

Doped TiO₂ Photocatalysts for the Photocatalytic Degradation Efficiency of Methylene Blue and Humic Acid under Solar Light

Nazli Turkten¹ and Miray Bekbolet²

¹Kirsehir Ahi Evran University, Department of Chemistry, Kirsehir, Turkey

²Bogazici University, Institute of Environmental Sciences, Istanbul, Turkey

ABSTRACT

In various advanced oxidation processes, photocatalysis is a promising and efficient way to remove natural organic matter consisting of humic acids and fulvic acids. The principle of this method involves both usage of a semiconductor photocatalyst and O₂ for the generation of radicals. Among them, TiO₂ photocatalysis is the most popular and studied one since TiO₂ has unique properties such as being chemically inert, photocatalytically stable, cheap, non-toxic, environmentally benign and exhibiting high oxidative power. However, despite all the advantages of using TiO₂ as a photocatalyst, there is a major disadvantage. Since TiO₂ has a broad band gap, its usage widely under solar light is limited and only allows to be active under UV light. Doping is one of the most popular methods to enhance the photocatalytic activity of TiO₂ via using metal or non-metal species as dopants. In this respect, solar light sensitive TiO₂ photocatalyst, C, N, S, Se doped and S/N codoped TiO₂ photocatalysts were synthesized by using wet-impregnation method. These doped photocatalysts were characterized by Raman spectroscopy to determine the crystal surface morphology. Moreover, methylene blue was used to investigate the photocatalytic performance of prepared doped TiO₂ photocatalysts in the presence or absence of organic matrix. Photocatalytic experiments were performed using a solar light simulating photoreactor. Humic acid characterization was monitored by UV-vis and fluorescence spectroscopy.

Keywords:

Raman spectroscopy; Metal/non-metal doped TiO₂; Humic acid; Photocatalysis.

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Correspondence to: Nazli Turkten,
Kirsehir Ahi Evran University, Chemistry,
40100, Kirsehir, Turkey
E-Mail: nazli.turkten@ahievran.edu.tr
Phone: +90 (386) 280 3104
Fax: +90 (386) 280 4525

INTRODUCTION

Wastewater is polluted with severe concentration of dyes in industries such as textile, cosmetic, paper, leather, food, etc. and this causes a critical environmental and health public issue [1, 2]. Accordingly, many studies have been reported for the removal of these colored effluents from wastewater using different methods such as physicochemical treatments, chemical methods, advanced oxidation processes (AOPs), and biological methods [3-8]. The application of the physicochemical treatments are limited because of the formation of sludge to be disposed of or the need of regeneration of the adsorbent materials. Although, biological methods are environmentally friendly and inexpensive, they are not effective to degrade the dyes in wastewaters and thus uncompleted degradation can cause secondary pollution. Even if ozonation is an effective process for the decolorization of dyes, this method causes very high operating costs [2, 9-11].

Among AOPs, heterogeneous photocatalysis in which a semiconductor, such as TiO₂, ZnO, SnO₂, etc. is used as a photocatalyst is an effective alternative method to conventional methods. TiO₂ photocatalysis is based on the formation of photogenerated charge carriers on the surface of titanium dioxide. Photocatalytic mechanism is initiated with the excitation and transfer of an electron from the valence band to the conduction band of TiO₂ and positively charged holes are formed in the valence band at the same time. These generated electron-hole reacts with water and O₂ or OH⁻ to form extremely reactive oxygen species (ROS) such as superoxide anions, and hydroxyl radicals. During the photocatalytic process, hydroxyl radicals react with surface adsorbed pollutants and leads them to degrade. Subsequently, further reactions with ROS could mineralize the organic matter to carbon dioxide and water [3, 4, 12].

TiO₂ is the most popular and promising photocatalyst with great photosensitivity and chemical stability. Moreover, it is non-toxic and a low-cost material. Nevertheless, TiO₂ with wide and gap of $E_{bg}=3.2$ eV limits its photocatalytic activity under solar light (This sentence needs correcting). Thus, doping method by using metal ions i.e. Cu, V, Se, Fe, etc., non-metal elements i.e. B, C, S, N, etc. and co-doping with metals and non-metals (N/S, N/Se, etc.) has been used to improve the photocatalytic activity of TiO₂ as an effective strategy under visible light [5, 7, 12-18].

