Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23812

151 (2019) 161–166
May

N-doped titanium dioxide nanoparticles activated under visible light achieve the photocatalytic degradation of textile azo dye remazol brilliant blue R

María C. Yeber*, Texia Zamora, Ricardo Álvarez, Paulina Medina

Faculty of Science, Department of Environmental Chemistry, Universidad Católica de la Santísima Concepción, Alonso de Ribera2850, Concepción, Chile, Tel. +56412345273; emails: mcyeber@ucsc.cl (M.C. Yeber), tazamora@qaciencias.ucsc.cl (T. Zamora), rdalvarez@qaciencias.ucsc.cl (R. Alvarez), pmedina@ucsc.cl. (P. Medina)

Received 14 June 2018; Accepted 20 January 2019

ABSTRACT

Dyes used in the textile industry have varied and complex structures are designed to resist degradation by external agents. Most are water soluble, resistant to chemical agents and not biodegradable, so they cannot be easily removed by wastewater treatment plants. Remazol Brilliant Blue R (RBBR) is one of the most important colorants in the textile industry, and it is frequently used as a starting material in the production of polymer dyes. This work studied the degradation of a textile dye by a heterogeneous photocatalysis process, using a titanium dioxide catalyst doped with nitrogen from urea, in the presence of visible light irradiation. For the optimization of the process a Box-Benhken experimental design was performed. Where, the TiO_2 was varied from 0.1 gL^{-1} (–1) to 1.0 gL^{-1} (+1), and the pH between 2.0 (–1) to 11(+1). With the optimal response it was possible to remove 86.3% of the dye ($R^2 = 0.987$ and $Q^2 = 0.873$, $p \leq 0.001$). The mineralization grade was determined through TOC analysis, which reached 50%, and the toxicity was evaluated with *Daphnia magna* nematodes, which was reduced considerably after photocatalytic treatment.

Keywords: N-doped TiO_2; Photocatalysis; Textile azo dye; Toxicity; Visible light

1. Introduction

When the colored effluents containing dyes are eliminated in aquatic systems, it causes an immediate impact in the environmental, due to the color, inhibiting photosynthesis and as a consequence producing harmful effects on aquatic environment.

These effluents are characterized by having a high chemical oxygen demand (COD), high color, solids in suspension and the presence of organic chlorinated compounds [1–3]. For this reason, the degradation of textile dyes by different methods has been studied [4–6], one of these is heterogeneous photocatalysis, because it is one of the advanced oxidation processes efficient in degrading organic matter.

Advanced oxidation processes using TiO_2 have been extensively studied in the degradation of a wide variety of organic compounds. However, the energy band gap the TiO_2 restricts its application due to its need of high energy radiation for the electronic jump to occur, limiting its use under visible light [7], and resulting in an increase of the investment cost in the application of these processes on a major scale. Hence, numerous methods of doping on the semiconductor have been studied, and a great variety of different semiconductors have been synthesized; with the aim of achieving lower energy gap and to be able to work with visible light or solar radiation [8–10].

Wen et al. [11] have studied p-n heterostructure in order to quicken the separation of electron–hole pairs using mixtures of strontium and bismuth via a hydrothermal method. The photocatalytic activity of new structure was tested in the degradation of different pollutants, including the textile dye methyl orange. Dong et al. [8] have also

---

* Corresponding author.

1944-3994/1944-3986 © 2019 Desalination Publications. All rights reserved.

studied the deposition of bismuth on the semiconductor as an alternative to the deposition of noble metals, those that have been used more widely as dopants [12–16]. Venditti et al. [17] used glucose as carbon source to doped titanium dioxide to degrade Caffeic acid under photocatalytic process activated by visible light, demonstrating that the whole process is governed by a synergic mechanism in which adsorption and photodegradation are involved. In addition, Rhodamine B, used as a model textile dye, degraded in the presence of carbon-doped TiO_2 through a photocatalytic process activated by visible light. In this case, the particles of the semiconductor were prepared by the hydrolysis of titanium isopropoxide [18]. Ren et al. [19] prepared TiO_2 photocatalyst through the sol gel method and doped by using glucose as carbon source, and achieved only a 55% of degraded compounds in 300 min of treatment.

