



PREPARATION OF DOPED TiO₂ PHOTOCATALYSTS AND THEIR DECOLORIZATION EFFICIENCIES UNDER SOLAR LIGHT

Dila KAYA^{1*}, Nazlı TÜRK TEN²

¹ Istanbul Medeniyet University, Faculty of Engineering and Natural Sciences, Department of Chemistry, Istanbul, Turkey

² Kırşehir Ahi Evran University, Faculty of Arts and Sciences, Department of Chemistry, Kırşehir, Turkey

Keywords

*Congo Red,
Decolorization,
Doped TiO₂,
Rhodamine B,
Solar Photocatalysis.*

Abstract

Photocatalysis has gained a great interest for the degradation of organic pollutants in aqueous media. This effective advanced oxidation technique is basically based on the oxidation of the target molecule by hydroxyl radicals. The most widely preferred and powerful photocatalyst is titanium dioxide (TiO₂), but it has limited use under solar light because of its band gap energy. This is a major drawback for various possible applications. In order to overcome this disadvantage, doping the photocatalyst with metals and non-metals to narrow the band gap can be applied. In this work, we have prepared visible light active photocatalysts by using wet-impregnation method. Decolorization of two different classes of dyes, Rhodamine B and Congo Red, was carried out under simulated solar light with doped TiO₂. The photocatalytic performances of non-metal doped (C, N, Se), metal doped (Cu, Fe) and codoped (N/S) TiO₂ photocatalysts were investigated by UV-vis studies and removal percentage calculations.

KATKILANDIRILMIŞ TiO₂ FOTOKATALİZÖRLERİNİN HAZIRLANMASI VE GÜNEŞ IŞIĞI ALTINDA DEKOLORİZASYON VERİMLİLİKLERİ

Anahtar Kelimeler

*Kongo Kırmızısı,
Dekolorizasyon,
Katkılandırılmış TiO₂,
Rodamin B,
Solar Fotokataliz.*

Öz

Organik kirleticilerin sulu ortamda bozunmasında etkili olan fotokataliz yöntemi oldukça ilgi çekmektedir. Bu ileri oksidasyon yönteminin esası, hedef molekülün hidroksil radikalleri tarafından yükseltgenmesidir. En yaygın olarak tercih edilen ve güçlü fotokatalizör titanyum dioksittir (TiO₂). Ancak bant boşluğu enerjisi nedeniyle güneş ışığı altında sınırlı kullanımı vardır. Bu durum, çeşitli olası uygulamalar için büyük bir dezavantajdır. Bu dezavantajın üstesinden gelmek için, fotokatalizörün bant boşluğunu daraltmak amacıyla metaller ve ametaller ile katkılandırma işlemi uygulanabilmektedir. Bu çalışmada, ıslak aşılama metodunu kullanarak simüle edilmiş solar ışıkta aktif olan fotokatalizörler hazırlanmıştır. Rodamin B ve Kongo Kırmızısı olmak üzere iki farklı boya sınıfının dekolorizasyonu (renginin giderilmesi) işlemi güneş ışığı altında katkı TiO₂ ile yapılmıştır. Ametal katkı (C, N, Se), metal katkı (Cu, Fe) ve ikili katkı (N/S) TiO₂ fotokatalizörlerin fotokatalitik performansları UV-vis verilerini takip ederek ve ortamdaki uzaklaşma yüzdeleri hesaplanarak incelenmiştir.

Alıntı / Cite

Kaya, D., Türkten, N., (2020). Preparation of Doped TiO₂ Photocatalysts and Their Decolorization Efficiencies Under Solar Light, Journal of Engineering Sciences and Design, 8(3), 655-663.

Yazar Kimliği / Author ID (ORCID Number)

D. Kaya, 0000-0003-1607-5317
N. Türkten, 0000-0001-9343-3697

Makale Süreci / Article Process

Başvuru Tarihi / Submission Date	08.01.2020
Revizyon Tarihi / Revision Date	09.06.2020
Kabul Tarihi / Accepted Date	21.06.2020
Yayın Tarihi / Published Date	24.09.2020

* İlgili yazar / Corresponding author: dila.kaya@medeniyet.edu.tr, +90-216-280-3333-4055

1. Introduction

The removal of organic pollutants in water and air, which cause environmental pollution, is an increasingly relevant subject in today's world. The subject has gained great importance and new environmentally friendly methods for removing these pollutants are being developed every day.

One class of pollutants is synthetic organic dyes which are widely used in different industries (Méndez-Martínez et al., 2012). Depending on their chemical constitutions, dyes can be classified as azo dyes that contain one or more azo bonds (-N= N-) and non-azo dyes. The release of azo dyes into the water streams can cause severe environmental problems. Furthermore, studies have shown that the toxicity and carcinogenic character of azo dyes can be threatening for human health (Turkten et al., 2017). Rhodamine dyes which are also known as fluorone dyes are used extensively for biotechnology applications because they show fluorescence and can be detected easily. Rhodamine dyes are also suspected to be carcinogenic and further studies are required for their removal from aqueous media.

