Mühendislik Bilimleri ve Tasarım Dergisi
8(3), 664 – 670, 2020
e-ISSN: 1308-6693

Journal of Engineering Sciences and Design
DOI: 10.21923/jesd.672750

Araştırma Makalesi Research Article

PHOTOCATALYTIC ACTIVITY OF IN-SITU FE-DOPED TIO_2 FOR NATURAL ORGANIC MATTER REMOVAL

Nazlı TÜRKTEN[1*], Ceyda S. UYGUNER DEMİREL[2]

[1] Kırşehir Ahi Evran University, Department of Chemistry, Faculty of Arts and Sciences, Kırşehir-Turkey
[2] Bogazici University, Institute of Environmental Sciences, Bebek, Istanbul-Turkey

Keywords

EEM,
Fe-Doped TiO_2,
Humic Acid,
In-Situ Sol Gel Method,
Photocatalytic Degradation.

Abstract

Humic acids represent a major fraction of natural organic matter (NOM) in aquatic environments. Having undefined composition and complex ill-defined structures, their presence in natural waters is undesirable. In this study, solar photocatalytic activity of synthesized Fe-doped TiO_2 photocatalysts was investigated for the degradation of a 100 kDa molecular size fraction of humic acid. For this purpose, catalysts comprised of 5 different molar ratios of Fe/Ti were prepared by in-situ sol gel method and characterized by FTIR and Raman spectroscopy. Optimum loadings of the catalysts were determined and the kinetics of humic acid removal was investigated focusing on UV–vis spectroscopic parameters. Moreover, fluorescence techniques such as excitation-emission matrix (EEM) were also acquired for elucidating induced structural changes of humic acid during photocatalytic degradation. Results revealed that, using photocatalysts prepared by in-situ sol-gel method 20 to 25% removal of humic acid could be attained after photocatalytic treatment of 120 min.

ORGANİK MADDE GİDERİMİ İÇİN EŞ ANLI (IN-SITU) FE-KATKILI $TİO_2$'NİN FOTOKATALİTİK AKTİVİTESİ

Anahtar Kelimeler

UEM,
Fe-Katkılı TiO_2,
Hümik Asit,
In-Situ Sol Jel Yöntemi,
Fotokatalitik Degradasyon.

Öz

Hümik asitler, su ortamlarındaki doğal organik maddenin (DOM) büyük bir kısmını temsil etmektedirler. Hümik asitlerin tam olarak tanımlanmamış kimyasal bileşimleri ve karmaşık yapıları sebebiyle doğal sularda bulunmaları istenmemektedir. Bu çalışmada, hümik asidin 100 kDa moleküler boyut fraksiyonunun degradasyonunun incelenmesi için sentezlenen Fe katkılı TiO_2 fotokatalizörlerinin simüle edilmiş güneş ışığı altındaki fotokatalitik aktivitesi incelenmiştir. Bu amaçla, beş farklı Fe/Ti molar oranından oluşan fotokatalizörler, eş-anlı (in-situ) sol jel yöntemi ile hazırlanmıştır. Hazırlanan Fe katkılı TiO_2 fotokatalizörlerinin karakterizasyonu FTIR spektroskopik yöntemi ve Raman spektroskopisi kullanılarak yapılmıştır. Katalizörlerin optimum dozlarının hümik asidin giderimine olan etkisi yapılan çalışmada belirlenmiştir. Buna ilaveten, UV-vis spektroskopisinin parametrelerine dayanılarak hümik asit gideriminin kinetiği incelenmiştir. Ayrıca, fotokatalitik degradasyon sırasında hümik asit yapısında gerçekleşen değişikliklerin açıklanabilmesi için uyarılma-emisyon matrisi (UEM) gibi spektroskopik floresans teknikleri kullanılarak yapılmıştır. Elde edilen sonuçlar eş-anlı (in-situ) sol-jel yöntemi ile hazırlanan fotokatalizörlerin kullanılması ile 120 dakika fotokatalitik işlem sonucunda hümik asit gideriminin % 20 ile % 25 aralığında olabileceğini göstermektedir.