Another technique using non-metals for doping is the incorporation of nitrogen atoms in the titanium dioxide, which promotes good photocatalytic activity; when the semiconductor is used under visible light irradiation, due to the nitrogen atoms being able to reduce the band gap energy of TiO_2 [20,21]. Asahi et al. [22] did substitutional doping of C, N, F, P, or S for O in the anatase TiO_2 crystal, which demonstrated that the substitutional doping of N was the most effective because its p states contribute to the band-gap narrowing by mixing with O 2p states.

Sacco et al. [23] prepared by the sol gel method TiO_2-N, incorporating nitrogen in the titanium dioxide, using ammonia as nitrogen source and the photocatalytic activity were tested degrading a textile dye. The dyes are good model compounds to prove the efficiency of the new material, due to its molecular structure which permits the conditions to be determined for a subsequent treatment of the real effluents and prevents the discharge of colored contaminants in aquatic systems.

The incorporation of nitrogen atoms in the TiO_2 generates localized states in the space of the band gap, just above the valence band. This allows the electrons to be promoted from these localized states to the conduction band with visible light. The sensitivity of the TiO_2 to visible light is due to the fact that some oxygen atoms are replaced by nitrogen atoms, thus resulting in the overlap of N_{2p} and O_{2p} [24,25].

In this research TiO_2 doped with nitrogen from urea was used, and its efficient activity was tested on textile dye degradation and the process was optimized by multivariate analysis.

2. Materials and methods

The TiO_2-N was prepared by adding different concentrations of urea to the catalyst and subjected to temperatures between 400ºC and 600ºC to obtain the catalyst with higher photoactivity under visible light. Yeber et al. [26] reported the characterization of the doped semiconductor in a previous paper.

To verify the efficiency of doping, the textile dye Remazol Brilliant Blue R (RBBR), was used as a model compound, and the effect of pH on the semiconductor was evaluated using a multivariate analysis, with the catalyst dose and the pH as the experimental variables. Experimental design through a matrix of 12 experiments, with the ranges of the variables to study between 0.1 gL^{-1} (–1) and 1.0 gL^{-1} (+1) by TiO_2-N and between 2 (–1) and 11 (+1) by pH. The time remained constant for 120 min in each experiment.

2.1. Reaction kinetics

The experiments were conducted in a reaction chamber, which is equipped with a magnetic stirrer, aerator and a 250 W and 230 V-50 Hz lamp. Photocatalytic degradation studies were carried out at both pH´s given by the experimental design, pH 2.5 and 3.0 and 1.0 gL^{-1} of TiO_2-N at time intervals of 30, 60, 90 and 120 min, using 50 mL of 50-ppm dye solution. All photocatalytic experiments were performed under room temperature with agitation, aeration and constant irradiation. After each treatment, dye samples were filtered using filter of 0.22 μ, and the degradation process was followed by UV-visible spectrophotometry.

2.2. Chemical oxygen demand (COD)

The chemical oxygen demand (COD mg O_2L^{-1}) was determined using the Merck Spectroquant kit with a measured range of 25–1,500 mg O_2 L^{-1}, Standard Methods 5220 D and ISO 15705.

2.3. Total organic carbon (TOC)

The Merck Spectroquant kit from 50–800 mg C $L^{-1}$was used for the determination of TOC. The carbon content in the sample was transformed with sulfuric acid and peroxodisulfate, to CO_2, when carried to reflux for 2 h in a thermal reactor (*Spectroquant TR620*) and *Spectroquant® NOVA 60*. TOC was expressed in mg of C L^{-1} (Method: ISO 84661-1 and DIN38402 A51).

2.4. Nitrogen

The determination of residual nitrogen after photocatalysis treatment was carried out by using the Merck method Spectroquant kit (ISO 11905-1).

2.5. Toxicity

The toxicity before and after photochemical treatment was determined using *Daphnia magna* nematodes. The analysis was performed with five dilutions of each sample, reconstituted water (water Class 4) was used as a control, and potassium dichromate was used as reference toxicant.

Bioassays were performed in duplicate for 24 h. The response was evaluated as mortality and expressed as a percentage of survival. To obtain the LC_{50} the Probit method was used (USEPA, 1991).