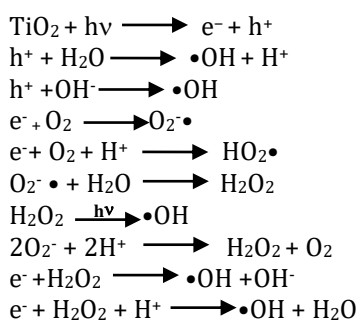
In this work, we have prepared visible light active photocatalysts by wet-impregnation method and carried out the decolorization of two different classes of dyes, Rhodamine B and Congo Red, under solar light. Evonik P25 powder, which is a mixture of anatase and rutile phases (79% anatase, 21% rutile) was chosen as the photocatalyst for doping. P25 TiO₂ which is the standard photocatalyst has high activity with a well-established structure and photocatalytic data. The photocatalytic performances of non-metal doped (C, N), metal doped (Cu, Fe, Se) and codoped (N/S) TiO₂ photocatalysts were investigated and compared by following UV-Vis data of the decolorization process and commenting on removal percentages.

2. Literature Survey

Advanced oxidation processes (AOP) stand out as alternative methods for the destruction of synthetic organic species resistant to conventional removal methods. The idea of AOP is based on the highly reactive hydroxyl radicals (Kudo et al., 2003, Gaya et al., 2008). Heterogeneous photocatalysis method which is one of the AOP, is a technique that enables the decomposition of organic pollutants in water and air into small molecules such as CO₂, H₂O, HCl in the presence of low energy UV-A light and a semiconductor. With the photocatalytic oxidation of the process, organic pollutants in the gas or liquid phase are partially or completely converted into harmless substances (Herrmann et al., 1993, Bahnemann et al., 1994, Mills et al., 1997, Pichat, 1997, Guillard et al., 1999, Bahnemann, 2004).

Since the first time the photocatalytic activity of TiO₂ was discovered (Fujishima et al., 1972), there has been an ongoing interest on its possible applications as a photocatalyst. The photocatalytic removal of organic pollutants is an economical method since it operates at ambient conditions, does not require energy input or additional chemicals other than atmospheric oxygen (Pelaez et al., 2012). There is a variety of reasons that TiO₂ is the most widely preferred and the most efficient photocatalyst. The advantages of TiO₂ include high stability, non-solubility in water, low-cost, chemical inertness and non-toxic as well as being a highly oxidative semi-conductor (Suib, 2013).

The basis of the accepted mechanism of TiO₂ photocatalysis can be explained by the formation of electron-hole (e⁻ / h⁺) pairs as a result of excitation by UV light and the obtained e⁻ / h⁺ pairs lead to oxidation and reduction reactions on the TiO₂ surface. The electrons are trapped in the distorted regions (Ti³⁺) on the particle surface and move away from the medium by reacting with molecular oxygen to form the superoxide anion radical and more hydroxyl radicals. The resulting holes react with the adsorbed water molecules or OH⁻ ions on the surface to form hydroxyl radicals. Hydroxyl radicals are thought to be the main reactive particles involved in the formation of photocatalytic reactions (Xu et al., 2007). The mechanism of photocatalytic degradation is given below;



However, the major drawback of titanium dioxide as a semiconductor-based photocatalyst is that it has a wide band gap energy of 3.2 eV and is able to absorb only 5% of sunlight. In order to overcome this disadvantage, numerous methods have been proposed and developed such as coupling with metal oxides (Ibhadon et al., 2008, Liao et al., 2008), depositing on magnetic ferrite activated carbon (Wang et al., 2010), synthesizing composite materials (Wang et al., 2007, Woan et al., 2009, Yüce et al., 2017) and surface modification (Kaya et al., 2017). One of these methods is doping the TiO₂ with metals or non-metals for an enhanced activity (Diebold, 2003, Gurkan et al., 2012, Birben et al., 2015).

Recently, doping with metal and non-metals has been carried out in order to increase the efficiency of TiO₂ photocatalysts under visible light. For this purpose, doping of TiO₂ with metal elements (Ag, Pt, Cr, V, Se, Fe, etc.) and non-metal elements (B, C, S, F, N, etc.) is conducted for increasing the visible photocatalytic activity. Metal ion doping enhances the photocatalytic activity by reducing the recombination of electron-space pairs and narrowing the charge distribution distance. Transition metal ions are the most commonly used dopants for reducing the band gap and increasing the activity of TiO₂. Metal ions are usually replaced by Ti⁴⁺ ions in the crystal network and make TiO₂ visible light active by adding electrons to the valence band or by placing additional electronic levels in the band space. In addition, metal ions slow the association rate of the charge carriers on the surface and play a role in increasing the photocatalytic activity of TiO₂. Dopant ions act as traps for electrons and holes. Numerous studies have been conducted on the effect of metal ions and while some researchers suggest that metal ions increase the activity of TiO₂, others have reported that metal ions have negative effects on the photocatalytic activity of TiO₂ (Karakitsou et al., 1993, Kang, 2003, Zhou et al., 2005, Wellia et al., 2011).