Alıntı / Cite

Türkten, N.,. Uyguner Demirel, C. S., (2020). Photocatalytic Activity of In-situ Fe-Doped TiO_2 for Natural Organic Matter Removal, Journal of Engineering Sciences and Design, 8(3), 664-670.

Yazar Kimliği / Author ID (ORCID Number)	Makale Süreci / Article Process	
N. Türkten, 0000-0001-9343-3697	**Başvuru Tarihi / Submission Date**	09.01.2020
C. S. Uyguner Demirel, 0000-0001-8782-7526	**Revizyon Tarihi / Revision Date**	11.06.2020
	Kabul Tarihi / Accepted Date	21.06.2020
	Yayım Tarihi / Published Date	24.09.2020

---

[*] Corresponding author: nazli.turkten@ahievran.edu.tr, +90-386-280-3104

1. Introduction

In recent twenty years, photocatalytic degradation of natural organic matter consisting of humic acids and fulvic acids have received great interest. Due to their role as precursors to the formation of disinfection by-products in chlorination process, their removal by various advanced oxidation processes have been studied in detail. Recently, the application of visible light activated photocatalyts for the removal of NOM and its fractions has been a popular research topic (Birben et al. 2017).

In this study, Fe-doped TiO_2 photocatalysts were prepared by an in-situ sol gel method changing the mole ratios of Fe to Ti, from 0.2 to 1.0. In a comparative approach to recent studies, solar photocatalytic activity of the synthesized catalysts were tested for the degradation of a 100 kDa molecular size fraction of humic acid. Kinetics of removal was explained by UV-vis parameters and specific fluorescence features.

2. Literature Survey

Recent findings revealed that Fe^{3+} was a good candidate for its photoactivity due to its band-gap (2.6 eV) and similar radius to that of Ti^{4+} (Yalçın et al., 2010). Taking into account the energy level of Fe^{2+}/Fe^{3+} that is close to that of Ti^{3+}/Ti^{4+}, the separation of photogenerated electron-hole pair was favored leading to a better quantum efficiency as given in Equatons (1)-(5) and explained in detail in various sources (Araña et al., 2003; Zhu et al., 2004; Zhang et al., 1998).

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \qquad (1)$$

$$Fe^{2+} + O_2\,(ads) \rightarrow Fe^{3+} + O_2^{-} \qquad (2)$$

$$Fe^{2+} + Ti^{4+} \rightarrow Fe^{3+} + Ti^{3+} \qquad (3)$$

$$Fe^{3+} + h_{vb}^{+} \rightarrow Fe^{4+} \qquad (4)$$

$$Fe^{2+} + h_{vb}^{+} \rightarrow Fe^{3+} \qquad (5)$$

Fe-doped TiO_2 photocatalysts could be synthesized by using different preparation methods such as a wet-impregnation method (Birben et al., 2017), a combination of sol-gel and wet-impregnation methods (Türkten and Cinar, 2019) and an in-situ sol gel method (Šijaković-Vujičić et al, 2004). In-situ sol gel method, the dopant agent was added into titanium(IV)isopropoxide (TIP) during hydrolysis process.

Literature survey reveals very few studies on the application of Fe doped TiO_2 specimens for the degradation of NOM or humic acids (HA) (Yuan et al., 2013 and Baek et al., 2014, Birben et al., 2017). In a recent paper by Yuan et al., (2013) the removal of HA by Al and Fe co-doped TiO_2 nanotubes was investigated under UV light. Birben et al. (2017) tested the solar photocatalytic activity of Fe-doped TiO_2 specimens (P-25 and UV-100) prepared by a wet impregnation method for the degradation of humic acid, where slower degradation rates were attained indicating the importance of substrate properties rather than the inefficiency of visible light activation by metal doping of photocatalyst.