3. Results and discussion

The experimental matrix with the response obtained for each treatment, according to the range of the variables (coded and uncoded) studied for the degradation of the dye RBBR (Fig. 1) is shown in Table 1. The responses obtained from the experimental design give a mathematical equation (Eq. (1)) plotted in Fig. 2, where one can observe that the first order variable has the most influence in the response, whereas when the semiconductor concentration increases and pH decreases the dye removal is greater. However, both variables reach a maximum as is observed with the bars representing the quadratic variables [TiO*TiO] and [pH*pH]. The observed response was determined experimentally and the mathematical model gave the predicted response. As observed, both values are similar so that the experimental response is in agreement with the prediction of the model.

$$Y\,(\%) = 49.6(\pm 1.5) + 15.25(\pm 1.4)X_1 - 21.6(\pm 1.4)X_2 - 7.1(\pm 2.0)X_1^2 - 3.7(\pm 2.0)X_2^2 - 0.6(\pm 1.7)X_1 \times X_2 \quad (p \leq 0.001) \qquad (1)$$

where Y is the RBBR removed (%), X_1 is the TiO_2 (gL^{-1}) and X_2 is the pH.

The response surface for the RBBR removal is shown in Fig. 3, as is observed in the contour plot representation the red zone indicates the values of the experimental variables that allowed the greatest removal, reaching 86.3% with 1.0 gL^{-1} of TiO_2– N and pH between 2.0 and 3.0. At the same time it is observed that when increasing the pH, the removal of the compound decreases, which is also observed in the polynomial equation, where the variable pH is negative. The effect of pH on the photocatalytic degradation is an important variable to be studied since an acidic pH the TiO_2 surface is positively charged, allowing absorption of

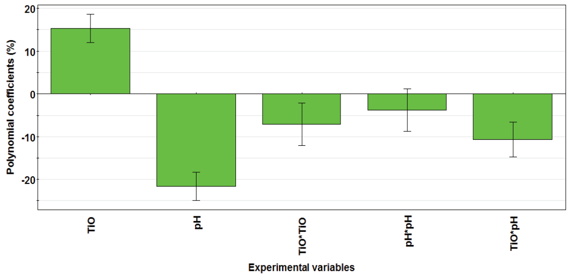

Fig. 2. Influence of each variable in the RBBR removal with TiO_2-N activated under visible light.

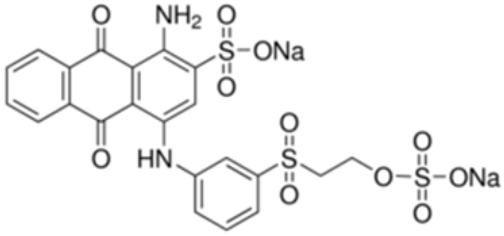

Fig. 1. Chemical structure of the textile dye Remazol Brilliant Blue R.

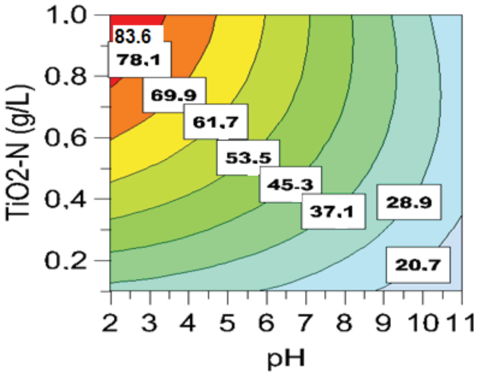

Fig. 3. Response surface for RBBR dye degradation.

Table 1
Experimental design of RBBR removal and the corresponding response

Experiment	Run order[a]	TiO_2-N (gL^{-1})	pH	RBBR-removed	
				Observed (%)	Predicted (%)
N1	6	0.1 (–1)	2.0 (–1)	43.3	57.0
N2	1	0.55 (0)	2.0 (–1)	71.0	74.6
N3	2	1.0 (+1)	2.0 (–1)	86.3	85.1
N4	5	0.1 (–1)	6.5 (0)	32.3	34.3
N5	10	0.55 (0)	6.5 (0)	49.0	48.4
N6	12	1.0 (+1)	6.5 (0)	55.5	55.4
N7	7	0.1 (–1)	11.0 (+1)	11.0	11.3
N8	9	0.55 (0)	11.0 (+1)	23.5	21.9
N9	3	1.0 (+1)	11.0 (+1)	24.0	25.4
N10	4	0.55 (0)	6.5 (0)	48.5	48.4
N11	8	0.55 (0)	6.5 (0)	49.3	48.4
N12	11	0.55 (0)	6.5 (0)	48.8	48.4

[a] Order in which the experiments should be performed

the anionic dye, which improves degradation [27]. In the red zone, where it is possible to find the major response to dye degradation, the experimental design gives a range for the pH variable, therefore the kinetic of reaction was realized at pH 2.5 value more focused on the midpoint of the red zone, where the removal is over 80% and pH 3.0 to observe the effect of a higher pH in the photocatalytic treatment.