Metal-doped photocatalysts have low thermal resistance and metal ions also may act as new coupling centers for charge carriers, which has led researchers to search for new dopant ions. Recent studies show that non-metals such as N, C, S, B and P are suitable doping ions (Ohno et al., 2004). Among them, nitrogen doping is the most widely preferred one of these studies (Asahi et al., 2001, Jagadale et al., 2008, Yalçın et al., 2010). This is due to the fact that the radius of nitrogen is very close to that of oxygen, is stable and has low ionization energy. Some researchers suggest that NO_x, NH_x and N²⁻ groups on the TiO₂ surface produce visible light activity, while others suggest that the energy of the valence band increases with the nitrogen contribution and thus the band gap is narrowed (Sakthivel et al., 2004, Sato et al., 2005). Subsequent studies with anion dopants have shown that carbon doping also shifts the absorption of TiO₂ into the visible region (Sakthivel et al., 2003). The results obtained with carbon doping were interpreted differently from nitrogen. Carbon acts as both a cation by replacing with Ti⁴⁺ in the crystal network and an anion by replacing with oxygen. However, the impurity levels in the non-metal doped TiO₂ act as charge recombination centers and reduce photocatalytic activity at high dopant concentrations.

Another doping approach is codoping the TiO₂ with two different ions (Sun et al., 2006, Yu et al., 2006, Gurkan et al., 2017). Codoping of TiO₂ has increased the photocatalytic activity as compared to single doping due to synergistic effects of two different non-metals (Li et al., 2005). Codoping with a metal and a non-metal is also found to increase the degradation of p-nitrophenol under both UV-A light and visible light (Gurkan et al., 2017).

3. Materials and Methods

In this work, we have prepared non-metal doped (C, N), metal doped (Cu, Fe, Se) and codoped (N/S) TiO₂ photocatalysts using the well-established wet impregnation method. Evonik P25 TiO₂ was used as the photocatalyst. TiO₂ was doped 0.50% wt using CH₄N₂O (urea), C₆H₁₂O₆ (glucose), Fe(NO₃)₃·9H₂O (iron (III) nitrate nonahydrate), Cu(NO₃)₂·3H₂O (copper (II) nitrate trihydrate), SeCl₄ (selenium tetrachloride) and CH₄N₂O and NH₂CSNH₂ (urea and thiourea, respectively) as N, C, Fe, Cu, Se and S/N sources, respectively. All doping sources were purchased from Merck. Congo Red and Rhodamine B was purchased from Sigma Aldrich. All chemicals were used as received without further purification. Deionized water was used for the preparation of the solutions.

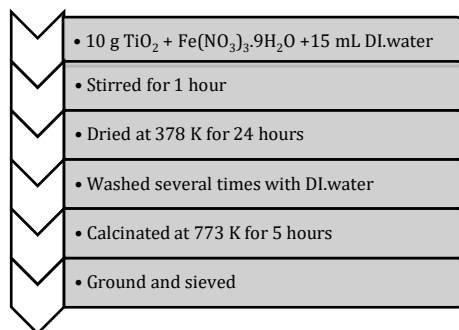
3.1. Preparation of the Doped Photocatalysts

The impregnation method can be briefly described as follows: 10 g TiO₂ Evonik P25 was mixed with 15 mL of aqueous solutions of dopant and stirred for 1 h at room temperature. Dopant concentration was decided as 0.50% wt. for all photocatalysts as it was determined in our previous work (Birben et al., 2015, Birben Nazmiye et al., 2016, Birben et al., 2017, Gurkan et al., 2017, Turkten et al., 2019). The prepared photocatalysts were washed several times with di. water and then dried at 378 K for 24 h to eliminate water completely. Dried photocatalysts were then calcinated at a predetermined temperature for several hours. Afterwards, the obtained samples were ground and sieved for a more homogeneous size distribution. Calcination temperatures and times were previously determined and are given in Table 1.

Table 1. Calcination Times and Temperatures for the Preparation of Doped Photocatalysts.

Photocatalyst	Calcination Temperature and Time
N-doped	500°C, 3 h
C-doped	500°C, 3 h
Fe-doped	500°C, 5 h
Cu-doped	500°C, 5 h
Se-doped	350°C, 3 h
N/S -codoped	350°C, 3 h

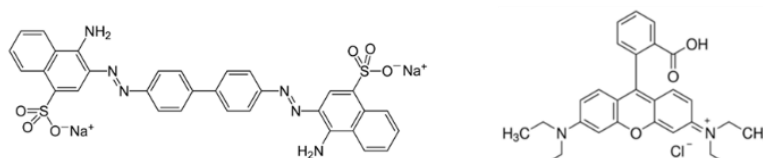
The preparation steps of Fe-doped TiO₂ is given in Figure 1 as an example to the wet impregnation method.

