**TUNING THE PHOTOACTIVITY OF TiO₂ NANOARCHITECTURES DOPED WITH
CERIUM OR NEODYMIUM AND APPLICATION TO COLOR REMOVAL FROM
WASTEWATERS**

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Abstract

The impact of cerium (Ce) and neodymium (Nd) rare-earth metal doping of TiO₂ prepared by hydrothermal method was investigated to tailor effective photocatalytic degradation of colored wastewater under UV or visible illumination. The hydrothermal treatment of TiO₂ decreased the pH_{pzc} from 6.3 to 3.1-3.8 favoring the affinity for cationic water contaminants. Doping with Ce and Nd modified the crystallinity and the morphology of the photocatalysts and significantly increased the BET surface area and the adsorption capacity of cationic dyes. The photocatalytic activity under UV light irradiation decreased due to shielding of the catalyst active area by excessive amount of dye adsorbed. Conversely, the photocatalytic activity of the Ce and Nd doped TiO₂ increased under visible light irradiation by 1.2 times as a result of the dye photosensitization effect. It was demonstrated that two-steps dark adsorption and photocatalytic reaction or one-step simultaneous adsorption and reaction can produce significantly different results for the photocatalytic degradation of dyes in coloured waters, the rate being controlled by the competitive adsorption of the reacting organics and the H₂O/OH⁻ species. The reaction is driven by the radical oxygen species (ROS) formed on the catalyst surface the nature of which, differs under UV or visible light irradiation. The Ce-doped TiO₂ and Nd-doped TiO₂ photocatalysts with 0.5% rare-earth content were found to be efficient in the degradation of MB in aqueous solution, removing the color and reducing the toxicity of wastewaters.

Keywords: Cerium; Neodymium; Colored Wastewaters; Adsorption; Photocatalysis.

1. Introduction

Colored effluents such as those produced by textile plants are often harmful to the environment and to the receiving waters, primarily because they impact the photosynthesis of aquatic plants due to reduced light penetration. In addition, dye degradation products can be toxic to aquatic organisms [1, 2]. Conventional treatment of colored waters by physico-chemical and biological processes often do not produce a dischargeable effluent textile, due to the high load of organic recalcitrant species and the high stability of dyes. In consequence, these effluents often require further treatment using alternative process, such as advanced oxidation processes (AOPs). Among these titanium dioxide (TiO_2) photocatalysis has been considered a promising process, since it can harvest renewable solar light to produce highly oxidative radical oxygen species (ROS) which degrade recalcitrant pollutants in contaminated waters [3-10].

TiO_2 is a semiconductor powder material primarily used as white pigment in paints but also in cosmetics, beauty products, toothpaste and as UV filter in sunblock formulations. Depending on its crystalline structure (anatase, rutile or brookite) TiO_2 can absorb photons in the UVA spectrum, causing the formation of electron-hole couples in the semiconductor material, which can initiate redox reactions [1]. According to the intended use, the photocatalytic activity of titanium dioxide (TiO_2) can be suppressed, such as in paints, or promoted, for instance, in environmental applications for the removal of aqueous or gaseous contaminants. Most studies reported in the literature have focused on increasing the photocatalytic activity of TiO_2 , reducing the recombination of charges or extending the absorption of TiO_2 into the visible spectrum of the solar light [3]. Conversely, in such cases in which the photocatalytic activity is undesirable, such as in textiles, paper, plastic films, paints and hygiene and beauty products, the photoactivity of TiO_2 must be suppressed throughout the solar light spectrum at the Earth surface [4].

Several metal dopants have been used to modify the morphology and photocatalytic activity of TiO_2 , including copper (Cu) [5,6], zinc (Zn) [5,6], iron (Fe) [7,8], silver (Ag) [5,9] and rare earth metals [10,11]. In particular, rare earth metals doping of TiO_2 produces materials with different

1 optical and catalytic properties, since they exhibit rich and unique spectroscopic and magnetic
2 properties. Cerium (Ce) is the most abundant of the rare earth elements, being found in the proportions
3 of 44% and 50% in the minerals monazite and bastnaesite, respectively. Neodymium (Nd) is the
4 second most abundant of the rare-earth elements and is almost as abundant as copper [12].