According to the ANOVA analysis $R^2 = 0.987$ (observed response) and $Q^2 = 0.873$ (predicted response), which indicates that the experimental response is correlated with the prediction of the model, indicating that there is no experimental error (Fig. 4). In the analysis of lack-of-fit and pure error, the critical F value is lower than the observed F value with a $p \leq 0.001$, which indicates that there are no random errors. All of the studied variables indicate the same results, giving statistical validity to the model. The same was observed by Tzikalos et al. [28] in the degradation of the reactive dye Red 195 using TiO_2 mesoporous nanoparticles under optimal conditions, but using twice the concentration of non-doped semiconductor.

3.1. Reaction kinetics

To check the optimal experimental variables given by the design, the kinetic reaction was performed with TiO_2-N (1.0 gL^{-1}) at pH 2.5 and 3.0. In accordance with this, high dye removal on the response surface was observed, at both pH levels (Fig. 5). However, as it is observed in the surface response, when pH was lowered greater removal occurred, which is in agreement with the kinetics, observing that at pH 2.5 the removal is faster and greater. In addition, the controls showed that the initial concentration of the dye remained constant in the kinetics when the treatment was carried out without light on doped semiconductor and without light and visible light on undoped semiconductor, indicating that the dye degradation is by photocatalysis on TiO_2-N. It is also observed in the photocatalytic system that during 30 min, only the absorption of the dye is produced on the semiconductor and later the photocatalysis occurs. The effective role of the adsorption on photodegradation process was well studied by Venditti et al. [17] where it shows the greatest efficiency in the degradation when this process occur. Cinelli et al. [18] observed the same process, indicating that the dye is first absorbed on the catalyst surface during the dark time, Eq. (2). When the visible light impinges on the semiconductor, the dye is adsorbed by the hole (h^+) generated in the valence band (VB). At the same time, the photogenerated hole oxidizes the adsorbed water molecule, generating OH radicals, which reacts with the organic matter promoting the mineralization process (Eq. (3)). On the other hand, the excited electrons (e−) that migrated to the conduction band (CB) are trapped by molecular oxygen generating superoxide radicals, which also collaborate in the mineralization process of the adsorbed organic matter, Eq. (4). Singh et al. [29] studied the methylene blue degradation under visible light using ZnO doped with nitrogen, removing 90% of dye in 140 min of reaction, demonstrating the effectiveness of nitrogen incorporation in the catalyst independent of the synthesis pathway.

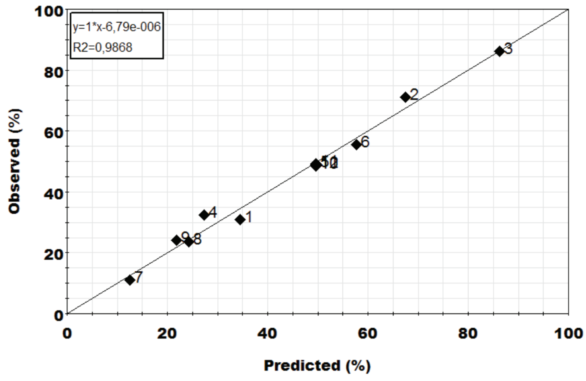

Fig. 4. Observed vs. predicted values from experimental design.

$$\text{MO-TiO}_{2} + \text{Visible light (400–500 nm)} \rightarrow \text{MO-TiO}_2\,(h^+ + e^-) \quad (2)$$

$$\text{MO-TiO}_2\,(h^+)\text{-H}_2\text{O} \rightarrow \cdot\text{OH} + \text{MO} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (3)$$

$$\text{MO-TiO}_2\,(e^-) + \text{O}_2 \rightarrow \text{O}_2^{\cdot-} + \text{MO} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (4)$$

COD and TOC removal are shown in Fig. 6, indicating dye oxidation and mineralization. As is observed in both