**Figure 1.** Wet Impregnation Steps for the Preparation of Fe-doped TiO₂ (DI.water: Deionized water)

In addition to previous characterization results, Fourier Transform Infrared (FTIR) spectra of the prepared catalysts were taken using a Perkin Elmer Spectrum Two with Universal ATR accessory with diamond/ Zn-Se crystal. Spectra were obtained from 8 scans with a resolution of 2 cm⁻¹ in the range of 4000 - 500 cm⁻¹.

3.2. Decolorization of the Chosen Dyes

Azo-dye Congo Red (CR) and fluorone dye Rhodamine B (RB) were chosen as model dyes for the determination of the decolorization efficiencies of the newly prepared photocatalysts under solar irradiation. The chemical structures of the dyes are given in Figure 2.

**Figure 2.** Congo Red, MW= 670 g/mole, λ_{\max} = 498 nm (left) and Rhodamine B, MW= 479 g/mole, λ_{\max} = 552 nm (right)

Photocatalytic decolorization of the dyes were performed in an ATLAS Suntest CPS+ simulator as solar photocatalytic reactor, equipped with an air cooled Xenon lamp (250 W m⁻² and wavelength range of 300–800 nm) as the light source. 50 mL of 20 mg L⁻¹ dye solution was put in a 150 mL cylindrical Pyrex reaction vessel and subjected to solar photocatalytic oxidation process in the presence of 0.25 mg mL⁻¹ photocatalyst. An ultrasonic water bath was used for the preparation of a homogenous suspension. Continuous stirring was applied during the experiments. After the experiments, samples were filtered through 0.45 μ m Millipore filters in order to remove TiO₂ specimens from the solution prior to analyses via UV-Vis spectrometer. λ_{\max} values were 498 nm for CR and 552 nm for RB.

4. Results and Discussion

4.1. Characterization of the Prepared Photocatalysts

In order to effectively characterize the doped photocatalysts, a variety of methods were used. BET surface area of doped TiO₂ samples were found to change in the range of 45-55 m²g⁻¹ and band gap energies were in the range of 2.55-2.90. The decrease in the band gap energies compared to 3.2 eV band gap energy of bare TiO₂ confirmed that the doping procedure shifted the band gap towards visible region (Gurkan et al., 2013, Birben et al., 2015, Birben Nazmiye et al., 2016, Birben et al., 2017, Gurkan et al., 2017, Turkten et al., 2019).

The FTIR spectra of doped TiO₂ photocatalysts are given in Figure 3. The main characteristic bands that are observed in similar wavenumbers include the broad band at 3300 cm⁻¹, which corresponds to the stretching

vibration of the hydroxyl group O-H of the TiO₂, the band at 1630 cm⁻¹ which is caused by the bending vibration of adsorbed water Ti-OH, and the bands between 800-600 cm⁻¹ corresponding to Ti-O-Ti bending (Yalçın et al., 2010). Any peaks corresponding to dopant phases were not detected. This was attributed to the low doping percentage. All spectra of doped samples were found to exhibit almost identical peak characteristics and intensity trend.

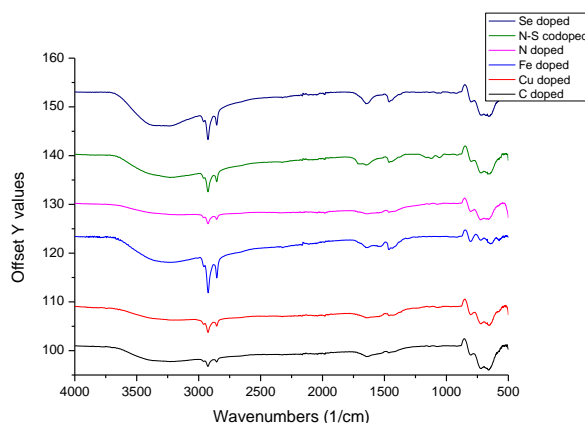


Figure 3. FTIR Spectra of the Prepared Photocatalysts

4.2. Photocatalytic Efficiencies

Photocatalyst performances were evaluated from the removal percentage values of CR and RB. Removal percentages were determined from Equation (1), where C_0 is the initial concentration of the dye and C is the dye concentration at time t .

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

Prior to solar irradiation, removal of dyes by adsorption onto the photocatalyst surface were investigated. In the following data, 0 min represents the adsorption values of dyes onto the photocatalysts without applying any solar light.

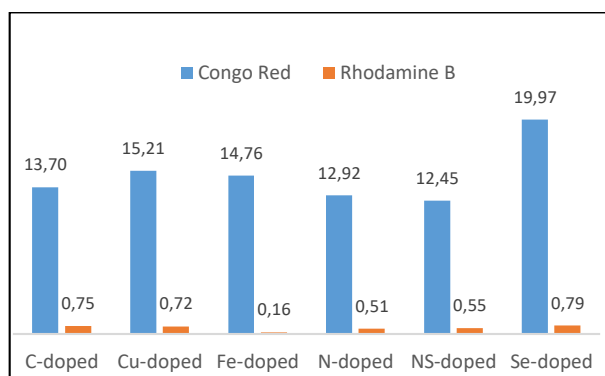


Figure 4. Removal % Values of CR and RB at 0 min

When the removal % values given in Figure 4 are taken into account, it can be said that adsorption of CR on the photocatalyst surface (without the application of solar light) is significantly higher than RB. This behavior can be explained by the higher affinity of two negative oxygen moieties (SO_3^-) on CR towards Ti atoms on the catalyst surface, making it prone to forming complexes. This causes approximately 12 – 20% of CR to be removed by adsorption depending on the catalyst. However, in the case of RB, it can be said that since only less than 1% dye is adsorbed on catalyst surface, RB removal can directly be attributed to photocatalytic decolorization rather than adsorption.