5 These two lanthanides have been used to modify the photocatalytic activity of TiO₂ and a
6 notably low doping percentage is usually sufficient to change the activity of TiO₂ both in a positive
7 [13,14] and in a negative way [15,16]. The suppressive effect on the activity, responsible for
8 maintaining the photostability of the lanthanide-doped TiO₂ particles, is usually attributed to the
9 ability of the dopants to act as electron and/or hole traps. However, the same explanation has been
10 reported to explain the increase in photocatalytic activity promoted by doping with rare earths [10,11].
11 Some studies propose that at lower rare earth concentrations (0.1-1% by mass) the trapping effect of
12 the charge carriers may decrease the recombination rate of the electron/hole pairs favoring redox
13 reactions, but at higher concentrations (1-10% by mass) the recombination process occurs so intensely
14 that there is a lack of electrons or holes to promote such redox reactions [13,17]. However, other
15 studies have shown that small amounts of these dopants (0.3-1% by mass) exert suppressive effects
16 on the photocatalytic activity of TiO₂ [15]. Metal doping could therefore be used to modulate the
17 photocatalytic activity of TiO₂ to selectively decompose toxic contaminants in industrial effluents as
18 a result of a more favorable surface chemistry [18].

19 Different routes of synthesis of TiO₂ nanoarchitected doped with rare earths are reported
20 [1-4,10], such as the sol-gel and hydrothermal methods. The most used methodology to produce
21 spherical Ce or Nd doped TiO₂ the sol-gel method, while the hydrothermal method provides
22 nanorods or nanosheets nanoparticles, depending on the temperature and synthesis time. Thus,
23 hydrothermal methodology was chosen for this study, since it has the advantage of being able to
24 control the photocatalysts morphology, increasing surface area, conductivity and, consequently,
25 reducing the recombination of the photogenerated pairs when compared to the photocatalysts
26 obtained by the sol-gel route [11].

In this study, a range of Nd or Ce-doped TiO_2 were prepared and the adsorption and photocatalytic properties were tuned for the selective treatment of synthetic and colored effluents, under both UV and visible light irradiation. The Nd or Ce-doped TiO_2 were prepared by the hydrothermal method to allows greater control of the surface area, morphology, and band-gap properties, to determine the most effective catalysts properties for the removal of contaminant from the dyeing wastewater. The toxicity of the treated effluent was evaluated to determine the environmental safety of the treated effluent.

2. Materials and Methods

2.1 Preparation of photocatalysts

TiO_2 P25 was purchased from Evonik (Germany). $\text{Ce}(\text{NO}_3)_3$ and $\text{Nd}(\text{NO}_3)_3$ were obtained from Sigma Aldrich. Analytically pure NaOH (NEON) and HCl (NEON) were used in the experiments. All of these chemicals were used without further purification. Distilled water was employed in the experiments.

The TiO_2 photocatalysts were prepared by a hydrothermal method [19,20]. Briefly, 60 mL of an aqueous solution of 10 M NaOH and 3 g of TiO_2 P25 were stirred magnetically for 1 h to complete homogenization. The solution was then transferred to a steel autoclave coated with polytetrafluoroethylene and placed in an oven under controlled temperature at 120 °C for 24 h. After completion, the sodium ion was removed by washing with a 0.1 M HCl solution and distilled water until the rising water reached neutral pH. Finally, the materials were dried at 60 °C overnight and calcined at 450 °C (heating rate of 10 °C min⁻¹) for 2 h and stored in sealed amber bottles. The Ce-doped and Nd-doped photocatalysts were prepared following a similar procedure but by adding different amounts of $\text{Ce}(\text{NO}_3)_3$ or $\text{Nd}(\text{NO}_3)_3$ during the first homogenization step along with NaOH and TiO_2 P25. Undoped TiO_2 , $\text{CeO}_2/\text{TiO}_2$ and $\text{Nd}_2\text{O}_3/\text{TiO}_2$ with different metal contents (0%, 0.15 %, 0.5% and 1% in mass) were prepared, the nomenclature of which is shown in Table 1.

