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## ORIGINAL ARTICLE

# Enhanced visible-light-driven photodegradation of Acid Orange 7 azo dye in aqueous solution using Fe-N co-doped TiO<sub>2</sub>



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## KEYWORDS

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Electric Energy  
Consumption

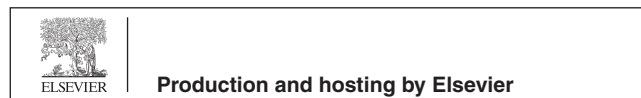
**Abstract** Fe–N co-doped TiO<sub>2</sub> photocatalysts are prepared by sol–gel method using titanium tetraisopropoxide, urea and iron(II) acetylacetonate as precursors of titania, nitrogen and iron, respectively. The prepared samples are analysed from chemical-physical point of view by X-ray diffraction (XRD), Raman spectroscopy, UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS), specific surface area measurements and scanning electron microscopy (FESEM). UV–Vis DRS spectra evidence that the co-doping of TiO<sub>2</sub> with N and Fe leads to the narrowing of the band gap value (2.7 eV) with respect to Fe-doped TiO<sub>2</sub> (2.8 eV) and N-doped TiO<sub>2</sub> (2.9–3 eV). XRD patterns show that photocatalysts are mainly in anatase phase and Fe and N ions are successfully incorporated into the TiO<sub>2</sub> lattice. The average crystallite size of Fe–N co-doped TiO<sub>2</sub> is slightly lower than the other samples and equal to about 7 nm and the specific surface area of the co-doped sample results to be 117 m<sup>2</sup> g<sup>−1</sup>. Photocatalytic performances of all prepared samples are evaluated by analysing the degradation of Acid Orange 7 azo dye under visible light irradiation. Photocatalytic efficiency obtained using Fe–N co-doped TiO<sub>2</sub> strongly increases compared to undoped TiO<sub>2</sub>, N-doped TiO<sub>2</sub> and Fe-doped TiO<sub>2</sub> photocatalysts. In detail, using the co-doped photocatalyst, dye discoloration and mineralization result equal to about 90 and 83% after 60 min of LEDs visible light irradiation, underlining the best performances of the Fe–N co-doped TiO<sub>2</sub> photocatalyst both in terms of treatment time and electric energy consumption.

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## 1. Introduction

Wastewater currently presents discharge problems due to the growing diffusion of non-biodegradable compounds, mainly resulting by industrial production processes (Gadipelly et al., 2014). The direct consequence of industrial activities is the

generation of liquid streams that, before to be returned to the environment, must necessarily undergo a purification treatment typically performed by biological oxidation processes (activated by microorganisms) (Manahan, 2017). However, these conventional methods are not able to remove bio-recalcitrant pollutants and, therefore, they require further treatment steps in order to eliminate non-biodegradable contaminants (Segneanu et al., 2013; Elshorbagy and Chowdhury, 2013; Zhou and Smith, 2002).

For this reason, the scientific research has focused attention on the application of innovative processes based on Advanced Oxidation Processes (AOPs) (Rokicka-Konieczna et al., 2019).

As far AOPs, heterogeneous photocatalysis based on semiconductor oxide has been strongly investigated in the latest recent years, because it is a technology able to completely degrade water pollutants into carbon dioxide, water and other non-toxic inorganic compounds (Klavarioti et al., 2009; Herrmann, 1999; Sannino et al., 2017; Al-Zahrani et al., 2020; Murcia et al., 2015; Tanji et al., 2020; Akhundi et al., 2019; Pirhashemi et al., 2018; Omrani and Nezamzadeh-Ejhih, 2020a; Ghattavi and Nezamzadeh-Ejhih, 2019; Senbari and Nezamzadeh-Ejhih, 2018; Omrani and Nezamzadeh-Ejhih, 2020b).

Different semiconductor oxides are widely used as photocatalysts. When a semiconductor is irradiated by light source with a wavelength greater than the band gap energy, electrons are promoted from the valence band (VB) to the conduction band (CB) with the simultaneous generation of positive holes in VB (Park et al., 2013; Zangeneh et al., 2015; Mousavi et al., 2018; Shekofteh-Gohari et al., 2018). The hole-electron pairs react with the pollutant molecules adsorbed on the semiconductor surface generating highly reactive radical species that are thus involved in oxidation and reduction processes of water pollutants (Fujishima and Honda, 1972). The most used semiconductor is titanium dioxide ( $\text{TiO}_2$ ), due to its properties, such as strong oxidizing power, high thermal stability, hydrophilicity, non-toxicity, high reactivity and environmental safety (Nakata and Fujishima, 2012). Photocatalytic activity of  $\text{TiO}_2$  depends on its morphology, crystalline structure, size distribution and porosity.  $\text{TiO}_2$  is a polymorphic material, whose crystalline forms are anatase, brookite and rutile. Among all, anatase is the most active because it has a greater affinity towards organic molecules (Nakata and Fujishima, 2012).

$\text{TiO}_2$  presents a wide band gap (3.2 eV for anatase) and therefore, it can be excited only by ultraviolet light irradiation ( $\lambda = 315\text{--}400\text{ nm}$ ), which represents 3–5% of solar radiation. (Nakata and Fujishima, 2012). Moreover, the efficient exploitation of  $\text{TiO}_2$  is limited by rapid recombination of electron/hole pair (Ejhih and Khorsandi, 2010). An important aim of the research is to make  $\text{TiO}_2$  active under visible light enhancing its photocatalytic activity also under the direct sunlight. To reach this goal, it is possible to couple  $\text{TiO}_2$  with other materials (Habibi-Yangjeh et al., 2020; Sedaghati et al., 2019; Feizpoor et al., 2019, 2018) or to reduce the band gap energy and therefore broaden the absorption spectrum of light radiation to the visible range by doping the  $\text{TiO}_2$  lattice with metallic and non-metallic elements (Cheng et al., 2018; Mohseni-Salehi et al., 2018). The possible expected action of  $\text{TiO}_2$  doped with metals like Fe, is that metal ions can play as hole and electron traps enhancing the generation of species at high oxidizing power, such as hydroxyl radicals and super-

oxides (Cheng et al., 2018). Thus, the generated highly oxidizing species further oxidize contaminants and intermediates up to the complete mineralization of the target pollutants. Moreover, non-metal dopants, such as N may substitute semiconductor lattice atoms or enter into the lattice interstices of  $\text{TiO}_2$  (Di Valentin et al., 2005; Di Valentin and Pacchioni, 2013). The introduction of a dopant in the lattice may allow the activation of  $\text{TiO}_2$  in the visible range (Di Valentin et al., 2004). Metallic or non-metallic elements in  $\text{TiO}_2$  structure can result in impurities promoting the recombination of photo-generated holes and electrons (Sharotri and Sud, 2017). For these reason, the research interest has been recently focused on the co-doping of  $\text{TiO}_2$  with two different ions (metal and non-metals), allowing a better separation of the photogenerated electrons and holes, assuring an effective enhancement of the visible light adsorption together with higher photocatalytic activity of  $\text{TiO}_2$ . (Su et al., 2011). Liu et al. (2007) reported the incorporation of nitrogen (N) and lanthanum (La) in  $\text{TiO}_2$  lattice. Such obtained systems showed better photocatalytic performances towards degradation of methyl orange dye under visible irradiation compared to N-doped or La-doped  $\text{TiO}_2$  (Wei et al., 2004; Sakatani et al., 2003). Moreover, nitrogen and cerium co-doped  $\text{TiO}_2$  showed a photocatalytic activity higher than undoped and N-doped  $\text{TiO}_2$  (Liu et al., 2008). A certain number of papers are devoted to the formulation of Fe-N co-doped  $\text{TiO}_2$  samples (Yen et al., 2011) and the evaluation of their photocatalytic activity towards the degradation of diphenylamine (Su et al., 2011), rhodamine B dye (Cong et al., 2007), methyl orange dye (Shen et al., 2008) and methylene blue dye (Zhou and Wang, 2014). In all cases, Fe-N co-doped  $\text{TiO}_2$  photocatalysts revealed a significant increase of photocatalytic activity under visible light with respect to undoped  $\text{TiO}_2$ , N-doped  $\text{TiO}_2$  and Fe-doped  $\text{TiO}_2$ . Unfortunately, to achieve a photodegradation performance higher than 85%, treatment times above 120 min are required. Therefore, further investigation should be required to improve the photocatalytic activity under visible irradiation of Fe-N co-doped  $\text{TiO}_2$  and to reduce the treatment time for the degradation of water pollutants. The aim of this work was to formulate titanium-based photocatalysts co-doped with both metal and non-metal elements (Fe and N). The prepared photocatalysts were tested in the discoloration and mineralization of Acid Orange 7 azo dye (AO7) under visible light irradiation. Azo dyes, such as AO7, are emerging

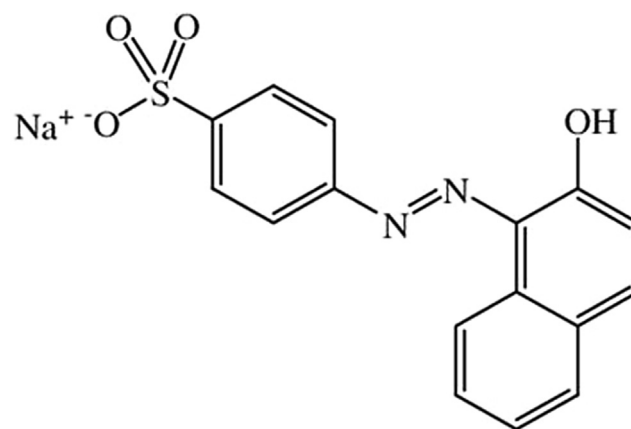


Fig. 1 Chemical structure of Acid Orange 7 azo dye (AO7).

contaminants widely used in the textile industries for dyeing cotton, wool and silk (Nezamzadeh-Ejhih and Zabihi-Mobarakeh, 2014). It is worth noting that, among the main synthetic dyes which characterize the effluents coming from the textile industry, AO7 is a colouring agent consisting of an azo group bound to aromatic rings (Fig. 1) (Liu et al., 2005). This azo dye can react with other chemical substances producing aromatic amines which cause toxic and carcinogenic effects. So, AO7 has been chosen as model dye pollutant to be removed through effective methods from aqueous solutions.