3. Material and Method

3.1. Catalyst Preparation

Fe-doped TiO_2 photocatalyts were synthesized by in- situ sol gel method. TiO_2 was synthesized using a modified sol-gel method (Shen et al, 2009). 0.1 mol of TIP was added dropwise into 100 mL ethanol within 30 min at room temperature under vigorous stirring to form Solution A. pH was adjusted to 2 during addition of TIP. $Fe(NO_3)_3.9H_2O$ was used as a Fe source. A certain amount of iron nitrate was dissolved in the mixture of 10 mL, 10 mL acetic acid and 80 mL ethanol to form Solution B. Solution A was added dropwise into Solution B within 60 min under continuous stirring for another 2 h at room temperature until a transparent solution was obtained. The resultant solution was aged for 48 h at room temperature in dark. The obtained gel was dried in an air oven at 378 K for 12 h and followed by extensive washing, at 773 K for 5 h and grinding. The sample was represented as x-FeTiO2. X being the mole ratios of Fe to Ti, it was labeled as 0.2-$FeTiO_2$, 0.4-$FeTiO_2$, 0.6-$FeTiO_2$, 0.8-$FeTiO_2$ and 1.0-$FeTiO_2$, respectively.

3.2. Humic Acid Characterization

50 mg L^{-1} HA (Aldrich humic acid sodium salt) was prepared and filtered through 0.45 μm cellulose acetate membrane filters. Subsequently, ultrafiltration (Amicon 8050 stirred cell unit) was applied to prepare 100 kDa molecular size fraction of humic acid.

Solar photocatalysis wasf carried out in a simulator (ATLAS Suntest CPS+) equipped with an air-cooled Xenon lamp (λ=300-800 nm, 250 W/m^2) as the light source. Photocatalyst specimens were removed from the reaction medium by immediate filtration through 0.45 μm membrane filter. Clear samples were subjected to UV-vis and fluorescence spectroscopic analysis.

3.3. Analytical Methods

FTIR spectroscopy was performed by Perkin Elmer Spectrum Two with Universal ATR accessory with diamond/ZnSe crystal. Spectra were obtained from 8 scans with a resolution of 2 cm^{-1} in the range of 4000-500 cm^{-1}. Raman spectra were acquired by a Thermo Scientific with NXR FT-Raman Module.

For humic acid characterization by UV–vis spectroscopy (Perkin Elmer Lambda35), parameters were described in terms of selected absorbance values measured at 254 nm (UV_{254}). In order to acquire fluorescence spectra as excitation-emission matrix (EEM), excitation wavelengths were incrementally increased from 250 to 600 nm at 10 nm steps; for each excitation wavelength,the emission at longer wavelengths was detected at 0.5 nm steps (Perkin Elmer LS 55). Excitation and emission slit widths were set to 10 nm and pho-tomultiplier tube voltage was 900 V. Three-dimensional contourplots were created by plotting fluorescence intensity as a functionof emission (x-axis) and excitation (y-axis) wavelengths. MatlabR2013a was used to process EEM data.

Moreover, doped TiO_2 specimens in deionized water were also exposed to irradiation to check the stability and release of Fe species. Fe concentration was mea-sured by ICP-OES (Perkin Elmer Optima 2100DV).

4. Experimental Results

4.1. FTIR Spectroscopy

The FTIR spectra of five different Fe-doped specimens show that they all have similar absorption patterns (Figure 1). The peak at 1643 cm^{-1} is attributed to the H-O-H bending vibration of adsorbed water, wheras absorption at ~1450cm^{-1} represents a stretching vibration of adsorbed carbon species. The absence of a broad peak in the region 3500–2400 cm^{-1} indicates that Fe-doped TiO_2 surface has less hydroxyl groups. Moreover, this finding points out that the surface of the Fe/Ti catalysts prepared by in situ sol gel method seems to be almost dehydrated/dehydroxylated. These results suggest that the degree of dehydroxylation could forecast a loss of photoactivity on these Fe-doped TiO_2 catalysts (Navio et al, 1996; Yalçın et al, 2010).