Table 1. Photocatalytic materials investigated.

Sample	% Metal (w/w)
TiO ₂ -P25	-
TiO ₂ -450	-
0.15Ce-TiO ₂ -450	0.15% Ce
0.5Ce-TiO ₂ -450	0.5% Ce
1Ce-TiO ₂ -450	1.0 % Ce
0.15Nd-TiO ₂ -450	0.15% Nd
0.5Nd-TiO ₂ -450	0.5% Nd
1Nd-TiO ₂ -450	1.0% Nd

2.2 Photocatalysts characterization

The crystalline properties of the photocatalysts were characterized by X-ray diffraction (XRD, Philips X'Pert) at room temperature using Cu K α radiation at 40 kV and 30 mA (geometry θ – 2θ and $\lambda = 1.54056 \text{ \AA}$). The morphology and the particle size were analyzed by transmission electron microscopy (TEM) on a JEM-2100. The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) was determined by nitrogen adsorption measurements at 77 K on a Quantachrome Autosorb-1 equipment. Prior to the analysis, the samples were heated to 100 °C and kept at this temperature for 12 h to desorb any adhering molecules and to remove any residual moisture. The zeta potential of the prepared photocatalysts was measured using a Stabino[®] Particle Charge Mapping analyzer (Particle Metrix, Germany). The optical characteristics were evaluated by diffuse reflectance ultraviolet-visible (DRUV) and diffuse reflectance spectroscopy on a Shimadzu UV-2450 spectrophotometer with an ISR-2200 Integrating Sphere attachment using BaSO₄ (Wako Pure Chemical Industries, Ltd.) as the baseline. In these measurements the samples were used as a powder. The fluorescence emission by the solid state was carried out on a Shimadzu RF-5301PC spectrofluorometer with a solid-state

holder. The measurements were performed using excitation/emission slits of 5.0 nm/5.0 nm (exc/em) in a spectral range of 300-700 nm. All measurements were performed at room temperature.

2.3 Photocatalytic activity

The photocatalytic activity of the sample materials was evaluated by monitoring the decolorization of methylene blue (MB) and that of a synthetic colored effluent (CE). The CE effluent was a commercial mixture of sodium chloride, marine blue dye and dispersant obtained from a product used to color cotton fabrics (Tingecor 0102.00, Guarany, Brazil).

The experiments were performed in a jacketed annular photoreactor (outer diameter 12 cm, inner diameter 9.5 cm, height 24 cm, useful volume 1 L, with 750 mL irradiated), similar to that described by [21], at 20 °C using a thermostatic bath equipment (Quimis, model: Q.214.D.12). The reactor was equipped with a visible light (model L3415 Brilia, 400-800 nm with a maximum emission at 620 nm, height 7.5 cm and diameter 3.5 cm) or a medium-pressure mercury lamp (model HQL E27 OSRAM, 200 nm to 800 nm with a maximum emission at 368 nm, height 7 cm and diameter 1.2 cm). The lamp was housed in a tube in the middle of the reactor, the visible light lamp and UV lamp were positioned 7.0 cm and 5.5 higher from the bottom, respectively. The photon irradiance at the reactor wall using the mercury lamp was 41 W m⁻² at 20 °C.

In a typical experiment, 750 mL of an aqueous solution of MB (20 mg L⁻¹) and the photocatalyst (500 mg L⁻¹) were mixed magnetically in the dark at 600 rpm until the adsorption equilibrium was reached. This was established when the concentration of MB remained constant (approximately 70 min). The lamp was then turned on and air was pumped into the aqueous suspension at a flow rate of 0.168 L min⁻¹. Samples collected at regular times were filtered through a GV membrane (Durapore, PVDF, 0.22 µm) and the absorbance was measured with a UV-Vis spectrophotometer (HACH DR5000) at 664 nm.