## 2. Experimental section

### 2.1. Materials

Titanium tetraisopropoxide ( $C_{12}H_{28}O_4Ti > 97\%$  Sigma Aldrich), urea ( $CH_4N_2O$  Sigma Aldrich), iron(II) acetylacetonate (99.95% Sigma Aldrich) and distilled water were utilized.

### 2.2. Photocatalysts preparation

N-doped  $TiO_2$  photocatalysts with different nitrogen content were synthesized through sol-gel method using urea as nitrogen precursor and titanium tetraisopropoxide as  $TiO_2$  precursor. Fe-doped  $TiO_2$  (Fe- $TiO_2$ ) photocatalyst was prepared by reaction between titanium tetraisopropoxide (TTIP) and an aqueous solution containing iron(II) acetylacetonate. In order to prepare photocatalysts doped with Fe and N, distilled water containing a certain amount of urea were mixed with a solution of titanium tetraisopropoxide and iron(II) acetylacetonate. The system was maintained at room temperature under continuous stirring for 10 min. The obtained suspension was centrifuged for the separation of a precipitates, which was washed with distilled water three times and finally placed in a furnace at 450 °C for 30 min in static air. The obtained samples were named (N- $TiO_2_x$  or Fe-N- $TiO_2_x$ ) where x indicates the amount of urea (in grams) used for synthesis. The Fe/Ti molar ratio used for the preparation of Fe- $TiO_2$  was equal to 0.0017 and corresponds to an optimized catalyst formulation as reported in a previous work (Zuorro et al., 2019). Table 1 reports the solution volume, the amount of N and Fe precursor used for the synthesis with together N/Ti and Fe/Ti molar ratio for each prepared photocatalyst samples.

### 2.3. Photocatalyst characterization techniques

Photocatalysts chemical-physical properties were analyzed using different characterization techniques. Specific surface

area ( $S_{BET}$ ) were measured from dynamic  $N_2$  adsorption at low-temperature ( $-196$  °C) by using a Costech Sorptometer 1042 instrument. Before the analysis, the samples were pre-treated at 150 °C for 30 min in He flow. UV-Visible reflectance spectroscopy (UV-Vis DRS) was used for the determination of the light absorption properties. The reflectance spectra were recorded by using a Perkin-Elmer spectrophotometer Lambda 35, using an 88 sample positioning holder (Labsphere Inc., North Sutton, NH). The reflectance data were reported in terms of Kubelka-Munk values ( $F(R_\infty)$ ) as a function of wavelength. The determination of the direct band gap was obtained by plotting  $[F(R_\infty) \cdot hv]^2$  vs  $hv$  (eV) (Derikvandi and Nezamzadeh-Ejhih, 2017; Ghattavi and Nezamzadeh-Ejhih, 2019). XRD patterns were acquired with a Bruker D8 diffractometer, employing Cu  $K\alpha$  radiation. The lattice parameter values were determined using the following equation:

$$\frac{1}{d_{(hkl)}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

where the value of  $d_{(hkl)}$  for an XRD peak was determined from Bragg's law:

$$2d_{(hkl)} \cdot \sin\theta = n \cdot \lambda \quad (2)$$

$h$ ,  $k$  and  $l$  are the crystal plane indices,  $d_{(hkl)}$  is the distance between crystal planes of  $(hkl)$ , while  $a$ , and  $c$  are the lattice parameters (for tetragonal anatase phase of  $TiO_2$ :  $a = b \neq c$ ). In order to calculate the lattice parameters values, the planes (1 0 1) and (2 0 0) for anatase were considered (Ganesh et al., 2012). The average crystallite size of the samples was calculated using Williamson-Hull method (Tamiji and Nezamzadeh-Ejhih, 2019). The common equation is shown in Eq. (3) where  $\lambda$  is the  $CuK\alpha$  radiation wavelength (1.5406 Å),  $d$  the crystallite size (nm),  $\beta$  the peak width at the half maximum (in Rad),  $\theta$  the diffraction angle,  $\varepsilon$  and  $A$  are constants with common value of 1.

$$\beta \cos\theta = \frac{0.9 \cdot \lambda}{d} + A \cdot \varepsilon \cdot \sin\theta \quad (3)$$

The average crystallite size  $d$  (nm) can be estimated from the intercept of the plot of  $\beta \cos(\theta)$  as a function of  $\sin(\theta)$ .

Raman spectra were obtained using a Dispersive MicroRaman spectrometer (Invia, Renishaw) equipped with a 514 nm laser in the range 150–900  $cm^{-1}$ . Mass titration method was used to estimate the point of zero charge (PZC) of all samples. PZC was measured using the mass titration method proposed by Noh and Schwarz (Noh and Schwarz, 1989; Rizzo et al., 2014). A field emission scanning electron microscope (FESEM, mod. LEO 1525, Carl Zeiss SMT AG, Oberkochen, Germany)

**Table 1** List of prepared photocatalyst, amount of chemicals used in the synthesis, Fe/Ti and N/Ti molar ratio.

Catalyst	TTIP volume (mL)	Urea weight (g)	Distilled water volume (mL)	Iron acetylacetonate weight (g)	Fe/Ti molar ratio	N/Ti molar ratio
$TiO_2$	12.5	0	50	0	0	0
N- $TiO_2_{0.3}$	12.5	0.3	50	0	0	0.243
N- $TiO_2_{0.6}$	12.5	0.6	50	0	0	0.485
N- $TiO_2_{1.2}$	12.5	1.2	50	0	0	0.970
N- $TiO_2_{2.4}$	12.5	2.4	50	0	0	1.940
Fe- $TiO_2$	12.5	0	50	0.025	0.0017	0
Fe-N- $TiO_2_{1.2}$	12.5	1.2	50	0.025	0.0017	0.970

was used to observe the morphology of powders that were previously dispersed on a carbon tab stuck to an aluminum stub (Agar Scientific, Stansted, United Kingdom) and then coated with gold-palladium (layer thickness 250 Å) using a sputter coater (mod. 108 A, Agar Scientific).

#### 2.4. Photocatalytic activity tests under visible light

Photocatalytic tests were performed in a cylindrical pyrex photoreactor (ID = 2.6 cm,  $L_{TOT} = 41$  cm and  $V_{TOT} = 200$  mL). Visible-LEDs strip (nominal power: 10 W; provided by LED lighting hut; emission in the range 400–800 nm; light intensity:  $13 \text{ mW cm}^{-2}$ ) was positioned in contact to the external surface of the photoreactor. The total volume of solution was 100 mL with  $10 \text{ mg L}^{-1}$  AO7 initial concentration (pH = 5.95). The photocatalyst dosage was equal to  $3 \text{ g L}^{-1}$ .

The suspension was left in dark conditions for 60 min to achieve the adsorption/desorption equilibrium of AO7 dye on the photocatalyst surface. After the dark phase, the LEDs were switched on and the photocatalytic test started. During the light irradiation, the reaction suspension was continuously mixed using a magnetic stirrer to avoid the sedimentation of the catalyst at the bottom of the photoreactor. An air distributor device ( $Q_{air} = 150 \text{ cm}^3 \text{ min}^{-1}$  (STP)) was also used to assure the presence of oxygen in the reaction medium and therefore to favor the oxidation reactions of the organic compound.

At regular time intervals, about 3 mL of the suspension was withdrawn from the photoreactor and centrifuged to remove the catalyst particle. The aqueous solution was then analyzed by UV-Vis spectrophotometer (Thermo Scientific Evolution 201) to monitor the reaction progress. In details, the color removal of the chosen dye was monitored by measuring the maximum absorbance value at 485 nm (Rodríguez et al., 2019). The mineralization of the target pollutant was assessed by the measure of the total organic carbon (TOC) content of the solutions during the irradiation time. The TOC of solution was measured from  $\text{CO}_2$  obtained by the high temperature ( $680 \text{ }^\circ\text{C}$ ) catalytic combustion (Franco et al., 2019).