4.2. Raman Spectroscopy

Raman spectroscopy is a powerful technique for the determination of crystallite phases of TiO_2. Figure 2 shows the Raman spectra of different mol ratios of Fe-doped samples where five modes of anatase are detected. Raman peak at about 146 cm^{-1} is observed for all samples, which is attributed to the main Eg anatase vibration mode. Moreover, vibration peaks at 198 cm^{-1} (E_g, weak), 396 cm^{-1} (B_{1g}), 518 cm^{-1} (A_{1g}), and 638 cm^{-1} (E_g) are present in all of the spectra of Fe-doped TiO_2 samples, which indicate that anatase is the predominant crystallite phase and no rutile or brookite impurity can be detected (Cong et al, 2007; Yalçın et al, 2010). Moreover, no bands are observed for oxides of iron. It is also evident that the intensities of anatase peaks decrease with the increase in doping concentration of the iron in the TiO_2 crystal lattice. This observation can be attributed to the increase in oxygen deficiencies as well as decrease in the crystalline size in the titania matrix (Delekar et al, 2012).

4.3. Humic Acid Removal and Characterization

Figure 3 shows % UV_{254} removal data of humic acid in the presence of Fe-TiO_2 specimens using two different doses.

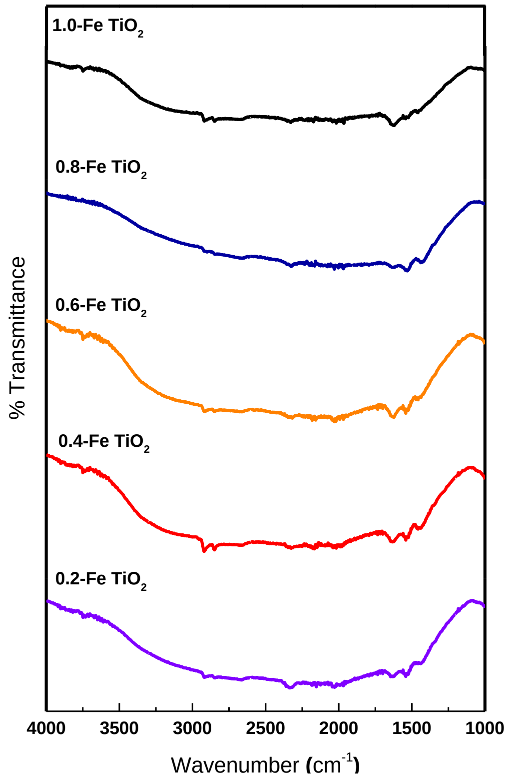


Figure 1. FTIR spectra of Fe-doped TiO$_2$ samples

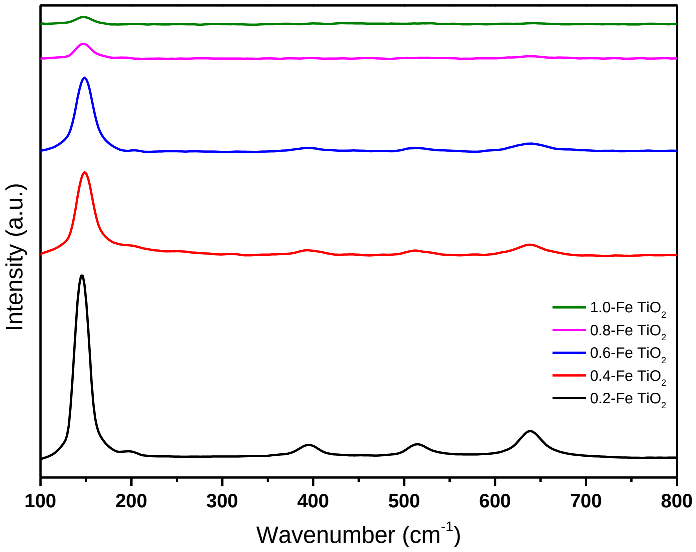


Figure 2. Raman spectra of Fe-doped TiO$_2$ samples.