A second set of photocatalytic experiments were performed in the absence of the dark equilibration adsorption phase (named as single-step test), to evaluate the relationship between the rates of adsorption and reaction. In such experiments, the adsorption and photocatalytic reaction steps occurred simultaneously in the presence of light irradiation. In these tests, 750 mL of the aqueous solution containing MB (20 mg L⁻¹) or CE (maximum absorbance at 554 nm~1.7±0.1, pH 6.0 - 7.0) was placed inside the photoreactor, the magnetic stirrer was switched on, the air flow was open, the photocatalyst was added and the lamp was immediately turned on. The experimental conditions and analytical procedures were as previously specified.

The pseudo-first-order rate constants (k_{1-MB} and k_{1-CE}) (min⁻¹) for the MB and CE decolorization were determined using Origin® software (Eqs. 1 - 2), respectively:

$$\ln(C_0/C) = k_{1-MB} t \quad (\text{Eq. 1})$$

$$\ln(A_0/A_t) = k_{1-CE} t \quad (\text{Eq. 2})$$

All measurements were carried out in triplicate. The data were expressed as the means ± standard deviations, and the t test or ANOVA were carried out to assess significant differences among the means. The 5% level ($p \leq 0.05$) was adopted as a criterion of significance.

2.3.1 Acute toxicity test with *Vibrio fischeri*

The acute toxicity of the water before and after photocatalytic treatment was determined with the bioluminescent bacteria *Vibrio fischeri* (lyophilized) according to the methodology proposed by ISO 11348-3 [22]. The toxicity was determined from the inhibition of the luminescence emitted by the bacteria after a contact time of 30 min for each sample. The toxicity tests were conducted under controlled temperature conditions in a Microtox® analyzer (Model 500) at 15.0 °C ± 1 °C for the exposure tests and 3 °C ± 1 °C for the bacterial reagent (control).

3. Results and Discussion

3.1 Morphology of undoped and Nb/Ce doped materials

The prepared photocatalysts presented nanometric particle sizes well below 100 nm with varying morphology ranging from nanoparticles, nanosheets and nanotubes as shown in Fig. 1. The properties of the nanomaterials are reported in Table 2. The untreated TiO₂ P25 displayed the typical nanoparticle morphology with average particle size of 20.75 nm. After hydrothermal treatment the vast majority of nanoparticles was transformed to nanowires and nanosheets, with evidence of nanosheets enveloping to form elongated structures resembling nanotubes. The length of the nanotubes decreased as the doping ratio increased, suggesting a new structural form of the clusters, which was not observed in the TEM images of the undoped samples.

Fig. 1. TEM images of photocatalytic materials (a) TiO₂-P25, (b) TiO₂-450, (c) 0.5Ce-TiO₂-450, (d) 1Ce-TiO₂-450, (e) 0.5Nd-TiO₂-450 and (f) 1Nd-TiO₂-450.

Table 2. BET surface area, cerium or neodymium surface density, crystallite size, band gap, point of zero charge (pH_{pzc}), zeta potential (ZP) and the morphology for different photocatalysts.

Photocatalysts	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Ce_{sd} or Nd_{sd} (atom nm^{-2}) ^b	Crystallite size (nm)	E_{g} (eV)	pH_{pzc}	ZP (mV)	Morphology
TiO ₂ -P25	50.10	-	20.75	3.20	6.3	44.6	Nanoparticles
TiO ₂ -450	80.28	-	14.31	3.05	3.1	-78.1	Nanoparticles and nanotubes
0.15Ce-TiO ₂ -450	92.53	6.97	18.54	3.21	a	a	a
0.5Ce-TiO ₂ -450	107.90	19.92	17.30	2.40	3.8	-51.0	Nanoparticles and nanotubes
1Ce-TiO ₂ -450	73.19	58.74	19.77	3.21	3.7	-70.8	Nanoparticles and nanotubes
0.15Nd-TiO ₂ -450	104.70	5.98	17.85	3.20	a	a	a
0.5Nd-TiO ₂ -450	87.46	23.87	16.36	3.05	3.3	-76.0	Nanosheets and nanotubes
1Nd-TiO ₂ -450	84.52	49.40	20.06	3.20	3.1	-75.7	Nanosheets and nanowires

a. not measured; b. Calculated according Eq. 3.