Photocatalytic decolorization results of the dye solutions after treatment with solar light for 60 minutes are given in Figure 5.

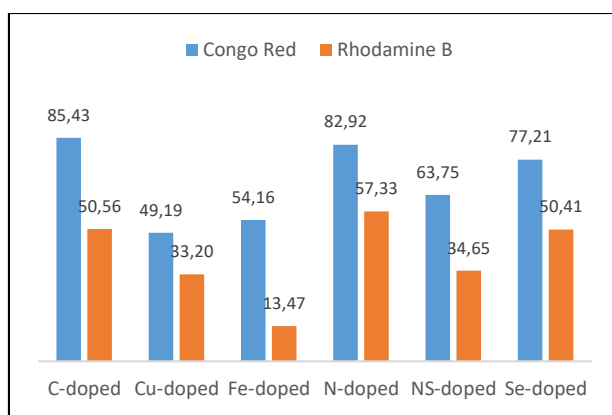


Figure 5. Removal % Values of CR and RB after 60 min Irradiation

Figure 5 shows that overall, CR removal was more efficient than RB removal reaching as high as 85 % for all investigated photocatalysts. This finding could implicate a better removal efficiency for azo dyes compared to fluorone dyes under solar light using doped photocatalysts.

When the photocatalysts were compared with respect to each dopant, both CR and RB had higher removal % for non-metal doped photocatalysts, namely C doped and N doped. For both dyes, co-doping was found to increase the removal efficiencies compared to metal doped photocatalysts. Overall, best decolorization performances were obtained with C-doped and N-doped photocatalysts for both CR and RB. This finding is in agreement with literature where carbon doped TiO₂ was found to have superior photocatalytic activity than unmodified TiO₂ for the solar light degradation of some phenol derivatives and azo dye remazol red (Sakhivel et al., 2003). Nitrogen doped visible light active photocatalysts were also investigated and found to be visible light active for the degradation of varying model pollutants such as phenols, dyes, and volatile organic compounds (Pelaez et al., 2012).

While C and N-doped photocatalysts have similar removal efficiencies between 83-85%, Se which is also a non-metal causes a somewhat lower removal percentage of 77%. This can be explained by the fact that Se is also considered as a metalloid with properties that are similar to sulfur, arsenic and tellurium. It was argued by Gurkan et. al. that Se doping produces additional electronic states and contributes to a higher visible light activity (Gurkan et al., 2013).

Although codoping with N and S provides a higher decolorization of the studied dyes compared to metal doped photocatalysts, the visible light activity of NS-doped catalyst was lower than non-metal doped ones. It was previously shown that while codoping is believed to be superior to single non-metal doping, codoping at two anionic sites could distort the crystal structure and promote the recombination rate of the charge carriers (Sun et al., 2013).

Metal doped photocatalysts were less efficient in terms of dye decolorization with 49-54% for CR and 13-33% for RB using Fe-doped and Cu-doped photocatalysts, respectively. It is known that incorporating transition metals into the TiO₂ crystal lattice could cause the formation of new energy levels between valence and conductance bands decreasing the band gap energy. Nonetheless, there are also explanations as to why photocatalytic activity or the visible light activity is not enhanced with metal ion doping as expected. This low visible light activity despite the decrease in band gap energy could be explained by the low incorporation of the metals into the TiO₂ lattice and the blocking of the surface by excess metal ions (Kang, 2005). Other possible drawbacks include photocorrosion and the promotion of charge recombination at metal sites (Pelaez et al., 2012).

Detailed decolorization values for both dyes at 0 min and 60 min are presented in Figure 6 for comparison. It can be said by removal % values of 0 min and 60 min, RB is only removed from the aqueous solution by photocatalysis with the prepared doped catalysts under solar light. CR on the other hand, clearly adsorbs onto the catalyst surface as high as 20%, indicated by the 0 min results. In order to clarify the means of removal from the solution and decolorization; 0 min, 60 min removal % results and the difference between them is given in Table 2.