In this study, C, N, S, Se doped and N/S codoped TiO₂ photocatalysts were synthesized by wet-impregnation method. Crystal surface morphology of the doped TiO₂ photocatalysts was determined by using Raman Spectroscopy. Photocatalytic activity of these specimens were investigated using methylene blue (MB) as a basic dye under simulated solar light in presence and absence of humic acid (HA).

MATERIAL AND METHODS

Materials

Commercial HA (humic acid sodium salt) was purchased from Aldrich. TiO₂ Evonik P25 was used as the photocatalyst for doping procedure. Doped TiO₂ photocatalysts were synthesized via an incipient wet-impregnation method using C₆H₁₂O₆ (glucose), CH₄N₂O (urea), NH₂CSNH₂ (thiourea), SeCl₄ (selenium tetrachloride) and CH₄N₂O coupled with NH₂CSNH₂ (urea and thiourea) as C, N, S, Se and S/N sources, respectively. All doping sources and MB were purchased from Merck. Distilled water was used for the preparation of the solutions. The chemical structures of MB and HA are given in Fig. 1.

Preparation of Doped TiO₂ Photocatalysts

Dopant concentration was selected as 0.50% wt. for all photocatalysts as it was determined in previous work [13-

18]. In incipient wet-impregnation method, 0.50% dopant agents in 15 mL water was added to 10 g TiO₂ Evonik P25 and stirred for 1 h at room temperature. Afterwards, doped photocatalysts were washed with distilled water, dried in air oven at 378 K for 24 h, and calcined at a predetermined temperature and time which were given in Table 1. Finally, the obtained samples were ground and passes through a sieve (32 Micron) to achieve a more homogeneous size distribution.

Table 1. Calcination time and temperature for the prepared photocatalysts.

| | Photocatalyst | Synonym | Temperature & Calcination |
|---|------------------------------|--|---------------------------|
| 1 | C-doped TiO ₂ | C-350-3-TiO ₂ C-500-3-TiO ₂ | 350°C 3h 500°C 3h |
| 2 | N-doped TiO ₂ | N-350-3-TiO ₂ N-500-3-TiO ₂ | 350°C 3h 500°C 3h |
| 3 | S-doped TiO ₂ | S-350-3-TiO ₂ S-500-3-TiO ₂ | 350°C 3h 500°C 3h |
| 4 | Se-doped TiO ₂ | Se-350-3-TiO ₂ | 350°C 3h |
| 5 | N/S-codoped TiO ₂ | N/S-350-3-TiO ₂ | 350°C 3h |

Solar Photocatalytic Experiments

Atlas-Suntest CPS+ solar simulator was used for the photocatalytic experiments [16]. The solar degradation of MB (20 mg/L) using doped TiO₂ specimens under solar light with 60 min irradiation time in presence and absence of HA (20 mg/L) was investigated. After the photocatalytic process, TiO₂ was removed by a filtration process. The photocatalytic experiments were carried out without pH adjustment (pH~5.5).

Characterization

Absorbance of filtered MB solutions at $\lambda=662$ nm was monitored by UV-vis spectrophotometry (Perkin Elmer lambda 35). EEM fluorescence spectra was measured by a Luminescence Spectrometer (Perkin Elmer LS 55). The detailed procedure was given in our previous work [16]. Raman spectra were acquired by a Thermo Scientific NXR FT-Raman spectrometer using Ar⁺ laser excitation at $\lambda=532$ nm, with a laser power 10 mW and a resolution 2 cm⁻¹.

RESULTS AND DISCUSSION

Raman Spectroscopy

Raman spectroscopy was employed for the characterization of the surface structure and identifying the phase transformation of doped TiO₂ photocatalysts. Moreover,

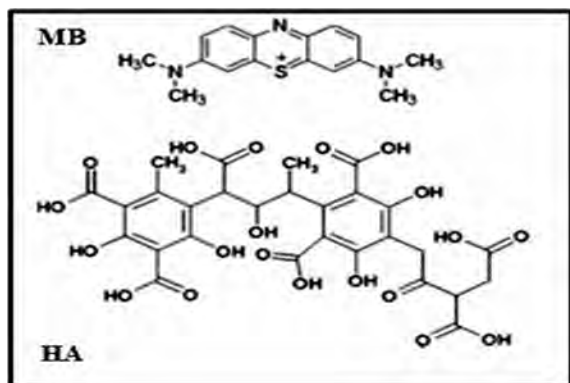


Figure 1. Chemical structures of MB and Steelink's proposed unit structure of HA [19].