The discoloration efficiency and mineralization (by TOC removal) were evaluated using the following relationships:

$$\text{Discoloration efficiency} = \left(1 - \frac{C}{C_0}\right) \cdot 100 \quad (4)$$

$$\text{TOC removal (mineralization)} = \left(1 - \frac{\text{TOC}}{\text{TOC}_0}\right) \cdot 100 \quad (5)$$

where

$C$  = pollutant concentration at the generic irradiation time ( $\text{mg L}^{-1}$ );

$C_0$  = initial AO7 concentration ( $\text{mg L}^{-1}$ );

TOC = total organic carbon at the generic irradiation time ( $\text{mg L}^{-1}$ );

$\text{TOC}_0$  = initial total organic carbon ( $\text{mg L}^{-1}$ ).

### 3. Results and discussion

#### 3.1. Photocatalytic materials characterization

Table 2 reports the specific surface area ( $S_{BET}$ ) of all samples evaluated by BET method. The undoped titania sample showed the lowest value of  $107 \text{ m}^2 \text{ g}^{-1}$ . All doped titania samples presented values of specific surface area higher than those of the undoped titania. Moreover, it seems that the  $S_{BET}$  values are not influenced by urea amount used as precursor for the preparation of N-TiO<sub>2-x</sub> samples. On the other hand, the specific surface area of Fe-N co-doped TiO<sub>2</sub> sample was found to be  $117 \text{ m}^2 \text{ g}^{-1}$ , very similar to the value observed for the N-doped TiO<sub>2</sub> sample prepared with the same amount of urea (N-TiO<sub>2-1.2</sub>).

The reflectance spectra of TiO<sub>2</sub> and N-TiO<sub>2-x</sub> samples are reported in Fig. 2.

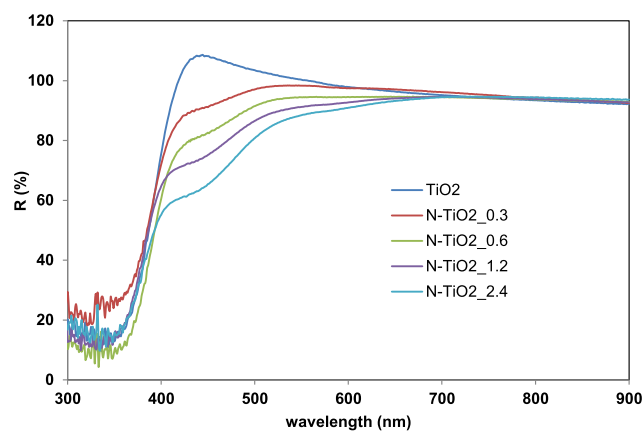
As expected, the main absorption edge of undoped titania lies in the range 390–400 nm (UV region). On the other hand, a marked shift toward the visible region for N-TiO<sub>2-x</sub> samples was achieved since the presence of a weak shoulder in the range 400–500 nm was observed and its intensity progressively enhanced with the increase of the urea content used for samples synthesis (Shao et al., 2008, Chainarong et al., 2011). Possibly, this result indicates that the doping with N led to new electron state above VB, shifting the absorption edge towards the visible light region, as already reported in literature (Chainarong et al., 2011, Cheng et al., 2012).

Fig. 3 displays the optical properties of undoped TiO<sub>2</sub>, N-TiO<sub>2-1.2</sub>, Fe-TiO<sub>2</sub> and Fe-N-TiO<sub>2-1.2</sub> photocatalysts.

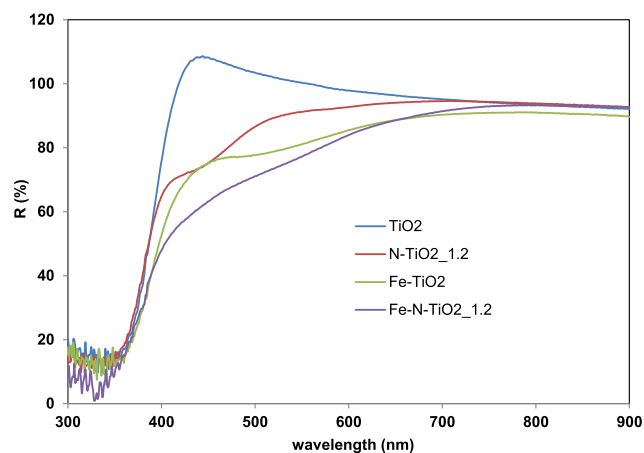
The reflectance spectra indicate that the doping of Fe into TiO<sub>2</sub> lattice shifts its optical absorption edge from UV into visible range (i.e. red shift) (Wu and Chen, 2004). This red shift is due to the charge transfer transitions between the metal ion d electrons and the CB of TiO<sub>2</sub> (Ganesh et al., 2012, Ali et al., 2017). It is worthwhile to note that Fe-N-TiO<sub>2-1.2</sub> sample

**Table 2** Crystallite size, lattice parameter, specific surface area ( $S_{BET}$ ), band gap ( $E_{bg}$ ) and zero point charge (ZPC) of all prepared samples.

Catalyst	Cristallite size (nm)	Lattice parameter (Å)		$S_{BET}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$E_{bg}$ (eV)	ZPC (pH unit)
		$a = b$	$c$			
TiO <sub>2</sub>	8	3.74	8.68	107	3.2	6.02
N-TiO <sub>2-0.3</sub>	6	3.79	9.20	139	3.0	5.14
N-TiO <sub>2-0.6</sub>	7	3.78	9.33	112	3.0	5.10
N-TiO <sub>2-1.2</sub>	7	3.77	8.81	115	2.9	5.12
N-TiO <sub>2-2.4</sub>	6	3.78	9.06	126	2.9	5.14
Fe-TiO <sub>2</sub>	6	3.77	9.21	122	2.8	5.15
Fe-N-TiO <sub>2-1.2</sub>	7	3.75	8.58	117	2.7	5.02



**Fig. 2** Reflectance spectra vs wavelength for  $\text{TiO}_2$  and  $\text{N-TiO}_2_x$  samples.

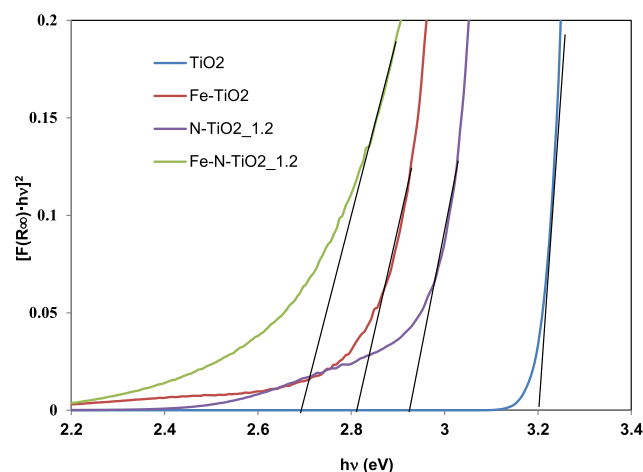


**Fig. 3** Reflectance spectra vs wavelength for  $\text{TiO}_2$ ,  $\text{N-TiO}_2_{1.2}$ ,  $\text{Fe-TiO}_2$  and  $\text{Fe-N-TiO}_2_{1.2}$  samples.

gives rise visible-light absorptions contributions higher than those of undoped  $\text{TiO}_2$ ,  $\text{N-TiO}_2_{1.2}$  and  $\text{Fe-TiO}_2$  photocatalysts, similarly to the results reported in a previous paper (Yen et al., 2011). Additionally, the  $\text{Fe-N-TiO}_2_{1.2}$  showed a noticeable absorbance at less than 500 nm and a marked increase of absorption properties in the range 400–500 nm compared to  $\text{N-TiO}_2_{1.2}$  or  $\text{Fe-TiO}_2$  (Yen et al., 2011).

Band gap values ( $E_{\text{bg}}$ ) were obtained by UV–Vis DRS measurements (Fig. 4 for undoped  $\text{TiO}_2$ ,  $\text{N-TiO}_2_{1.2}$ ,  $\text{Fe-TiO}_2$  and  $\text{Fe-N-TiO}_2_{1.2}$  samples) and the obtained data are included in Table 2.