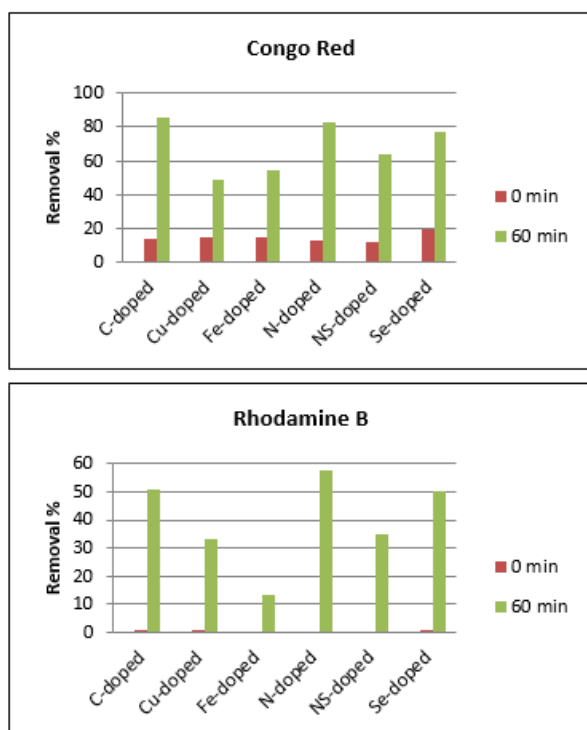


Figure 6. Comparative Removal % Values for CR and RB at 0 min and 60 min

Table 2. Removal % Differences Depending on Adsorption or Photocatalytic Decolorization

	Removal %					
	C-doped	Cu-doped	Fe-doped	N-doped	N,S-codoped	Se-doped
Congo Red						
0 min	13.70	15.21	14.76	12.92	12.45	19.97
60 min	85.43	49.19	54.16	82.92	63.75	77.21
Difference	71.73	33.98	39.4	70.00	51.30	57.24
Rhodamine B						
0 min	0.75	0.72	0.16	0.51	0.55	0.79
60 min	50.56	33.20	13.47	57.33	34.65	50.41
Difference	49.81	32.48	13.31	56.82	34.10	49.62

In Table 2, differences between 0 and 60 min results yield the normalized value of removal which solely originates from heterogeneous photocatalytic degradation of the dyes. These results indicate that C-doped TiO₂ and N-doped TiO₂ show the highest visible light activity for CR and RB, respectively. The lowest visible light active photocatalyst was determined to be Fe-doped catalyst for the removal of both dyes, with removal values of 39.4 % and 13.3 % for CR and RB.

5. Conclusion

In this work we have shown that Evonik P25 TiO₂ can successfully be doped with metals and non-metals using wet impregnation method. We have conducted a comparative investigation on the decolorization performance of the doped photocatalysts and shown that the newly prepared catalysts can indeed perform decolorization of the chosen dyes under simulated solar light. When adsorption onto the doped TiO₂ surfaces were taken into account, CR was found to be more prone to adsorbing to the surface of TiO₂ than RB. This was attributed to the affinity of negative moieties on CR towards Ti atoms. Both CR and RB had higher removal % for non-metal doped photocatalysts. For both dyes, co-doping increased the removal efficiencies compared to metal doped photocatalysts. Overall, best decolorization performances were obtained with C-doped and N-doped photocatalysts for CR and RB, respectively. Future work includes evaluating the photocatalysis kinetics in order to shed light on the reaction mechanism.

Acknowledgements

The authors express their thanks to Kirsehir Ahi Evran University Research Foundation for their financial support (Project No. FEF.A4.19.009-A4). Authors also would like to express their gratitude to Professor Miray Bekbolet for allowing them to conduct photocatalytic experiments at the laboratories of Boğaziçi University, Institute of Environmental Sciences.

Conflict of Interest

No conflict of interest was declared by the authors.