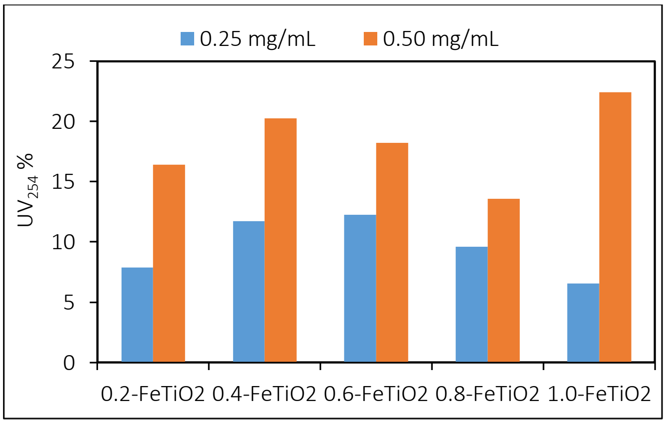


Figure 3. Humic acid removal (60 min) in the presence of 0.25 and 0.50 mg/mL Fe-TiO$_2$.

In general, humic acid removal increased with increasing photocatalyst dose. In the presence of 0.25 mg/mL of catalyst, changing the mole percentage of Fe-TiO_2 from 0.2 to 0.6 slightly increased removal of HA from 8 to 12%. Further increase in the mole ratio had a detrimental effect on the photocatalytic removal of humic acid probably due to recombination of Fe with electrons and holes. However, a completely different trend was observed in the presence of 0.5 mg/mL of photocatalyst loading that reached a maximum removal of 23 % using the highest mole ratio of Fe-TiO_2. Considering better removal efficiencies attained in the presence of 1.0 Fe-TiO_2, irradiation time dependent changes were presented in Figure 4.

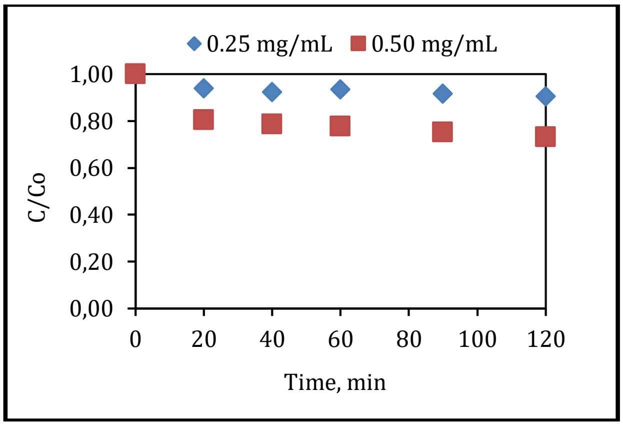
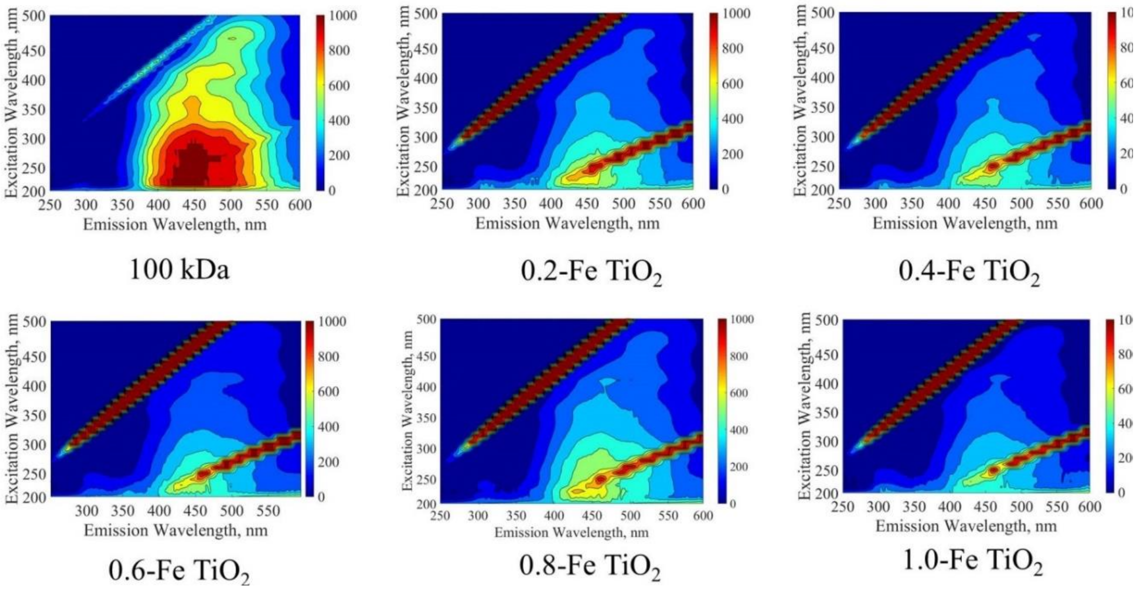