$E_{\text{bg}}$  value was 3.2 eV for undoped titania and 2.9–3 eV for  $\text{N-TiO}_2_x$  samples. This change in  $E_{\text{bg}}$  values can be attributed to the presence of nitrogen in the  $\text{TiO}_2$  lattice (Cheng et al., 2012). Moreover, from the  $E_{\text{bg}}$  values and the trend of the reflectance curves, undoped  $\text{TiO}_2$  is expected to be active under UV irradiation, while  $\text{Fe-TiO}_2$  under visible light.  $E_{\text{bg}}$  was about 2.8 eV for  $\text{Fe-TiO}_2$  sample while it was possible to obtain a further decrease in  $E_{\text{bg}}$  up to the value of 2.7 eV with  $\text{Fe-N-TiO}_2_{1.2}$  photocatalyst. The narrow band gap of  $\text{Fe-N-TiO}_2_{1.2}$  may be therefore an indication of the possible

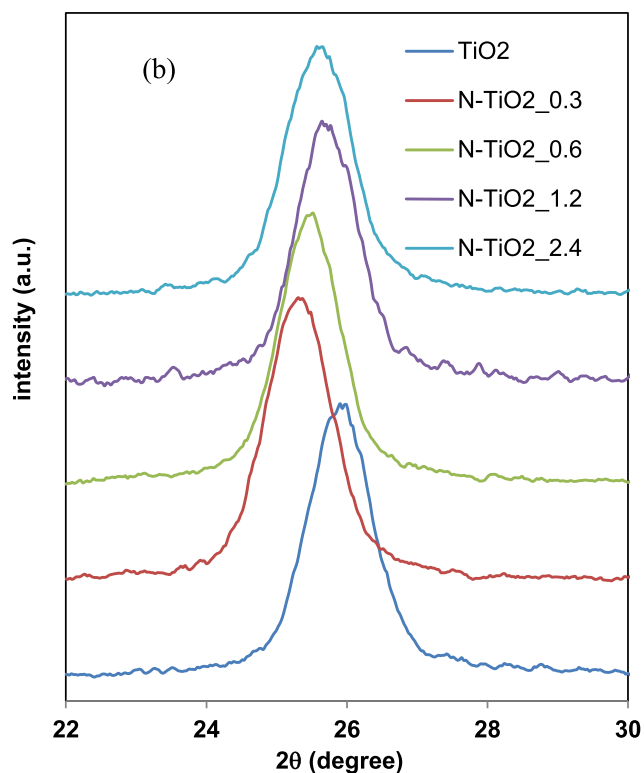
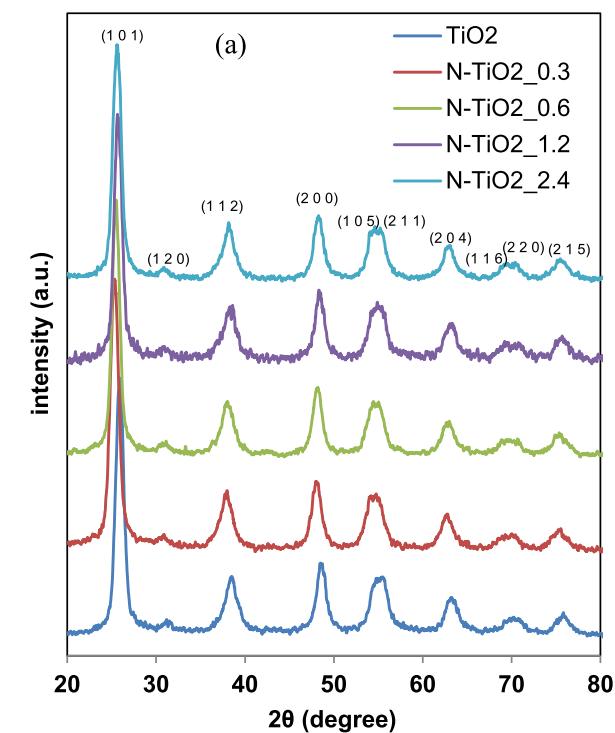


**Fig. 4** Band gap calculation by UV–VIS DRS spectra for  $\text{TiO}_2$ ,  $\text{N-TiO}_2_{1.2}$ ,  $\text{Fe-TiO}_2$  and  $\text{Fe-N-TiO}_2_{1.2}$  samples.

enhancement of the photocatalytic activity in the visible light region with respect to both  $\text{Fe-TiO}_2$  and  $\text{N-TiO}_2_{1.2}$  samples (Cong et al., 2007).

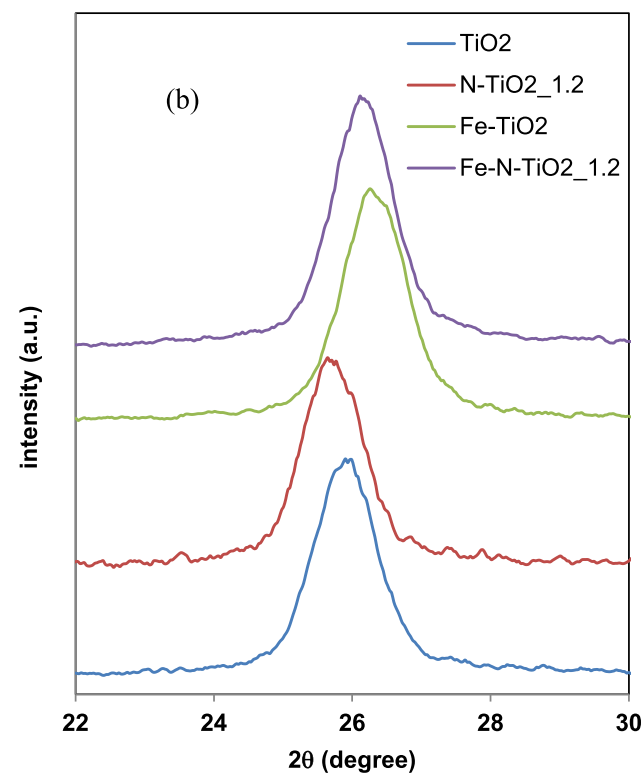
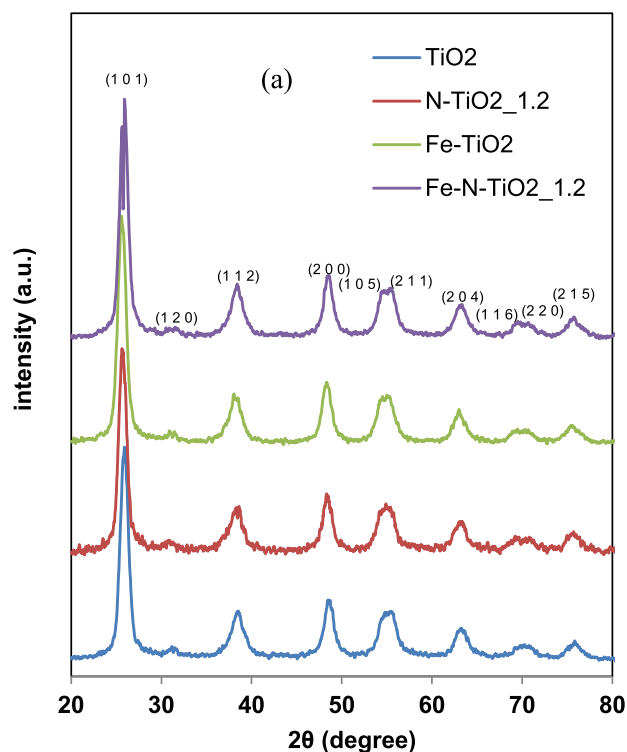
Figs. 5a and 6a report the XRD patterns of all prepared samples.

In particular, the sharp peaks of anatase phase at  $2\theta = 25.91^\circ$  (1 0 1) and  $2\theta = 48.62^\circ$  (2 0 0) for undoped titania are evident (JCPDS Card No. 21-1272). Similarly the XRD patterns all doped samples exhibited the characteristic peaks of  $\text{TiO}_2$  anatase phase (Ramalingam et al., 2017). The peak corresponding to the (1 0 1) crystalline plane was the most intense (Ramalingam et al., 2017). No peaks of rutile phase was observed in all the  $\text{N-TiO}_2_x$  samples prepared with different urea loadings (Fig. 5a) and in  $\text{Fe-TiO}_2$  (Fig. 6a) (Cheng et al., 2008, Zuorro et al., 2019). This result indicates that the phase transformation from anatase to rutile does not take place when nitrogen doped titania powders are calcined at temperature of 450 °C. In fact, as reported in literature, the use of urea as a nitrogen precursor inhibits the transformation from anatase to rutile phase (Cheng et al., 2008). Furthermore, traces of brookite phase were observed in the XRD pattern at about  $2\theta = 31^\circ$  (1 2 0) (Figs. 5a and 6a) (Lee and Yang, 2006, Bhawe, 2007, Yanqing et al., 2000). The XRD patterns of all  $\text{N-TiO}_2_x$  samples were analyzed more in detail in the  $2\theta$  range between 22 and 30° (Fig. 5b). It is possible to observe a shift to lower values of  $2\theta$ , from  $2\theta = 25.91^\circ$  (undoped  $\text{TiO}_2$ ) to  $2\theta = 25.30^\circ$  ( $\text{N-TiO}_2_{0.3}$ ). This shift is consistent with literature and it can be associated to distortion and strain phenomena in the  $\text{TiO}_2$  crystal lattice induced by the incorporation of the nitrogen ions (Smirniotis et al., 2018, Sun et al., 2008). In particular, this phenomenon may occur because nitrogen ions replace oxygen in the  $\text{TiO}_2$  structure due to differences in binding properties (Vaiano et al., 2015a, Batzill et al., 2006), indicating that the crystalline structure of  $\text{TiO}_2$  was doped with nitrogen. The  $a$  and  $c$  lattice parameters calculated for the  $\text{N-TiO}_2_x$  samples are reported in Table 2. The values of  $a$  and  $c$  parameters for the  $\text{N-TiO}_2$  samples are both higher than those observed for the undoped titania. It has also been possible to consider that the increase of N/Ti ratio does not influence both the value of  $a$  parameter (3.79–3.78 Å) and  $c$  parameter (9.20–



**Fig. 5** XRD patterns for TiO<sub>2</sub> and N-TiO<sub>2</sub>\_0.3, N-TiO<sub>2</sub>\_0.6, N-TiO<sub>2</sub>\_1.2 and N-TiO<sub>2</sub>\_2.4 samples in the range  $2\theta = 20\text{--}80^\circ$  (a) and in the range  $2\theta = 22\text{--}30^\circ$  (b).