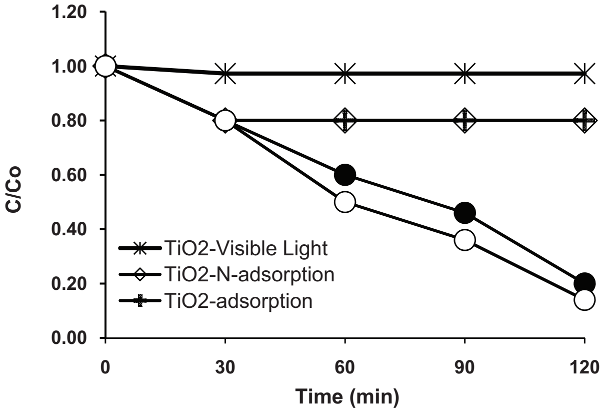

Fig. 5. Kinetics of RBBR dye removal (50 ppm) by TiO_2-N under visible light.

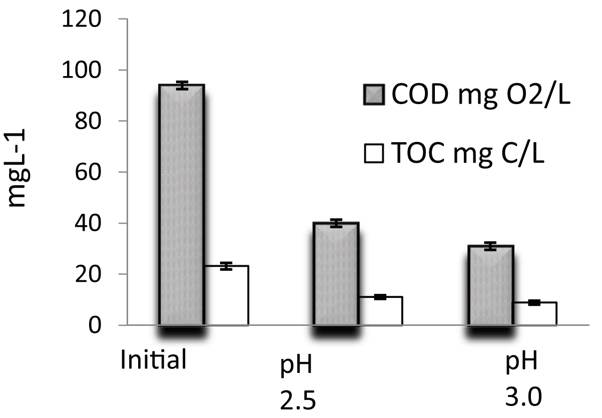

Fig. 6. Chemical oxygen demand (COD) and total organic carbon (TOC) before and after treatment with TiO_2-N-visible light.

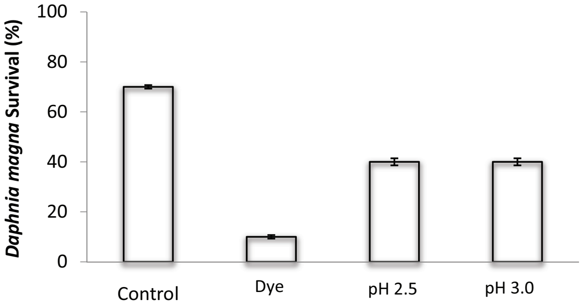

Fig. 7. Survival of *D. Magna* before and after treatment by photocatalysis with TiO_2- N under visible light irradiation.

systems 60% of COD and 50% of TOC were removed, indicating that the photocatalytic system using TiO_2 doped with nitrogen under visible light is efficient degrading textile dyes and mineralizing the remaining organic matter. In addition, residual nitrogen was checked to observe the stability of doping, through analysis of total nitrogen in solution after photochemical treatment. In this process, no nitrogen was observed in solution indicating that the incorporation of nitrogen in the structure of the semiconductor is stable. The same was observed by other author [30] in the preparation of N-doped TiO_2 with zeolita where the research showed excellent catalytic activity and good recycling stability of the catalyst.

3.2. Toxicity on Daphnia magna

Toxicity tests with *D. magna* were used to assess the acute toxicity of RBBR, using nematodes (i.e. less than 24 h of life) *D. magna* (Fig. 7). *D. magna* survival was 40% when kept in the samples that were treated with TiO_2-N. In the initial sample, the percentage of survival did not exceed 10%, which confirms that by submitting dye to the action of the TiO_2-N in the presence of visible light, mineralization occurs, generating less toxic compounds. On the contrary, using the degradation of azo dyes by Electro-Fenton did not reduce the toxicity after treatment due to the formation of more toxic intermediate compounds [31]. On the other hand, Cifci (2016) [5] observed that the decolorization of two dyes under visible light irradiation using Ag-TiO_2 as a catalyst does not generate more toxic compounds, when the post-treated dyes are assessed with toxicity test of *D. magna*.

4. Conclusions

The textile dye RBBR, presented a positive response to the action of the TiO_2-N in presence of visible light. Using the photocatalityc process at acidic pH for 120 min, 86.3% of the dye was removed.

To compare the photocatalytic activity of the TiO_2 and TiO_2-N, it was observed that a higher removal was obtained using the titanium dioxide doped with nitrogen, which shows that the doping of TiO_2 changes its response to visible light, allowing the generation of active sites, which are responsible for degradation. The results showed that both pH 2.5 and 3.0, result in a high response of dye degradation and mineralization, showing high efficiency in the action of the TiO_2-N under visible light.