3.2 Band gap of TiO₂ photocatalysts

Diffuse reflectance UV-Vis absorption (DRUV) and diffuse reflectance spectroscopy were used to determine the optical response and band-gap of undoped TiO₂ and Ce and Nd doped TiO₂ (Fig. 2a). Since the objective was to evaluate the difference between cerium and neodymium doping, the photocatalysts TiO₂-450, 0.5Ce-TiO₂-450 and 0.5Nd-TiO₂-450 were selected for this analysis.

Fig. 2. (a) Diffuse reflectance UV-Vis absorption (DRUV) spectra of doped TiO_2 . Inset: magnification of the Vis-NIR region (400-900 nm); (b) Diffuse reflectance (%) spectra of doped TiO_2 . Pure titanium dioxide is included for comparison.

In Fig. 2a, all samples show an intense absorption in the UV region located around 300 nm (4.13 eV), regardless of the doping metal, which may be related to the TiO_2 . Below 450 nm, similar absorbance behaviors are observed for the TiO_2 and Nd-doped TiO_2 , the sharp increase being attributed to the absorption edge. The optical band-gap energies were obtained for these two oxides based on the onset of the DRUV spectra, determined from the energy associated with the separation of the valence and conduction bands of these materials. Values of around 3.05 eV were obtained, as expected for TiO_2 . The most significant change in the DRUV spectra was located in the visible-NIR region (400-900 nm) in correspondence with the characteristic absorption bands of Nd. The doped TiO_2 presented several optical absorption bands, related to the $f-f$ electron transitions of Nd ions, [24] located at 475, 515, 528, 586, 628, 660, 684, 706, 744 and 803 nm, as previously reported [17], with a band gap transition similar to that observed with the undoped TiO_2 . The broader absorption window of the Nd- TiO_2 extending in the visible-NIR region could be exploited in photocatalytic reactions under direct solar light. Concerning the Ce- TiO_2 , the absorption in the visible region (400-500 nm)

was more intense than the undoped material [1,24]. This result is probably related to the generation of electron-hole pairs with visible light absorption, provided by the 4f electronic configuration of Ce. The Ce-TiO₂ presented an optical band gap (2.40 eV) significantly lower than that of TiO₂ and Nd-TiO₂.

Fig. 2b shows that despite the final reflectance in the UV region of all samples was approximately 5%, only the undoped TiO₂ was transparent in the visible region (400 nm - 800 nm). The diffuse reflectance of Nd-TiO₂ in the green-NIR regions was 90%, while the reflectance of Ce-TiO₂ in the blue-green region reduced up to 70%, indicating significant optical absorption in this region.

3.3 BET surface area and metal surface density

The surface area of TiO₂ P25 increased by 60% after hydrothermal treatment (TiO₂-450 sample, Table 1) and further increased in the doped photocatalysts especially at lower doping percentages, with the exception of 1Ce-TiO₂-450. The photocatalyst with the largest areas were 0.5Ce-TiO₂-450 and 0.15Nd-TiO₂-450.

The Ce or Nd surface density over the TiO₂ surface, was estimated from Eq. 3 [25]:

$$X_{sd} = \frac{\% \text{mass of X} \times A}{S_{BET} \times MM_X} \quad (\text{Eq. 3})$$

where the X_{sd} is the number of Ce or Nd atoms per nanometer squared of surface area (atom nm⁻²); %mass of X is the nominal mass percentage of Ce or Nd doping; A is Avogadro's number; S_{BET} is the surface area (nm² g⁻¹) of the TiO₂ photocatalyst; and MM_X is the molar mass of Ce or Nd (mol g⁻¹) [26].