References

- Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K. and Taga, Y., 2001. Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides. *Science*, 293 (5528): 269-271.
- Bahnemann, D., 2004. Photocatalytic water treatment: solar energy applications. *Solar Energy*, 77 (5): 445-459.
- Bahnemann, D., Cunningham, J., Fox, M., Pelizzetti, E., Pichat, P., Serpone, N., Helz, G., Zepp, R. and Crosby, D., 1994. Aquatic and surface photochemistry. Lewis, Boca Raton, FL: 261.
- Birben Nazmiye, C., Uyguner-Demirel Ceyda, S., Sen-Kavurmaci, S., Gürkan Yelda, Y., Türkten, N., Kılıç, M., Çınar, Z. and Bekbolet, M., 2016. Photocatalytic Performance of Anion Doped TiO₂ on the Degradation of Complex Organic Matrix. *Journal of Advanced Oxidation Technologies*. 19: 199.
- Birben, N. C., Uyguner-Demirel, C. S., Kavurmaci, S. S., Gürkan, Y. Y., Türkten, N., Cinar, Z. and Bekbolet, M., 2017. Application of Fe-doped TiO₂ specimens for the solar photocatalytic degradation of humic acid. *Catalysis Today*, 281: 78-84.
- Birben, N. C., Uyguner-Demirel, C. S., Sen-Kavurmaci, S., Gurkan, Y. Y., Turkten, N., Cinar, Z. and Bekbolet, M., 2015. Comparative evaluation of anion doped photocatalysts on the mineralization and decolorization of natural organic matter. *Catalysis Today*, 240, Part A: 125-131.
- Diebold, U., 2003. The surface science of titanium dioxide. *Surface Science Reports*, 48 (5-8): 53-229.
- Fujishima, A. and Honda, K., 1972. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature*, 238 (5358): 37-38.
- Gaya, U. I. and Abdullah, A. H., 2008. Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 9 (1): 1-12.
- Guillard, C., Disdier, J., Herrmann, J.-M., Lehaut, C., Chopin, T., Malato, S. and Blanco, J., 1999. Comparison of various titania samples of industrial origin in the solar photocatalytic detoxification of water containing 4-chlorophenol. *Catalysis Today*, 54 (2-3): 217-228.
- Gurkan, Y., Kasapbasi, E., Turkten, N. and Cinar, Z., 2017. Influence of Se/N Codoping on the Structural, Optical, Electronic and Photocatalytic Properties of TiO₂. *Molecules*, 22 (3): 414.
- Gurkan, Y. Y., Kasapbasi, E. and Cinar, Z., 2013. Enhanced solar photocatalytic activity of TiO₂ by selenium(IV) ion-doping: Characterization and DFT modeling of the surface. *Chemical Engineering Journal*, 214: 34-44.
- Gurkan, Y. Y., Turkten, N., Hatipoglu, A. and Cinar, Z., 2012. Photocatalytic degradation of cefazolin over N-doped TiO₂ under UV and sunlight irradiation: Prediction of the reaction paths via conceptual DFT. *Chemical Engineering Journal*, 184: 113-124.
- Herrmann, J. M., Guillard, C. and Pichat, P., 1993. Heterogeneous photocatalysis : an emerging technology for water treatment. *Catalysis Today*, 17 (1): 7-20.
- Ibhadon, A., Greenway, G. and Yue, Y., 2008. Photocatalytic activity of surface modified TiO₂/RuO₂/SiO₂ nanoparticles for azo-dye degradation. *Catalysis Communications*, 9 (1): 153-157.
- Jagdale, T. C., Takale, S. P., Sonawane, R. S., Joshi, H. M., Patil, S. I., Kale, B. B. and Ogale, S. B., 2008. N-Doped TiO₂ Nanoparticle Based Visible Light Photocatalyst by Modified Peroxide Sol-Gel Method. *The Journal of Physical Chemistry C*, 112 (37): 14595-14602.
- Kang, M., 2003. Synthesis of Fe/TiO₂ photocatalyst with nanometer size by solvothermal method and the effect of H₂O addition on structural stability and photodecomposition of methanol. *Journal of Molecular Catalysis A: Chemical*, 197 (1-2): 173-183.
- Kang, M., 2005. The superhydrophilicity of Al-TiO₂ nanometer sized material synthesized using a solvothermal method. *Materials Letters*, 59 (24-25): 3122-3127.
- Karakitsou, K. E. and Verykios, X. E., 1993. Effects of Altrivalent Cation Doping of Titania on its Performance as a Photocatalyst for Water Cleavage. *The Journal of Physical Chemistry*, 97 (6): 1184-1189.
- Kaya, D. and San, N., 2017. Heterogeneous Photocatalytic Degradation of 4-Nitrophenol via TiO₂ Surface-Modified with Salicylic Acid. *Fresenius Environmental Bulletin*, 26 (8): 4953-4962.
- Kudo, T., Nakamura, Y. and Ruike, A., 2003. Development of rectangular column structured titanium oxide photocatalysts anchored on silica sheets by a wet process. *Research on Chemical Intermediates*, 29 (6): 631-639.
- Li, D., Ohashi, N., Hishita, S., Kolodiazny, T. and Haneda, H., 2005. Origin of Visible-Light-Driven Photocatalysis: A Comparative Study on N/F-Doped and N-F-Codoped TiO₂ Powders by means of Experimental Characterizations and Theoretical Calculations. *Journal of Solid State Chemistry*, 178 (11): 3293-3302.
- Liao, D. L., Badour, C. A. and Liao, B. Q., 2008. Preparation of Nanosized TiO₂/ZnO Composite Catalyst and its Photocatalytic Activity for Degradation of Methyl Orange. *Journal of Photochemistry and Photobiology A: Chemistry*, 194 (1): 11-19.
- Méndez-Martínez, A. J., Dávila-Jiménez, M. M., Ornelas-Dávila, O., Elizalde-González, M. P., Arroyo-Abad, U., Sirés, I. and Brillas, E., 2012. Electrochemical reduction and oxidation pathways for Reactive Black 5 dye using nickel electrodes in divided and undivided cells. *Electrochimica Acta*, 59: 140-149.
- Mills, A. and Le Hunte, S., 1997. An overview of semiconductor photocatalysis. *Journal of Photochemistry and Photobiology A: Chemistry*, 108 (1): 1-35.
- Ohno, T., Akiyoshi, M., Umeyayashi, T., Asai, K., Mitsui, T. and Matsumura, M., 2004. Preparation of S-Doped TiO₂ Photocatalysts and their Photocatalytic Activities Under Visible Light. *Applied Catalysis A: General*, 265 (1): 115-121.
- Pelaez, M., Nolan, N. T., Pillai, S. C., Seery, M. K., Falaras, P., Kontos, A. G., Dunlop, P. S. M., Hamilton, J. W. J., Byrne, J. A., O'Shea, K., Entezari, M. H. and Dionysiou, D. D., 2012. A Review on the Visible Light Active Titanium dioxide Photocatalysts for Environmental Applications. *Applied Catalysis B: Environmental*, 125: 331-349.