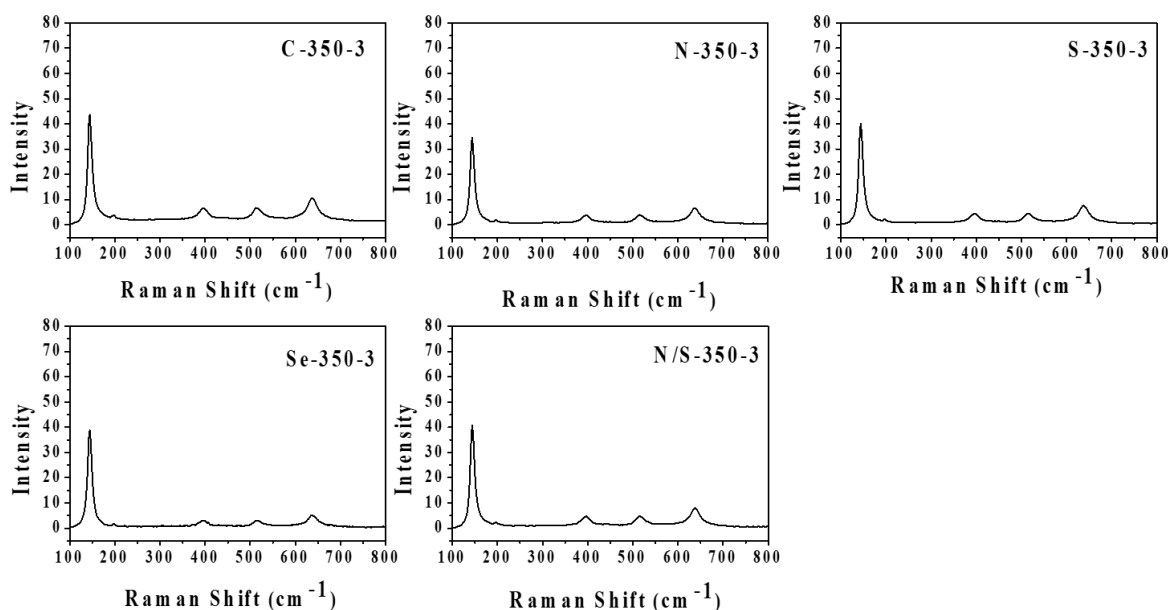


Figure 2. FT-Raman spectra of doped TiO₂ samples calcined at 350°C for 3h.

the effect of different dopant agents and different calcination temperatures on the transformation of crystallographic phases were identified. The FT-Raman spectra of the doped TiO₂ samples calcined at 350°C for 3h are displayed in Fig. 2.

Raman peaks were acquired at 144 (E_g), 197 (E_g), 397 (B_{1g}), 515 (A_{1g}, B_{1g}), and 637 (E_g) cm⁻¹ in the spectra of each sample, indicating the presence of anatase phase [16, 20]. Similarly, Raman spectroscopy of the samples calcined at 500°C for 3h (Fig. 3) revealed the presence of only anatase phase.

Any phase transformation from anatase phase to rutile phase and any significant shift in the Raman bands were not observed as expected. The reason could be explained by the anatase phase transformation to rutile phase starting at 550°C [21].

Photocatalytic Experiments

Photocatalyst performances were estimated by the removal percentage values of MB in the absence and presence of HA. Removal percentages were determined from Equation (1), where C₀ is the initial concentration of MB and C is concentration at time t of MB.

