsification on the data collected. In addition, she declares that Sakarya University Journal

of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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