Figure 4. UV_{254} removal of humic acid in the presence of 1.0 Fe-TiO_2.

Kinetic modelling of humic acid removal data revealed pseudo first order rate constants (k) as 1.1x10^{-3} min^{-1} and 3.93x10^{-3} min^{-1}, in the presence of 0.25 mg/mL and 0.50 mg/mL of Fe-TiO_2, respectively. Using the same substrate even under similar experimental conditions, photocatalytic activity of in-situ doped Fe-TiO_2 versus Fe-TiO_2 (prepared from P-25 or UV-100) synthesized by wet impregnation (Birben et al., 2017) showed significant differences. Compared to previous results of Birben et al., (2017), in the presence of in-situ doped Fe-TiO_2, one order of magnitute retardation in rate constants were noted for the photocatalytic removal of 100 kDa HA.

In Figure 5, EEM contour plots of humic acid subsequent to photocatalysis of 60 min using five different mole ratios Fe- TiO_2 samples (constant dose: 0.5 mg/ml) were shown. It is notable from the figure that humic like as well as fulvic like features decreased in all spectra, but the most significant change was observed in the presence of 1.0-Fe TiO_2 sample.



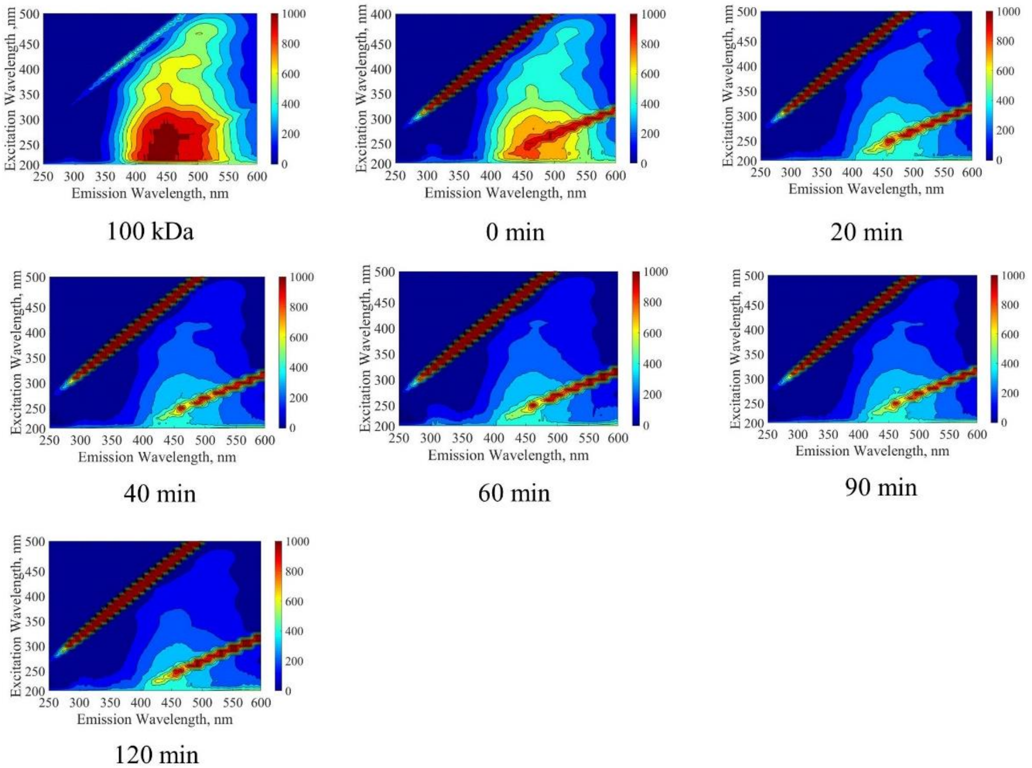
100 kDa 0.2-Fe TiO_2 0.4-Fe TiO_2

0.6-Fe TiO_2 0.8-Fe TiO_2 1.0-Fe TiO_2

Figure 5. EEM contour plots of humic acid degradation using different mole ratios of Fe-doped TiO_2 samples.

The change in EEM contour plots of humic acid with respect to photocatalytic irradiation time was also illustrated for 1.0-Fe-TiO_2 sample in Figure 6. In accordance with UV_{254} removal data, change of EEM spectra with decrease in intensity is noticable. Moreover, analysis of EEM fluorescence contour plots attained for an irradiation period of 120 min show gradual disappearance of humic-like (λ_{exc} 220–470 nm and λ_{emis} 380–580 nm) features and evolution of protein-like fluorophores (λ_{exc} 220–250 nm and λ_{emis} 280–332 nm). Considering the higher removal efficiency attained, as followed by UV_{254}, using 1.0 Fe-TiO_2 photocatalyst, EEM contour plots similarly illustrated significant loss of humic like moieties after photocatalysis of 120 min.