9.06 Å). As shown in the Fig. 6b, the presence of Fe led to a slight shift of the peak related to the anatase phase for Fe-TiO<sub>2</sub> at higher value ( $2\theta = 26.31^\circ$ ) with respect to undoped TiO<sub>2</sub> ( $2\theta = 25.91^\circ$ ) (Morales et al., 2018). Generally, the Fe



**Fig. 6** XRD patterns for TiO<sub>2</sub> and N-TiO<sub>2</sub>\_1.2, Fe-TiO<sub>2</sub> and Fe-N-TiO<sub>2</sub>\_1.2 samples in the range  $2\theta = 20\text{--}80^\circ$  (a) and in the range  $2\theta = 22\text{--}30^\circ$  (b).

doping does not change the crystalline structure of TiO<sub>2</sub>, while a small change in the lattice parameters can be observed as

reported in Table 2. The  $a$  and  $c$  lattice constant values for undoped  $\text{TiO}_2$  are 3.74 Å and 8.68 Å, respectively, whereas with the addition of Fe ions, the value of  $a$  parameter was 3.77 Å, while the  $c$  parameter changed to 9.21 Å. These lattice parameter values suggest that the iron doping caused the decrease of  $\text{TiO}_2$  crystallite size along  $c$ -axis because the ionic radius of Fe (0.64 Å) is relatively smaller compared to the ionic radius of Ti (0.68 Å) (Ganesh et al., 2012). Probably, due to the almost similar ionic radius, some portion of Ti ions in  $\text{TiO}_2$  lattice was replaced with Fe ions (Ganesh et al., 2012). When Fe ions substitute Ti ions, defective sites are formed which act as a long-lasting space charge region. Consequently, the electrical energy of these defects improves the efficiency of the carriers separation and the charge transfer (Prajapati et al., 2017). Thus, the XRD results indicate that the crystallinity of the iron and nitrogen doped materials is not affected by the presence of the dopant element. The XRD patterns of Fe-N- $\text{TiO}_2$ \_1.2 sample (Fig. 6a) showed the presence of all diffraction peaks related to the anatase phase and a small signal associated to brookite, similarly to the other analyzed samples. The peak corresponding to anatase (1 0 1) plane evidenced a shift up to  $2\theta = 26.11^\circ$ , as also observed for Fe- $\text{TiO}_2$  sample (Fig. 5b) (Ramalingam et al., 2017). Finally,  $a$  and  $c$  lattice parameters for Fe-N- $\text{TiO}_2$ \_1.2 are 3.75 Å and 8.58 Å, respectively (Table 2). The  $a$  lattice parameter for this sample seems to be similar to undoped  $\text{TiO}_2$  (3.74 Å) and lower than N- $\text{TiO}_2$ \_1.2 and Fe- $\text{TiO}_2$  (3.77 Å), whereas the  $c$  lattice parameter for Fe-N- $\text{TiO}_2$ \_1.2 (8.58 Å) is lower with respect to undoped  $\text{TiO}_2$  (8.68 Å), N- $\text{TiO}_2$ \_1.2 (8.81 Å) and Fe- $\text{TiO}_2$  (9.21 Å).

The average crystallite size is in the range 6–8 nm (Table 2). Photocatalysts exhibiting the lowest values of crystallite size, showed the highest values of  $S_{\text{BET}}$ , as expected.

Raman spectra in the range of 100–900  $\text{cm}^{-1}$  for undoped and N-doped  $\text{TiO}_2$ \_x photocatalysts are presented in Fig. 7.

Raman bands were observed at 144, 397, 516 and 638  $\text{cm}^{-1}$  together with a weak shoulder at 195  $\text{cm}^{-1}$  in the spectra of all samples, indicating that anatase was the predominant crystalline structure. No Raman signals associated to TiN bonds were detectable in the N- $\text{TiO}_2$ \_x samples (Gurkan et al., 2012). This result may be an indication that N anions did not react with  $\text{TiO}_2$  surface, meaning that the dopant element is placed in the interstitial or the substitutional sites of the titania structure (Gurkan et al., 2012), as also evidenced by XRD (Fig. 5) and UV-Vis DRS results (Fig. 2).  $\text{TiO}_2$  common signals related to the anatase phase were also evident for Fe- $\text{TiO}_2$  sample (Fig. 8).

No bands due to iron oxides were detected (Zuorro et al., 2019). Fe-doped  $\text{TiO}_2$  maintained the  $\text{TiO}_2$  structure indicating that the  $\text{Fe}^{3+}$  ions are present into the  $\text{TiO}_2$  framework, replacing  $\text{Ti}^{4+}$  cations (Ali et al., 2017). Additionally, the intensity of the Raman bands for Fe- $\text{TiO}_2$  sample was lower than those observed for undoped  $\text{TiO}_2$ , indicating the possible incorporation of  $\text{Fe}^{3+}$  into the substitutional sites of the  $\text{TiO}_2$  lattice (Prajapati et al., 2017), in agreement with XRD results. Fe-N- $\text{TiO}_2$ \_1.2 photocatalyst (Fig. 8) also showed the typical Raman signals related to anatase  $\text{TiO}_2$  and the intensity of these bands is lower than that of undoped  $\text{TiO}_2$ , Fe- $\text{TiO}_2$  and N- $\text{TiO}_2$ \_1.2 photocatalysts.

The surface acidity of the prepared samples was estimated using the mass titration method. The pH values (representative of PZC) are reported in Table 2. In particular, the PZC value

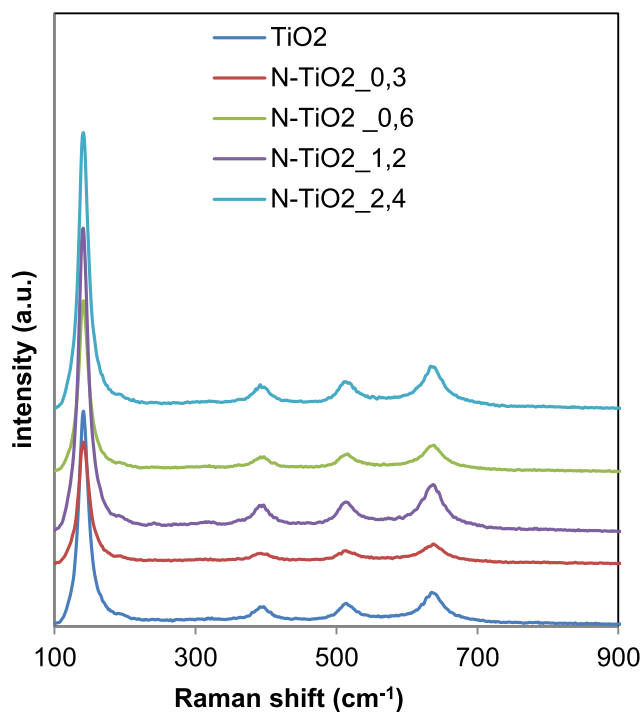


Fig. 7 Raman spectra of  $\text{TiO}_2$ , N- $\text{TiO}_2$ \_0.3, N- $\text{TiO}_2$ \_0.6, N- $\text{TiO}_2$ \_1.2 and N- $\text{TiO}_2$ \_2.4 samples.