- Pichat, P. (1997). Handbook of Heterogeneous Catalysis. in: G. Ertl, H. Knözinger, Wiley-VCH, Weinheim.
- Sakthivel, S., Janczarek, M. and Kisch, H., 2004. Visible Light Activity and Photoelectrochemical Properties of Nitrogen-Doped TiO₂. The Journal of Physical Chemistry B, 108 (50): 19384-19387.
- Sakthivel, S. and Kisch, H., 2003. Daylight Photocatalysis by Carbon-Modified Titanium Dioxide. Angewandte Chemie International Edition, 42 (40): 4908-4911.
- Sato, S., Nakamura, R. and Abe, S., 2005. Visible-Light Sensitization of TiO₂ Photocatalysts by Wet-Method N Doping. Applied Catalysis A: General, 284 (1-2): 131-137.
- Suib, S., 2013. New and Future Developments in Catalysis: Solar Photocatalysis Amsterdam, The Netherlands Elsevier.
- Sun, H., Bai, Y., Cheng, Y., Jin, W. and Xu, N., 2006. Preparation and Characterization of Visible-Light-Driven Carbon-Sulfur-Codoped TiO₂ Photocatalysts. Industrial & Engineering Chemistry Research, 45 (14): 4971-4976.
- Sun, H., Zhou, G., Liu, S., Ang, H. M., Tadó, M. O. and Wang, S., 2013. Visible Light Responsive Titania Photocatalysts Codoped by Nitrogen and Metal (Fe, Ni, Ag, or Pt) for Remediation of Aqueous Pollutants. Chemical Engineering Journal, 231: 18-25.
- Turkten, N. and Cinar, Z., 2017. Photocatalytic decolorization of azo dyes on TiO₂: Prediction of mechanism via conceptual DFT. Catalysis Today, 287: 169-175.
- Turkten, N., Cinar, Z., Tomruk, A. and Bekbolet, M., 2019. Copper-doped TiO₂ photocatalysts: application to drinking water by humic matter degradation. Environ Sci Pollut Res Int.
- Wang, F. and Min, S. X., 2007. TiO₂/polyaniline composites: An efficient photocatalyst for the degradation of methylene blue under natural light. Chinese Chemical Letters, 18 (10): 1273-1277.
- Wang, S. and Zhou, S., 2010. Titania deposited on soft magnetic activated carbon as a magnetically separable photocatalyst with enhanced activity. Applied Surface Science, 256 (21): 6191-6198.
- Wellia, D. V., Xu, Q. C., Sk, M. A., Lim, K. H., Lim, T. M. and Tan, T. T. Y., 2011. Experimental and theoretical studies of Fe-doped TiO₂ films prepared by peroxo sol-gel method. Applied Catalysis A: General, 401 (1-2): 98-105.
- Woan, K., Pyrgiotakis, G. and Sigmund, W., 2009. Photocatalytic carbon-nanotube - TiO₂ composites. Advanced Materials, 21 (21): 2233-2239.
- Xu, T., Kamat, P. V., Joshi, S., Mebel, A. M., Cai, Y. and O'Shea, K. E., 2007. Hydroxyl radical mediated degradation of phenylarsonic acid. J Physical Chemistry A, 111 (32): 7819-7824.
- Yalçın, Y., Kılıç, M. and Çınar, Z., 2010. Fe³⁺-doped TiO₂: A combined experimental and computational approach to the evaluation of visible light activity. Applied Catalysis B: Environmental, 99 (3-4): 469-477.
- Yalçın, Y., Kılıç, M. and Çınar, Z., 2010. The Role of Non-Metal Doping in TiO₂ Photocatalysis. Journal of Advanced Oxidation Technologies, 13 (3): 281-296.
- Yu, J., Zhou, M., Cheng, B. and Zhao, X., 2006. Preparation, Characterization and Photocatalytic Activity of in situ N,S-Codoped TiO₂ Powders. Journal of Molecular Catalysis A: Chemical, 246 (1-2): 176-184.
- Yüce, E., Mert, E. H., Krajnc, P., Parin, F. N., San, N., Kaya, D. and Yıldırım, H., 2017. Photocatalytic Activity of Titania/Polydicyclopentadiene PolyHIPE Composites. Macromolecular Materials and Engineering, 302 (10): 1700091.
- Zhou, M., Yu, J., Cheng, B. and Yu, H., 2005. Preparation and photocatalytic activity of Fe-doped mesoporous titanium dioxide nanocrystalline photocatalysts. Materials Chemistry and Physics, 93 (1): 159-163.