$$\text{Removal}\% = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

In Fig. 4 (a), removal % values of MB by using doped TiO₂ photocatalysts under solar light at 60 min are shown. Se-350-3 and N-350-3 TiO₂ photocatalysts exhibited the

highest removal of MB as 87.30% and 89.31%, respectively. It was found that N/S-350-3 TiO₂ has the lowest ability for the decolorization of MB compared to other doped photocatalysts. Moreover, the effect of calcination temperature on the anion doped photocatalysts (C-doped TiO₂, N-doped TiO₂ and S-doped TiO₂ photocatalysts) were investigated and shown in Fig. 4 (b). N-doped and C-doped TiO₂ photocatalysts almost exhibited the same removal efficiency, while S-doped TiO₂ samples performed a lowered photocatalytic activity with increasing calcination temperature. The reason may be explained by its having a large surface area compared to N-doped and C-doped TiO₂ samples which were reported in our previous work [13]. A larger surface area could promote an increment on the photogenerated electrons and photocatalytic activity [22]. For this reason, a further study is needed to investigate the removal percentage of anionic dyes by using anion doped TiO₂ photocatalysts.

In Fig. 4 (c), the removal % efficiency of MB with the presence of HA is shown. HA caused a retardation effect on the photocatalytic system. The reason of this retardation could be explained by two assumptions.

- i) HA could reduce the light transmittance thereby effects photo-oxidation process.
- ii) The competition between HA and MB for the active sites of TiO₂ surface [23].

Fig. 5 displays the UV-vis spectra of MB solution with the absence and presence of HA after 60 min for doped TiO₂ photocatalysts. The spectrum of MB was characte-

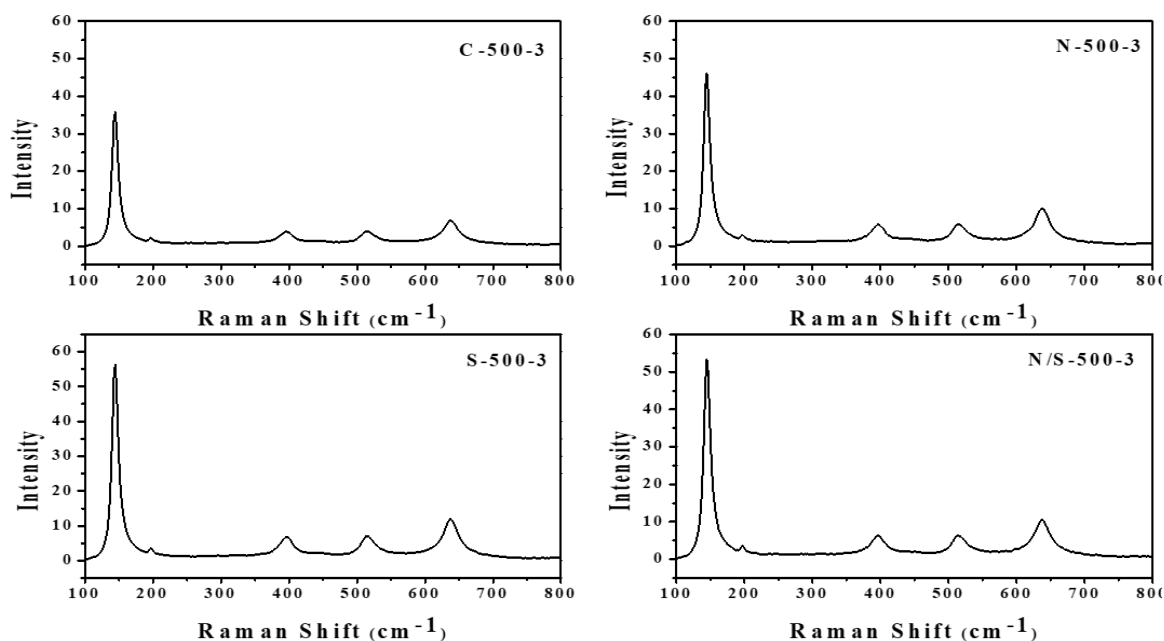


Figure 3. FT-Raman spectra of doped TiO₂ samples calcined at 500°C for 3 h.