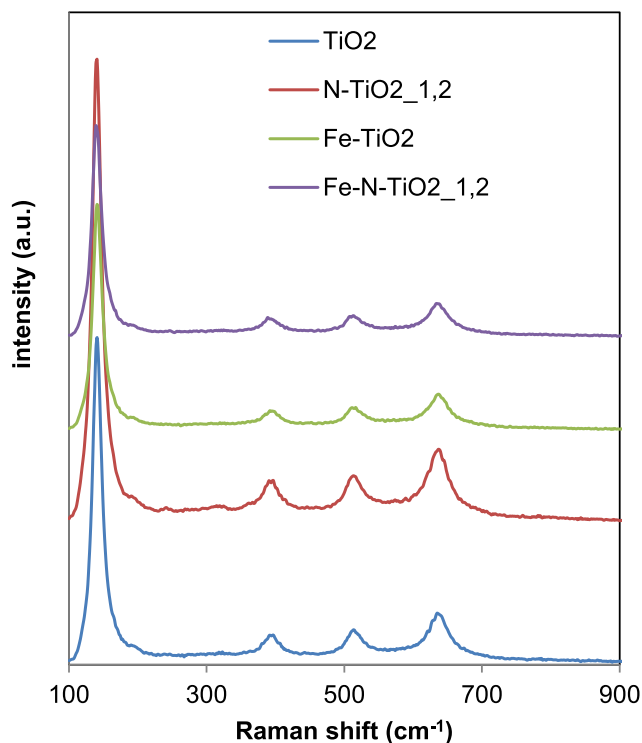


Fig. 8 Raman spectra of  $\text{TiO}_2$ , N- $\text{TiO}_2$ \_1.2, Fe- $\text{TiO}_2$  and Fe-N- $\text{TiO}_2$ \_1.2 samples.

of undoped  $\text{TiO}_2$  is 6.02, very close to those reported in literature for  $\text{TiO}_2$  in anatase phase (Ciambelli et al., 2005). On the other hand, N- $\text{TiO}_2$ \_x, Fe- $\text{TiO}_2$  and Fe-N- $\text{TiO}_2$ \_1.2 photo-

catalysts showed an acidic character, being the ZPC values equal to 5.10, 5.15 and 5.02 pH unit, respectively (Ganesh et al., 2012). It is worth to underline that the result obtained for the N-TiO<sub>2-x</sub> samples could be an indication about the absence of surface nitrogen groups, which typically induce a basic character to the surface of TiO<sub>2</sub> samples modified with nitrogen (Sorrentino et al., 2001). Fig. S1 (reported in Supplementary Material) shows the FESEM images of TiO<sub>2</sub>, Fe-TiO<sub>2</sub>, N-TiO<sub>2\_1.2</sub> and Fe-N-TiO<sub>2\_1.2</sub> photocatalysts. In particular, from the images it is possible to observe that all the samples are characterized by a non-uniform structure of macro aggregates indicating that the doping process does not influence the photocatalysts morphology.

### 3.2. Photocatalytic activity results under visible light

#### 3.2.1. Effect of photocatalyst formulation

The visible light driven degradation of AO7 was investigated for all prepared photocatalysts. Fig. 9 reports the AO7 relative concentration as a function of irradiation time showing the influence of the amount of urea in N-TiO<sub>2-x</sub> in the photocatalytic discoloration efficiency.

The AO7 relative concentration did not change under visible irradiation for 60 min in the absence of photocatalyst, indicating that the photolysis effect is negligible. In the presence of the photocatalysts, the AO7 relative concentration progressively decreased. In detail, after 60 min, AO7 discoloration efficiency was equal to about 10% with undoped TiO<sub>2</sub>. All N-TiO<sub>2-x</sub> samples were more active than undoped TiO<sub>2</sub> under visible light irradiation: the increase in the amount of urea from 0.3 to 1.2 g in the preparation causes an increase of photocatalytic activity. A further increase in the urea content shows a worsening of the photocatalytic performance. The optimal colour removal efficiency (about 62%) was obtained using the photocatalyst prepared with a urea amount equal to 1.2 g (N-TiO<sub>2\_1.2</sub>). The influence of N presence and its content on photocatalytic activity of N-doped TiO<sub>2</sub> is widely reported in literature (Kim et al., 2018; Haoli et al., 2007; Qin et al., 2008; Sacco et al., 2018, 2015; Vaiano et al., 2015b; Cheng et al., 2016; Reda et al., 2020; Wojtaszek et al., 2019). It is reported that the incorporation of N in the TiO<sub>2</sub> structure induces the formation of an N 2p band above the original O 2p valance band leading to the band gap decrease and enhancing the photocatalytic activity under visible light (Kim et al., 2018, Vaiano et al., 2015a). On the other hand, the existence of an optimal N content can be explained considering that the oxygen sites of TiO<sub>2</sub> can be partially replaced with nitrogen ions (Shin et al., 1991) inducing oxygen vacancies and, as a consequence, the amount of Ti<sup>3+</sup> increases with the increase of N content (Haoli et al., 2007; Qin et al., 2008). Both oxygen vacancies and Ti<sup>3+</sup> species acted as hole traps, inhibiting the recombination of electron-hole pairs and, therefore, improving the photocatalytic activity under visible light (Linschinger et al., 1995). However, when the concentration of N in N-doped TiO<sub>2</sub> is excessively high, the recombination of the photogenerated electron-hole pairs became easier (Li et al., 2004) since the excessive amount of oxygen vacancies and Ti<sup>3+</sup> species act as recombination cen-

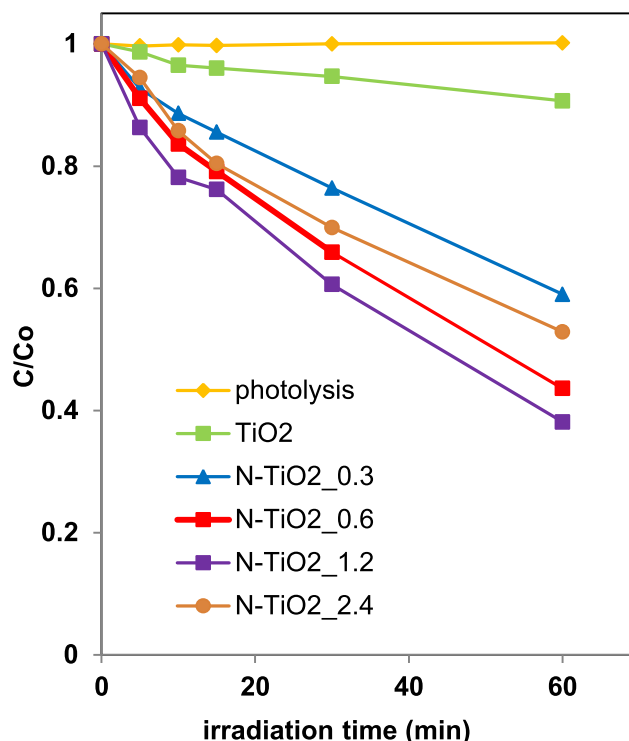


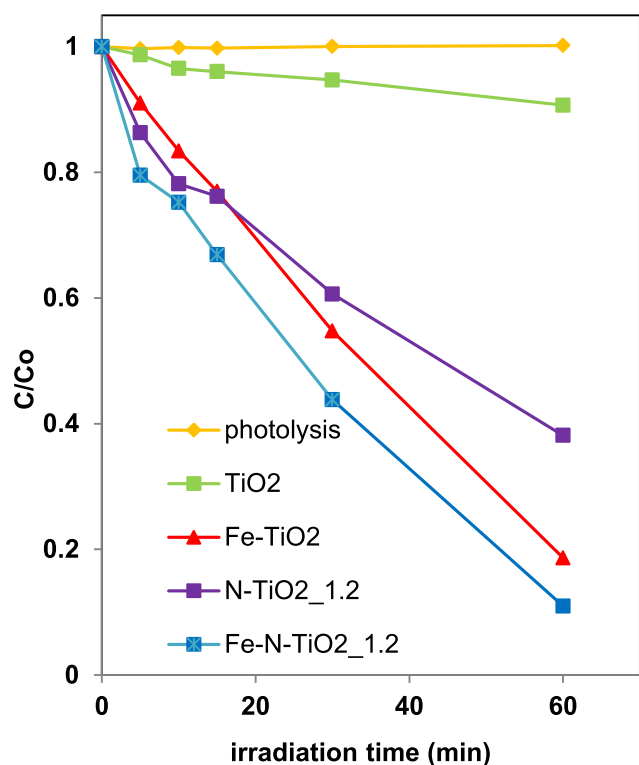
Fig. 9 Photocatalytic discoloration of TiO<sub>2</sub>, N-TiO<sub>2\_0.3</sub>, N-TiO<sub>2\_0.6</sub>, N-TiO<sub>2\_1.2</sub>, N-TiO<sub>2\_2.4</sub> photocatalysts under visible light irradiation.

tres for electron-hole pairs (Haoli et al., 2007; Qin et al., 2008). The previous observations can explain why the AO7 discoloration efficiency becomes lower when the N content was higher than the optimal amount (1.2 g).

Fe-TiO<sub>2</sub> sample was much more active than undoped TiO<sub>2</sub> under visible light. From Fig. 10, it is also possible to notice a substantial enhancement of the photocatalytic performances for Fe-TiO<sub>2</sub> sample with a discoloration efficiency of about 80%, compared to 62% achieved using N-TiO<sub>2\_1.2</sub> photocatalyst.