Acute toxicity testing with *D. magna* determined that the wastewater containing RBBR dye decreases its toxicity after treatment performed with TiO_2-N, reaching 40% survival of nematodes. On the other hand, it shows that the multivariate analysis is a good tool to obtain fast and optimal responses in the processes of degradation.

This research is an important contribution because it demonstrated that doping by a simple and cheap method can occur and be efficient in the degradation of contaminants such as textile dyes using visible light, which would make the process possible to be used at an industrial scale.

Acknowledgments

The authors acknowledge the financial support from the University research direction.

References

[1] T. Hadibarata, R.A. Kristanti, Effect of environmental factors in the decolorization of Remazol Brilliant Blue R by polyporus SP. S133, J. Chil. Chem. Soc., 57 (2012) 1095–1098.

[2] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresour. Technol., 77 (2001) 247–255.

[3] F. Vacchi, J.Vendemiatti, V. Brosselin, B. Da Silva, M. Zanoni, M. De Meo, S. Bony, A. Devaux, G. Umbuzeiro, Combining different assays and chemical analysis to characterize the genotoxicity of waters impacted by textile discharges, Environ. Mol. Mutagen., 57 (2016) 559–571.

[4] A. Asghar, A. Aziz, A. Raman, W. Ashri, W. Daud, Advanced oxidation processes for in-situ production of hydrogen peroxide/hydroxyl radical for textile wastewater treatment: a review, J. Cleaner. Prod., 87 (2015) 826–838.

[5] D.I. Çifçi, Decolorization of methylene blue and methyl orange with Ag doped TiO_2 under UV-A and UV-Visible conditions: process optimization by response surface method and toxicity evaluation, Global Nest J., 18 (2016) 371–380.

[6] J. Hwanga, S. Kalanurb, H. Seo, Identification of visible photocatalytic and photoelectrochemical properties of I-TiO_2 via electronic band structure, Electrochim. Acta., 252 (2017) 482–489.

[7] S. Dong, J. Feng, M. Fan, Y. Pi, L. Hu, X. Han, M. Liu, J. Sun, J.H. Sun, Recent developments in heterogeneous photocatalytic water treatment using visible light-responsive photocatalysts: a review, R.S.C. Advances., 19 (2015) 14610–14630.

[8] X. Dong, W. Zhang, Y. Sun, J. Li, W. Cen, Z. Cui, H. Huang, F. Dong, Visible-light-induced charge transfer pathway and photocatalysis mechanism on Bi semimetal@defectiveBiOBr hierarchical microspheres, J. Catal., 357 (2018) 41–50.

[9] D. Nassoko, Y. Li, H. Wang, J. Li, Y. Li, Y. Yu, Nitrogen-doped TiO_2 nanoparticles by using EDTA as nitrogen source and soft template: simple preparation, mesoporous structure, and photocatalytic activity under visible light, J. Alloys. Compd., 540 (2012) 228–235.

[10] P. Pattanaika, M. Sahoob, TiO_2 photocatalysis: progress from fundamentals to modification Technology, Desal. Wat. Treat., 52 (2014) 6567–6590.

[11] X. Wen, N. Cheng, L. Zhang, Ch. Liang, G. Zeng, An in depth mechanism insight of the degradation of multiple refractory pollutants via a novel $SrTiO_3$/BiOI heterojunction photocatalysts, J. Catal., 356 (2017) 283–299.

[12] T. Putta, M. Lu, J. Anotai, Characterization and activity of visible-light driven TiO_2 photocatalyst doped with tungsten, Water. Sci. Technol., 62 (2010) 2128–2133.

[13] R. Khoshnavazi, S. Fereydouni, L. Bahrami, Enhanced photocatalytic activity of nanocomposites of TiO_2 doped with Zr, Y or Cepolyoxometalates for degradation of methyl orange dye, Water. Sci. Technol., 73 (2016) 1746–1755.

[14] P. Nyamukamba, L. Tichagwa, S.Mamphweli, L.Petrik, Silver/carbon codoped titanium dioxide photocatalyst for improved dye degradation under visible light, Int. J. Photoenergy., (2017) 1–9. doi:10.1155/2017/3079276.

[15] U. Pal, A. Sandoval, S. Madrid, G. Corro, V. Sharma, P. Mohanty, Mixed titanium, silicon, and aluminum oxide nanostructures as noveladsorbent for removal of rhodamine 6G and methylene blue ascationic dyes from aqueous solution, Chemosphere, 163 (2016) 142–152.