As expected, the results shown in Table 2 indicate that the Ce or Nd surface density is dependent on the amount of Ce or Nd used in the doping and the BET surface area. 1Ce-TiO₂-450 has more atoms of Ce well-distributed over the material surface, but it has the lowest surface area. On the other and, 0.5Nd-TiO₂-450 has a considerable quantity of Nd atoms well-distributed over its surface and a high surface area.

3.4 Crystallinity (XRD) and Ce/Nd doping (XRF) of photocatalysts

Figure 3 shows the XRD spectra of the doped and undoped samples. The diffraction peaks at 2 theta values of 25.17°, 37.60°, 47.76°, 54.01° and 62.60° are indexed to the (101), (004), (200), (105) and (204) planes of the anatase phase of TiO₂ [25]. This indicates that during the hydrothermal reaction the rutile phase is not formed.

The absence of Ce in the XRD patterns was attributed to the small percentage in the samples. The cerium species were either successfully doped into the TiO₂ lattice or well dispersed, since small particles of CeO₂ on the surface of TiO₂ with a low Ce content were not detected by the XRD technique. As the ionic radii of Ce⁴⁺ and Ce³⁺ (0.093 and 0.103 nm, respectively) are larger than that of Ti⁴⁺ (0.068 nm), it is difficult to envisage that the cerium ions would be able to enter the TiO₂ lattice. Therefore, only a small number of Ce³⁺/Ce⁴⁺ ions may penetrate the lattice and the remaining dopant ions were most likely located at the grain boundary/grain junctions [27]. In the presence of Ce, there was a significant increase in the intensity of the peaks, and there was no phase change, which gives the material a higher stability, as previously reported [24].

Likewise, the absence of Nd in the XRD patterns suggest that a very small percentage of the Nd added replaced the Ti⁴⁺ in the TiO₂ lattice. The very different ionic radii of Nd³⁺ and Ti⁴⁺ (0.99 and 0.68 Å, respectively) supports this hypothesis. Instead of replacing the substituent Ti⁴⁺ positions, the Nd species may be preferentially located on the TiO₂ surface and/or in the octahedral interstices

of the titania lattice [27]. Doping with Nd also increased the intensity of the peaks and did not cause phase change, giving the material greater stability, as previously reported [24,29].

The peaks at 31.65° and 45.41° identified in selected samples related to the residues formed with the NaCl reagent used during the hydrothermal synthesis and the peak at 29.12° is associated to the formation of sodium titanate (Na₂Ti₉O₁₉).

The photocatalysts crystallites sizes were determined using the Scherrer equation (Eq. 4). The results (Table 2) confirm that the hydrothermal method and the doping with cerium and neodymium did not have a significant influence on the crystallite size. The doping with Ce or Nd inhibited the growth of the crystallite and with low concentrations of the metal, which is an advantage [24].

$$D = \frac{K \lambda}{\beta \cos(\theta)} \quad (4)$$

where D is the crystallite length in the direction of the d spacing, K is the shape factor of the particle (consider to be 1), λ and θ are the wavelength and incident angle of the X-rays, respectively, and β is the line width at half maximum of the peak.

Fig. 3. XRD patterns obtained for photocatalysts prepared. The symbols ♥, ✕, • and ♦ indicate anatase TiO_2 phase, NaCl, sodium titanate and rutile TiO_2 phase, respectively.