A further increase in visible light driven AO7 discoloration was obtained using Fe-N co-doped TiO<sub>2</sub> prepared with the optimal amount of urea, as assessed from the photocatalytic tests carried out on N-TiO<sub>2-x</sub> photocatalysts. In particular, after 60 min of irradiation time, the relative AO7 concentration for Fe-N-TiO<sub>2\_1.2</sub> photocatalyst was lower than Fe-TiO<sub>2</sub> and N-TiO<sub>2\_1.2</sub> photocatalysts, reaching a discoloration efficiency of about 90%. The higher photocatalytic activity of Fe-TiO<sub>2</sub> with respect to undoped TiO<sub>2</sub> should be due to the substitution of Ti<sup>4+</sup> ions with Fe<sup>3+</sup>, which acts as electron acceptors promoting the charge separation of photogenerated electrons and holes and yielding more hydroxyl radicals on the surface of the oxide lattice, as reported in literature (Delekar et al., 2012; Zhang et al., 2011). Additionally, Fe-TiO<sub>2</sub> showed a higher S<sub>BET</sub> and a lower E<sub>bg</sub> with respect to N-TiO<sub>2\_1.2</sub> (Table 2), justifying the better performances of Fe-TiO<sub>2</sub> photocatalyst under visible light. On the other hand, the enhanced photocatalytic activity by modification of the TiO<sub>2</sub> structure with N and Fe may be associated with the





**Fig. 10** Photocatalytic discoloration of TiO<sub>2</sub>, N-TiO<sub>2</sub>\_1.2, Fe-TiO<sub>2</sub> and Fe-N-TiO<sub>2</sub>\_1.2 photocatalysts under visible light irradiation.

simultaneous action of Fe<sup>3+</sup> (previously underlined) and N anions, which are able to replace the oxygen sites of TiO<sub>2</sub> lattice, generating Ti<sup>3+</sup> sites and oxygen vacancies (Ramalingam et al., 2017). At the same time, despite Fe-N-TiO<sub>2</sub>\_1.2 sample presented a S<sub>BET</sub> slightly lower than Fe-TiO<sub>2</sub>, the co-doped photocatalyst displayed a lower E<sub>bg</sub> value (Table 2). Therefore, it is not surprising that Fe-N-TiO<sub>2</sub>\_1.2 showed the best photocatalytic activity under visible light irradiation. It is worthwhile to note that, with Fe-N-TiO<sub>2</sub>\_1.2 sample, about 90% of AO7 discoloration was achieved in a very short time (60 min), if compared to the treatment time reported in several papers, about the AO7 degradation under visible light using also different photocatalyst formulations (Li et al., 2016; Wu et al., 2010c, 2010b, 2010a; Ji et al., 2012).

The TOC of solutions was measured to assess the mineralization performances of the photocatalysts. TOC removal efficiency after 60 min of treatment time using N-TiO<sub>2</sub>\_x samples was shown in Fig. 11. The highest mineralization efficiency (55%) was observed for the N-TiO<sub>2</sub>\_1.2 sample, confirming that 1.2 g of urea was the optimal value also for the mineralization of the target pollutant.

Fig. 12 reports the TOC removal of Fe-N-TiO<sub>2</sub>\_1.2 photocatalyst that was found to be equal to 83%. The co-doped sample (Fe-N-TiO<sub>2</sub>\_1.2) was certainly more efficient than the undoped titania (5%), but it also showed a better efficiency in the AO7 mineralization compared to N-TiO<sub>2</sub>\_1.2 (55%) and Fe-TiO<sub>2</sub> (73%) samples.

So, it is worthwhile to note that discoloration and mineralization occurs simultaneously under visible light irradiation of N-doped and Fe-N co-doped photocatalysts.

### 3.2.2. Kinetics evaluation of AO7 discoloration and mineralization

The apparent kinetic constant for AO7 discoloration and mineralization was evaluated in order to better evidence the influence of co-doping on photocatalytic performances. It was considered that AO7 photodegradation reaction follows a pseudo first-order kinetic, as reported in literature (Li et al., 2016; Wu et al., 2010c; Omrania et al., 2019). The photocatalytic degradation rate ( $r$ ) depends on AO7 concentration or TOC in aqueous solution according to the following relationship:

$$r = k \cdot s \quad (6)$$

where

$$s = \text{concentration of AO7 (mg L}^{-1}\text{) or TOC (mg}_c\text{ L}^{-1}\text{);}$$

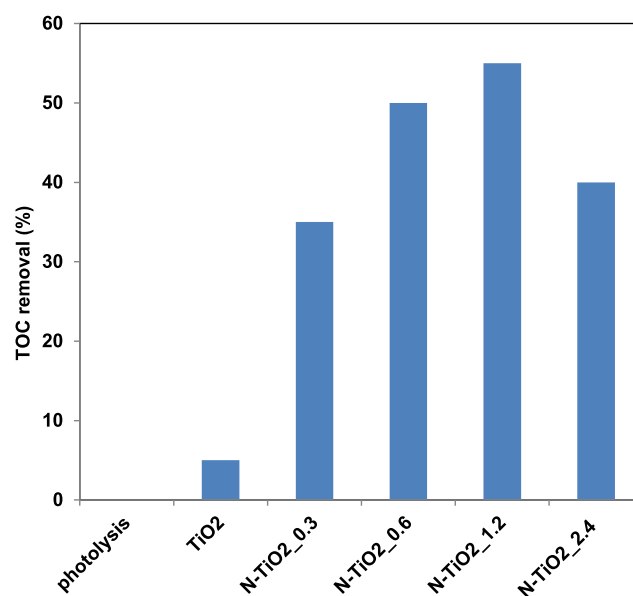
$$k = \text{apparent kinetic constant (min}^{-1}\text{).}$$

Integrating the mass balance (Eq. (7)) equation between the initial time ( $t = 0$ ) and a generic irradiation time  $t$ , it is possible to obtain the equation Eq. (8).

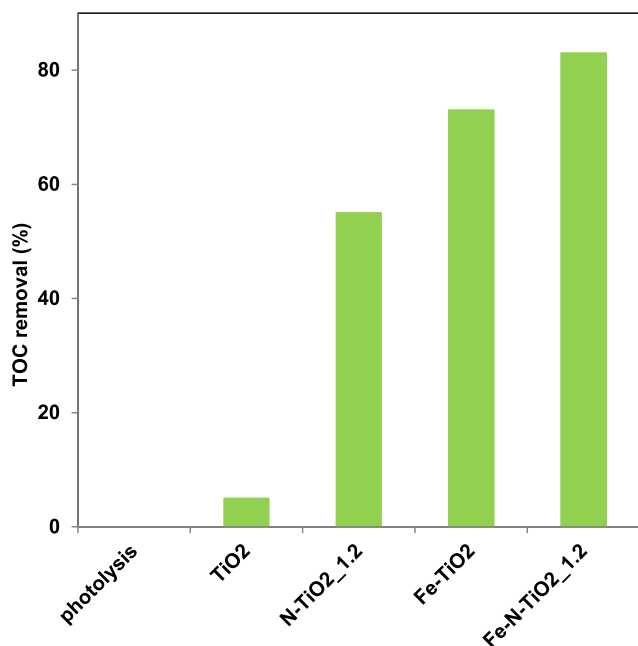
$$\frac{ds}{dt} = -k \cdot s \quad (7)$$

$$-\ln\left(\frac{s}{s_0}\right) = k \cdot t \quad (8)$$

The values of the apparent kinetic constant  $k$  are calculated by plotting  $-\ln\left(\frac{s}{s_0}\right)$  as a function of the irradiation time ( $t$ ) (Figs. S2 and S3 of Supplementary Material).



**Fig. 11** TOC removal (%) after 60 min of visible light irradiation of TiO<sub>2</sub>, N-TiO<sub>2</sub>\_0.3, N-TiO<sub>2</sub>\_0.6, N-TiO<sub>2</sub>\_1.2 and N-TiO<sub>2</sub>\_2.4 photocatalysts.



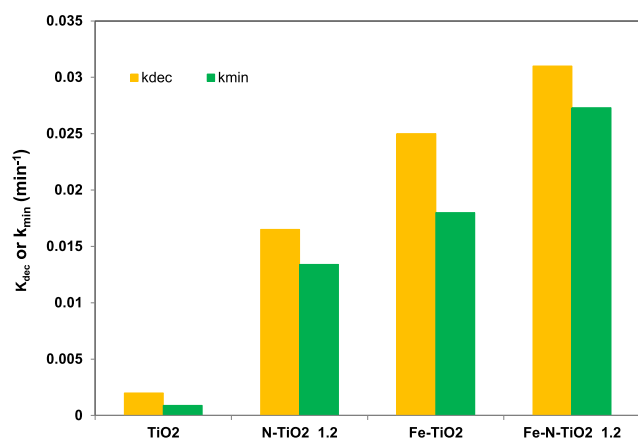
**Fig. 12** TOC removal (%) after 60 min of visible light irradiation of TiO<sub>2</sub>, N-TiO<sub>2</sub>\_1.2, Fe-TiO<sub>2</sub> and Fe-N-TiO<sub>2</sub>\_1.2 photocatalysts.

The obtained values ( $k_{\text{dec}}$  for discoloration and  $k_{\text{min}}$  for mineralization) are reported in Fig. 13 for the TiO<sub>2</sub>, N-TiO<sub>2</sub>\_1.2, Fe-TiO<sub>2</sub> and Fe-N-TiO<sub>2</sub>\_1.2 samples.