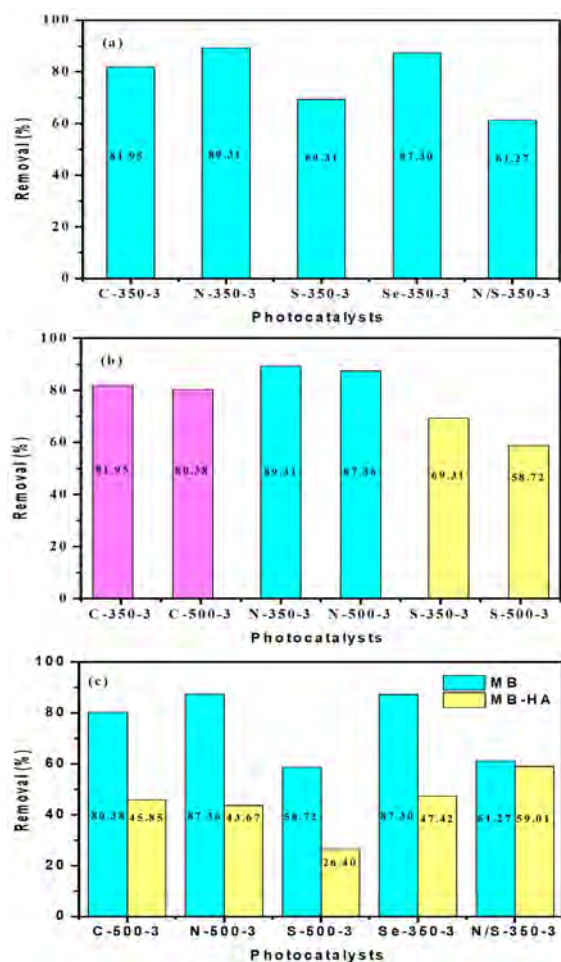


Figure 4. The removal % values of MB (a) 350°C 3h, (b) 350°C and 500°C 3h, (c) the retardation effect of HA.

ized by an absorption band $\lambda=662$ nm and a shoulder at 612 nm in visible light region. This absorption band was attributed to a chromophore including an elongated conjugate system. The absorption bands located in the UV region at 292 nm and 245 nm were corresponded to the conjugated system of the benzene ring structure [24, 25].

In Fig. 5 (a) and (b), the characteristic absorption peak of MB solution at 662 nm was significantly lowered in intensity with solar light irradiation and the shoulder was disappeared. Furthermore, a decrease in the intensity of benzene rings after irradiation, confirmed that decolorization and degradation of MB occurs at the same time. Among all doped TiO₂ photocatalysts, N-TiO₂ was the most effective one and decolorize approximately 87-89% of MB after 60 min. In Fig. 5 (c), the presence of HA effected the disappearance of hump at 612 nm after irradiation. Besides, the intensity of aromatic peaks and maximum absorption peak were decreased as expected after 60 min. However, the retardation effect of HA caused an adverse impact by decreasing the intensity of peaks compared to the peaks in absence of HA spectra.

EEM Fluorescence Contour Plots

Regional specification of the EEM spectra of HA was expressed in four regions. Region I, II and III were defined as aromatic proteins I, aromatic proteins II and fulvic-like in the excitation wavelength region of $\lambda_{exc}=200-250$ nm with emission wavelength regions of $\lambda_{emis}=280-332$ nm, $\lambda_{emis}=332-380$ nm and $\lambda_{emis}=380-580$ nm respectively.