Humic acids have the capability of complexation with iron. Therefore, leaching of iron species were determined for 0 min and 60 min solar light irradiation in the presence of HA. The released iron concentration was detected in the range 0.054- 0.095 mg L^{-1} for 0 min. On the other hand, after 60 min solar light irridiation, leaching of iron increased to values ranging from 0.101 mg L^{-1} to 0.413 mg L^{-1}. The reason could be explained by chelation with humic acids and releasing of iron to the aqueous medium. The amount leached could be considered as negligible due to the presence of a high amount of iron in photocatalyst samples.



100 kDa

0 min

20 min

40 min

60 min

90 min

120 min

Figure 6. EEM contour plots of humic acid with respect to irradiation time using 1.0-Fe TiO_2.

5. Result and Discussion

Results revealed that, using Fe-doped photocatalysts prepared by in-situ sol-gel method, 20 to 25% removal of humic acid could be attained after photocatalytic treatment of 120 min.

EEM fluorescence spectroscopy showed notable decrease in both humic and fulvic like fluorescence features during photocatalysis, the most prominent being the one carried out in the presence of 1.0-Fe TiO_2 sample.

Improvement of the photocatalytic activity of Fe-doped TiO_2 using different methods can be possible. Considering the origin based structural complexity of NOM, different fractions of humic acid could reveal various removal efficiencies that requires further testing.

Acknowledgement

The authors express their thanks to Kırşehir Ahi Evran University Research Foundation for financial support (Project No. FEF.A4.19.009).