[16] G. Pozan, M. Isleyen, S. Gokcen, Transition metal-coated TiO_2 nanoparticles: synthesis, characterization and their photocatalytic activity, Appl. Catal., B., 140–141 (2013) 537–545.

[17] F. Venditti, F. Cuomo, A. Ceglie, P. Avino, M. Russo, F. Lopez, Visible light caffeic acid degradation by carbon-doped titanium dioxide, Langmuir, 31 (2015) 3627−3634.

[18] G. Cinelli, F. Cuomo, L. Ambrosone, M. Colella, A. Ceglie, F. Vendittia, F. Lopez, Photocatalytic degradation of a model textile dye using Carbon-doped titanium dioxide and visible light, J. Water. Process. Eng., 20 (2017) 71–77.

[19] W. Ren, Z. Ai, F. Jia, L. Zhang, X. Fan, Z. Zou, Low temperature preparation and visible light photocatalytic activity of mesoporous carbon-doped crystalline TiO_2, Appl. Catal., B., 69 (2007) 138–144.

[20] H. Wang, X. Gao, G.Duan, X. Yang, X. Liu, Facile preparation of anatase-brookite-rutile mixed-phase N-doped TiO_2 with high visible-light photocatalytic activity, J. Environ. Chem. Eng., 3 (2015) 603–608.

[21] M. Mohamad, W. Salleh, J. Jaafar, A. Ismail, Photodegradation of phenol by N-doped TiO_2 anatase/rutile nanorods assembled microsphere under UV and visible light irradiation, Mater. Chem. Phys., 162 (2015) 113–123.

[22] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Visible-light photocatalysis in nitrogen-doped titanium oxides, Science, 293 (2001) 269–271.

[23] O. Sacco, V. Vaiano, L. Rizzo, D. Sannino, Photocatalytic activity of a visible light active structured photocatalyst developed for municipal wastewater treatment, J. Cleaner. Prod., 175 (2018) 38–49.

[24] Y. Liu, X. Chen, J. Li, C. Burda, Photocatalytic degradation of azo dyes by nitrogen-doped TiO_2 nanocatalysts, Chemosphere, 61 (2015) 11–18.

[25] L. Gomathi, R. Kavitha, A review on non-metal ion doped titania for the photocatalytic degradation of organic pollutants under UV/solar light: role of photogenerated charge carrier dynamics in enhancing the activity, Appl. Catal., B., 140–141 (2013) 559–587.

[26] M.C. Yeber, C. Escalona, A. Núñez, P. Medina, Photocatalytic activity under visible light to transform As (III) with Nitrogen-doped TiO_2 nanoparticles, using urea as a nitrogen source. Optimization by multivariate analysis, Desal. Wat. Treat., 107 (2018) 218–222.

[27] N. Kaur, S. Kaur, V. Singh, Preparation, characterization and photocatalytic degradation kinetics of Reactive Red dye 198 using N, Fe codoped TiO_2 nanoparticles under visible Light, Desal. Wat. Treat., 57 (2015) 1–10.

[28] N. Tzikalos, V. Belessi, D. Lambropoulou, Photocatalytic degradation of reactive Red 195 using brookite/anatase TiO_2 mesoporous nanoparticles: optimization using response surface methodology (RMS) and kinetics studies, Environ. Sci. Pollut. Res., 20 (2013) 2305–2320.

[29] S. Singh, R. Sharma, B. Mehta, Enhanced surface area, high Zn interstitial defects and band gap reduction in N-doped ZnO nanosheets coupled with $BiVO_4$ leads to improved photocatalytic performance, Appl. Surf. Sci., 411 (2017) 321–330.

[30] Z. Cheng, S. Han, Preparation and photoelectrocatalytic performance of N-doped TiO_2/NaY zeolite membrane composite electrode material, Water. Sci. Technol., 73 (2016) 486–492.

[31] T. Le, T. Nguyen, Z. Yacouba, L. Zoungrana, F. Avril, E. Petit, J. Mendret, V. Bonniol, M. Bechelany, S. Lacour, G. Lesage, M. Cretin, Toxicity removal assessments related to degradation pathways of azo dyes: toward an optimization of Electro-Fenton treatment, Chemosphere, 161 (2005) 308–318.