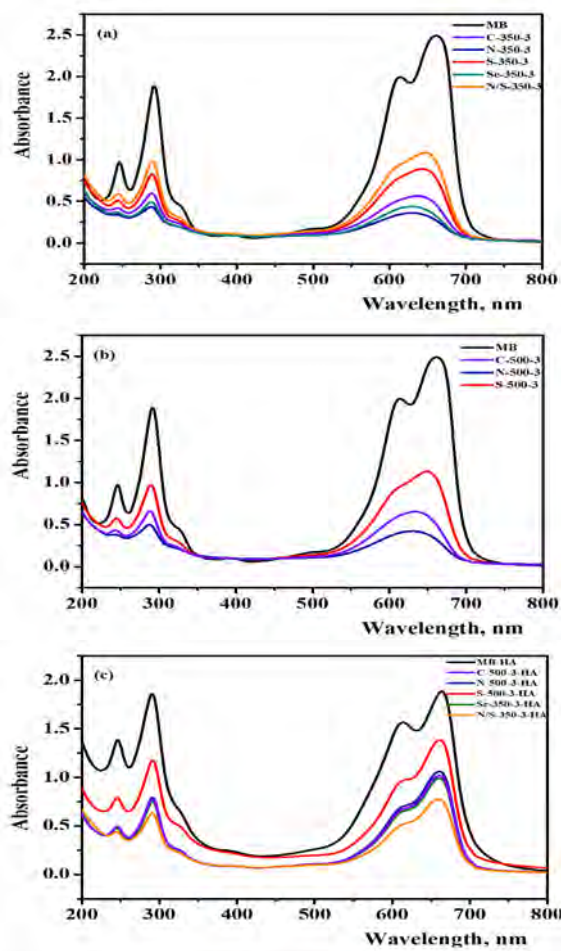


Figure 5. UV-vis spectra of MB dye solution by doped TiO_2 photocatalysts (a) 350°C 3h, (b) 350°C and 500°C h, (c) presence of HA.

Region IV and V were expressed by microbial byproducts and humic-like in the excitation wavelength region of $\lambda_{\text{exc}}=250\text{--}470$ nm with an emission wavelength region of $\lambda_{\text{emis}}=280\text{--}380$ nm and $\lambda_{\text{emis}}=380\text{--}580$ nm respectively [26].

In Fig. 6, EEM contour plots of HA and MB subsequent to photocatalysis of 60 min using doped- TiO_2 samples are shown. It is notable from the figure that humic-like features decreased in all spectra after 60 min irradiation, but the most significant changes were observed in the presence of N- TiO_2 , C- TiO_2 , and Se- TiO_2 samples. The humic-like region was slightly decreased in S- TiO_2 and N/S- TiO_2 samples compared to anion doped TiO_2 samples.

CONCLUSION

In this study, C, N, S, Se doped and N/S codoped TiO_2 photocatalysts were prepared using wet-impregnation method. It was found that Se-350-3 and N-350-3 TiO_2 photocatalysts exhibited the highest removal of MB. The removal efficiency % was decreased in HA medium because of the retardation effect of HA on the photocatalytic system. In Raman spectra, any phase transformation from anatase phase to rutile phase was not observed due to different calcination temperature as expected. The results in Raman spectra confirmed that all doped TiO_2 photocatalysts exhibited anatase phase. In accordance with removal data, the change of EEM spectra with a decrease in intensity of the humic-like region was noticeable after 60 min irradiation especially in anion doped TiO_2 photocatalysts.

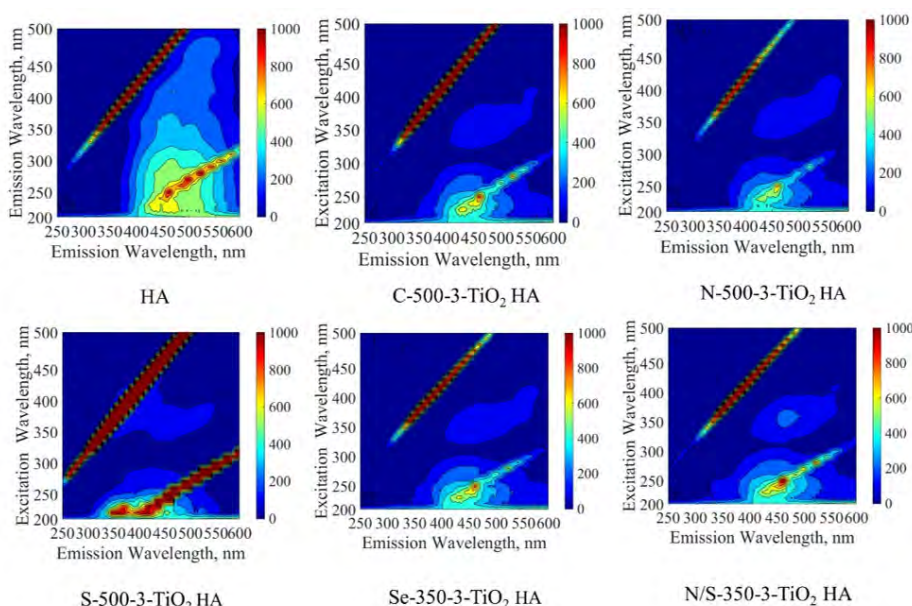


Figure 6. EEM contour plots of HA and MB with respect to irradiation 60 min using doped TiO_2 .

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