Conflict of Interest

No conflict of interest was declared by the authors.

References

Araña, J., Gonzalez Diaz, O., Dona Rodriguez, J.M., Herrera Melian, J.A., Garrigai Cabo, C., Perez Pena, J., Carman Hidalgo, M. and Navio-Santos, J.A., 2003. Role of Fe3+/Fe2+ as TiO_2 dopant ions in photocatalytic degradation of carboxylic acids. Journal of Molecular Catalysis A: Chemical, 197, 157-171.

Baek, M.-H., Hong, J.-S., Yoon, J.-W., and Suh J.-K., 2013. Photocatalytic degradation of humic acid by Fe-TiO_2 supported on spherical activated carbon with enhanced activity. International Journal of Photoenergy, 2013, 1-5.

Birben, N.C., Uyguner-Demirel, C.S., Sen-Kavurmaci, S., Gurkan, Y.Y., Turkten, N., Cinar, Z., Bekbolet, M., 2017. Solar photocatalytic degradation of natural organic matter in the presence of Fe^{3+}-doped TiO2 specimens, Catalysis Today, 281, 78–84.

Cong, Y., Zhang, J., Chen, F., Anpo, M., He, D., 2007. Preparation, Photocatalytic Activity, and Mechanism of Nano-TiO_2 Co-Doped with Nitrogen and Iron (III), Journal of Physical Chemistry C, 111, 10618-10623.

Delekar, S.D., Yadava, H.M., Achary, S.N., Meenac, S.S., Pawar, S.H., 2012. Structural refinement and photocatalytic activity of Fe-doped anatase TiO_2, Applied Surface Science, 263, 536–545.

Navio, J.A. Colh, G.D., Litter, M. I, Bianco, G.N., 1996. Synthesis, characterization and photocatalytic properties of iron-doped titania semiconductors prepared from TiO_2, and iron (III) acetylacetonate. Journal of Molecular Catalysis A: Chemical. 106, 267-176

Šijaković-Vujičić, N., Gotić, M., Musić, S., Ivanda, M., Popovıc´, S., 2004. Synthesis and microstructural properties of Fe-TiO_2 nanocrystalline particles obtained by a modified sol-gel method. Journal of Sol-Gel Science and Technology, 30, 5–19.

Shen, X.-Z., Liu, Z.-C., Xie, S.-M., Guo, J., 2009. Degradation of nitrobenzene using titania photocatalyst co-doped with nitrogen and cerium under visible light illumination. Journal of Hazardous Materials, 162, 1193-1198.

Türkten, N., Çınar, Z., 2019. Preparatıon, Characterızatıon and photocatalytıc propertıes of iron-doped TiO_2 photocatalysts. The Proceedings of the 4th International Porous and Powder Materials Symposium and Exhibition PPM.

Yalçın, Y., Kılıç, M. Çınar, Z., 2010. Fe^{3+}-doped TiO_2: A combined experimental and computational approach to the evaluation of visible light activity. Applied Catalysis B: Environmental, 99, 469-477.

Yuan, R., Zhou, B., Hua, D. and Shi, C., 2013. Enhanced photocatalytic degradation of humic acids using Al and Fe co-doped TiO_2 nanotubes under UV/ozonation for drinking water purification. Journal of Hazardous Materials, 262, 527-538.

Zhang, Z., Wang, C.-C., Zakaria, R. and Ying, J.Y., 1998. Role of particle size in nanocrystalline TiO_2-based photocatalysts. Journal of Physical Chemistry B, 102, 10871-10878.

Zhu, Z., Zheng, W., He, B., Zhang, J. and Anpo, M., 2004. Characterization of Fe-TiO_2 photocatalysts synthesized by hydrothermal method and their photocatalytic reactivity for photodegradation of XRG dye diluted in water. Journal of Molecular Catalysis A: Chemical, 216, 35-43.