3.5 Zeta Potential

The aqueous suspension stability of the solids and the point of zero charge (pH_{pzc}) of the photocatalysts were determined by measuring the zeta potential in a suspension in distilled water (Table 2). A significant reduction of the point of zero charge of TiO_2 P25 ($\text{pH}_{\text{pzc}} = 6.3$) was observed after the hydrothermal treatment ($\text{pH}_{\text{pzc}} = 3.1$) due to the presence of NaOH which increased the amount of OH groups on the solid surface. In contrast, the presence of Ce or Nd had an insignificant

1 impact on the hydrothermally treated sample. Therefore, the aqueous suspension stability of the
2 catalyst after hydrothermal treatment increased the pH range that the catalyst is active. The affinity
3 between the photocatalysts and the contaminants over the neutral and basic pH range increased. Such
4 effect would increase the adsorption and oxidation capacity of the photocatalyst for common cationic
5 contaminants.

7 *3.6 Photoluminescence analysis*

9 The photoluminescence (PL) spectra, in the range of 300-700 nm, measured with different
10 excitation wavelengths at room temperature are shown in Fig. 4. A broad PL emission band was
11 observed in the visible region (~ 500 nm), probably related to the transitions occurring due to the
12 recombination of the electron-hole pairs in surface defects/surface oxygen vacancies [29]. A similar
13 intensity and shape were observed in the PL spectra for all samples, regardless of the excitation
14 wavelength and doping metal. These results indicate that the presence of the doping metal, as well as,
15 the preparation methodology do not significantly affect the recombination centers and do not create
16 new entrapment sites on the surface of TiO_2 .

Fig. 4. PL spectra for TiO_2 , $0.5\text{Ce-TiO}_2\text{-450}$ and $0.5\text{Nd-TiO}_2\text{-450}$ using (a) 280 nm, (b) 300 nm and (c) 330 nm as the excitation wavelength. The pure titanium dioxide is presented for comparison. The asterisk indicates the scattering from the solid sample holder.

3.7 Impact of Ce or Nd doping of TiO_2 on photodegradation of MB

A relatively high amount of MB was adsorbed at pH 8.4 in the darkness on the hydrothermally treated TiO_2 in comparison to the untreated sample (Table 3). Under these conditions, the

photocatalyst surface has a negative charge ($\text{pH} > \text{pH}_{\text{pzc}}$, Table 2) which attracts the cationic MB dye. During the adsorption process the pH decreased to 6.0, which is lower than the point of zero charge of untreated TiO_2 P25, therefore negligible MB adsorption occurred on the slightly positive charged surface. Surface area plays a minor role on the adsorption process in this case, although this can explain well the small differences observed in hydrothermally treated samples (Fig. 5). It has been reported that the doping of rare earths generally increases the MB adsorption capacity as shown in Table 3, and the literature reports values from 0.0038-88.4 mg/g (undoped TiO_2) to 0.0081-95.4 mg/g (Ce, Sm, La, Nd doped TiO_2) [30-37].

In addition to the surface area, adsorption capacity is also influenced by other characteristics of the material, such as the zeta potential and charge density. Surface charge density represents the amount of electrical charges present on the surface of each photocatalyst, showing a greater or lesser attraction for water contaminants [37]. This parameter is calculated by Eq. 5 [38]:

$$\sigma = \frac{E_r E_o ZP}{\sqrt{\frac{E_r E_o k_b T}{q z n}}} \quad (\text{Eq. 5})$$

where $E_r E_o$ is the permittiveness of the solution (for distilled water = $7.07 \times 10^{-10} \text{ F m}^{-1}$); ZP is the zeta potential of the particle (V) (see table 2); k_b is the constant of Boltzmann ($1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-1} \text{ K}^{-1}$); T is absolute temperature ($294.8 \pm 0.33 \text{ K}$); q is the elemental charge ($1.6 \times 10^{-19} \text{ C}$); z is the valence of ions (4, without unity); and n is the concentration of particles in the solution (2 kg m^{-3}).