The overall rate constants for AO7 discoloration were given in the following order:

$k_{\text{dec Fe-N-TiO}_2_{1.2}} > k_{\text{dec Fe-TiO}_2} > k_{\text{dec N-TiO}_2_{1.2}} > k_{\text{dec N-TiO}_2_x} > k_{\text{dec TiO}_2}$ , indicating the faster AO7 discoloration and therefore the higher photocatalytic activity for Fe-N-TiO<sub>2</sub>\_1.2 photocatalyst. The mineralization rate constants also increased in the following order:

$k_{\text{min Fe-N-TiO}_2_{1.2}} > k_{\text{min Fe-TiO}_2} > k_{\text{min N-TiO}_2_{1.2}} > k_{\text{min N-TiO}_2_x} > k_{\text{min TiO}_2}$ , thus proving that also the AO7 mineralization with Fe-N-TiO<sub>2</sub>\_1.2 photocatalyst is faster than



**Fig. 13** Apparent kinetics constant for AO7 discoloration ( $k_{\text{dec}}$ ) and mineralization ( $k_{\text{min}}$ ) using TiO<sub>2</sub>, N-TiO<sub>2</sub>\_1.2, Fe-TiO<sub>2</sub> and Fe-N-TiO<sub>2</sub>\_1.2 photocatalysts.

that with undoped TiO<sub>2</sub>, N-TiO<sub>2</sub>\_1.2 and Fe-TiO<sub>2</sub> photocatalysts.

### 3.3. Calculation of electric energy consumption

In order to compare the system under investigation (Fe-N-TiO<sub>2</sub>\_1.2) with the literature dealing with the Fe-N doped TiO<sub>2</sub> formulation, the electric energy consumption ( $E_{E/O}$ ) was estimated. It is recognized that  $E_{E/O}$  (given in kWh in European Countries) represents a scale-up parameter required to remove a pollutant by one order of magnitude (90%) in 1 m<sup>3</sup> of polluted water (YASAR and YOUSAF, 2012). The  $E_{E/O}$  values were calculated using the following proposed equation (Azbar et al., 2004, Vaiano et al., 2019):

$$E_{E/O} = \frac{P \cdot t \cdot 1000}{V \cdot 60 \cdot \ln\left(\frac{C_o}{C_f}\right)} \quad (9)$$

where

$P$  = nominal power of the light source (kW);

$t$  = irradiation time (minutes);

$V$  = solution volume (L);

$C_o$  = AO7 initial concentration (mg L<sup>-1</sup>);

$C_f$  = AO7 final concentration (mg L<sup>-1</sup>).

The  $E_{E/O}$  value for Fe-N-TiO<sub>2</sub>\_1.2 is reported in Table 3 and compared with the energy consumption required to remove different contaminants using Fe-N co-doped TiO<sub>2</sub> as reported in other papers (Cong et al., 2007, Shen et al., 2008, Zhou and Wang, 2014).

The  $E_{E/O}$  values confirm that the electric energy consumption for the AO7 degradation by Fe-N-TiO<sub>2</sub>\_1.2 photocatalyst under investigation is drastically less than  $E_{E/O}$  data related to the removal of water pollutants under visible light with similar photocatalysts.

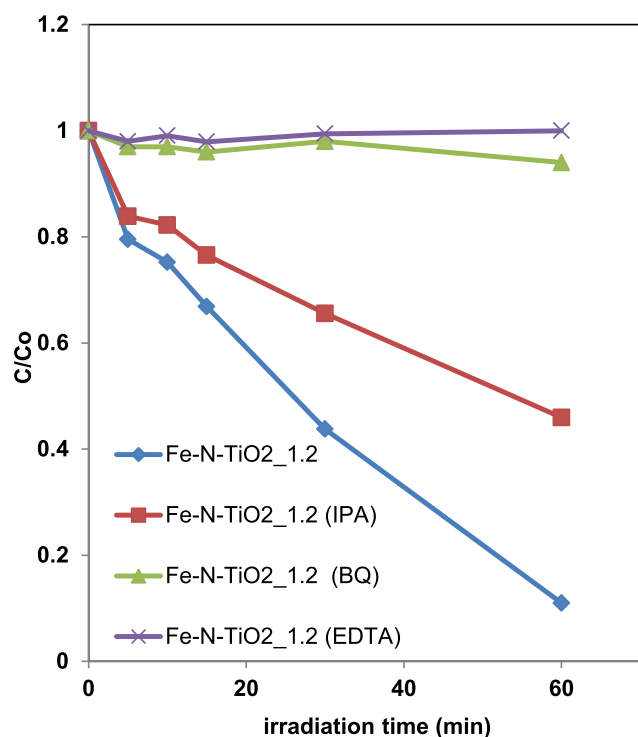
### 3.4. Possible role of reactive oxygen species towards the AO7 discoloration under visible light

The possible role of reactive oxygen species (ROS), such as hydroxyl radicals, superoxide and positive holes has been investigated during the AO7 photocatalytic discoloration process using Fe-N-TiO<sub>2</sub>\_1.2. The scavenger probe molecules were: isopropanol (IPA, 10 mmol L<sup>-1</sup>) for hydroxyl radicals (Zhang et al., 2018), benzoquinone (BQ, 1 μmol L<sup>-1</sup>) for superoxide (Zhang et al., 2017) and disodium ethylenediamine tetra-acetate (EDTA, 10 mmol L<sup>-1</sup>) for positive holes. Fig. 14 shows the effects of the scavengers presence on photocatalytic performances.

It can be seen as the addition of IPA, BQ and EDTA influenced the AO7 discoloration rate. In particular, it was found that the IPA presence slightly decreased the AO7 discoloration efficiency while, the addition of BQ and EDTA completely inhibited the photocatalytic process. These results demonstrate that the main reactive oxygen species involved in the AO7 discoloration mechanism were represented by superoxide and positive holes. They are consistent with the literature reporting the role of ROS on visible light driven photodegradation of AO7 (Styliadi et al., 2004).

**Table 3** Comparison of  $E_{E/O}$  ( $\text{KWh m}^{-3}$ ) with studies reported in the literature about the degradation of different contaminants using Fe-N co-doped  $\text{TiO}_2$ .

Contaminant	Types light source	Power input (W)	$E_{E/O}$ ( $\text{KWh m}^{-3}$ )	Reference
Acid Orange 7	Visible-LEDs	10	43	Present work
Rhodamine B	halogen lamp	1000	$3.5 \cdot 10^4$	Cong et al. (2007)
Methylene Blue	xenon lamp	450	$1.6 \cdot 10^4$	Zhou and Wang (2014)
Methyl Orange	xenon lamp	300	$1.3 \cdot 10^3$	Shen et al. (2008)
Phenol	metal halide lamp	575	250	Sun et al. (2013)
Ciprofloxacin	LEDs lamp	12	120	Suwannaruang et al. (2020)

**Fig. 14** Effects of different scavengers on AO7 photodegradation using Fe-N-TiO<sub>2</sub>\_1.2 photocatalyst under visible light irradiation.

#### 4. Conclusions

The photocatalytic performances under visible light irradiation of Fe-N codoped  $\text{TiO}_2$  photocatalysts were investigated in the treatment of aqueous solutions containing AO7. The photocatalysts were prepared by sol-gel method and analyzed by different characterization techniques. UV-vis DRS spectra showed that Fe-N-TiO<sub>2</sub>\_1.2 sample gives visible-light absorption contributions higher than those of undoped  $\text{TiO}_2$ , N-TiO<sub>2</sub>\_1.2 and Fe-TiO<sub>2</sub> photocatalysts. It was observed a decrease in  $E_{bg}$  up to the value of 2.9 eV for N-TiO<sub>2</sub>\_1.2 and 2.8 eV for Fe-TiO<sub>2</sub>, with respect to undoped  $\text{TiO}_2$  (3.2 eV). The further narrowing of Fe-N-TiO<sub>2</sub>\_1.2  $E_{bg}$  to value of 2.7 eV may be a possible indication of the enhancement of the photocatalytic activity in the visible light region with respect to both Fe-TiO<sub>2</sub> and N-TiO<sub>2</sub>\_1.2 samples. Furthermore, the XRD results indicate that the crystalline phase of

the iron and nitrogen doped materials is not influenced by the presence of the dopant elements, showing the presence of all diffraction peaks related to the anatase phase and a small signal associated to brookite. It was observed an enhancement of photocatalytic AO7 discoloration and mineralization under visible light irradiation using Fe-N-TiO<sub>2</sub>\_1.2 photocatalyst, also confirmed by the kinetic constants values for AO7 degradation. In particular, Fe-N-TiO<sub>2</sub>\_1.2 was able to achieve 90% of discoloration efficiency and 83% of TOC removal in 60 min of LEDs light irradiation. This enhancement of photocatalytic activity should be due to the modification of the  $\text{TiO}_2$  structure with N and Fe associated with the simultaneous action of  $\text{Fe}^{3+}$  ions that inhibit the hole and electron recombination and nitrogen ions, which are able to replace the oxygen sites of  $\text{TiO}_2$  lattice, generating  $\text{Ti}^{3+}$  sites and oxygen vacancies. The main reactive oxygen species responsible of AO7 photocatalytic degradation are superoxide and positive holes generated under visible light irradiation. Finally, the optimized Fe-N-TiO<sub>2</sub>\_1.2 evidenced photocatalytic performances better than other Fe-N co-doped  $\text{TiO}_2$  formulations investigated in literature, both in terms of treatment time and electrical energy consumption.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.arabj.2020.05.019>.

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