The surface area and charge density of TiO_2 photocatalysts were compared with the amount of MB adsorbed (Table 3). The amount of MB adsorbed is almost independent of the doping amount of cerium or neodymium while it is a function of surface area or affinity (zeta potential and surface charge density) between the photocatalyst and the dye. The natural pH of the MB solution (8.4) is greater than the zero charge point of all photocatalysts, however, after the adsorption process was completed the pH decreased to 6.0. Under these conditions, the photocatalysts surface, other than that

of TiO₂-P25, had a negatively charged ($\text{pH} > \text{pH}_{\text{pcz}}$), which explain the large amount of MB adsorbed on the hydrothermally treated TiO₂ samples.

Fig. 5. Relationship between (a) BET surface area, (b) surface charge density and (c) charge density by surface area with adsorption capacity for photocatalysts prepared in this study.

The photocatalytic activity of the photocatalysts after the completion of the adsorption process of MB was evaluated under UV and under visible light irradiation and the results are shown in Fig. 6. The pseudo-first-order kinetic model and the kinetic constants fitting the degradation of MB are shown in Table 3.

Fig. 6. Photocatalytic degradation of MB by the photocatalysts under UV (a – b) and visible (c – d) light ($C_0 = 20 \text{ mg L}^{-1}$; $C_{\text{cat}} = 500 \text{ mg L}^{-1}$).

Table 3. Amount of MB adsorbed in the dark, pseudo-first-order kinetic constant for MB photodegradation under UV and visible light using different photocatalysts.

Photocatalysts	In the dark		Under UV light		Under visible light	
	Charge density by Surface area (C g ⁻¹)	Amount of MB adsorbed (mg g ⁻¹)	k _{1-MB} x 10 ² (min ⁻¹)	R ²	k _{1-MB} x 10 ² (min ⁻¹)	R ²
Photolysis	-	-	0.09 ± 0.01	0.93	0.12 ± 0.03	0.82
TiO ₂ -P25	0.0011	1.67	8.10 ± 0.80	0.96	0.25 ± 0.03	0.84
TiO ₂ -450	0.0030	32.91	5.71 ± 0.33	0.97	1.73 ± 0.11	0.96
0.15Ce-TiO ₂ - 450	a	34.75	4.03 ± 0.25	0.94	0.46 ± 0.02	0.99
0.5Ce-TiO ₂ -450	0.0026	34.46	3.24 ± 0.24	0.97	2.14 ± 0.17	0.92
1Ce-TiO ₂ -450	0.0024	33.08	4.87 ± 0.48	0.88	1.13 ± 0.16	0.84
0.15Nd-TiO ₂ - 450	a	35.58	0.93 ± 0.04	0.99	1.35 ± 0.25	0.88
0.5Nd-TiO ₂ -450	0.0032	36.10	3.79 ± 0.52	0.93	1.92 ± 0.31	0.90
1Nd-TiO ₂ -450	0.0031	35.23	2.99 ± 0.42	0.93	1.83 ± 0.18	0.96

a. not measured

The highest photocatalytic activity under UV light was found for TiO₂-P25 (0.08102 min⁻¹) although, while the photocatalysts prepared by the hydrothermal method displayed reduced photocatalytic activity under UV light irradiation. Such effect resulted by the competitive adsorption of MB which adsorbed extensively on the surface of these photocatalysts reducing the number for active sites for H₂O/OH⁻ ions adsorption and therefore the rate of hydroxyl radical formation.

The Ce and Nd doped TiO₂ photocatalysts, under visible light irradiation showed significantly higher photocatalytic activity than the undoped photocatalyst and the TiO₂-P25 sample. The smaller band gap in the Ce and Nd doped TiO₂ supports this results. In other studies, Ce and Nd doped TiO₂ showed similar trends for the photocatalytic oxidation of 4-chlorophenol [14], rhodamine B and phenol [39], under visible light irradiation. However, in this study we have shown that the application

1 of the hydrothermal method increases the surface area and the adsorption capacity due to a reduction
2 of pH_{pzc} (Tables 2 and 3). Therefore, in the presence of Ce and Nd doping metals an improved visible
3 light catalyst is demonstrated in comparison to other studies [14,39], although the greater amount of
4 dye adsorbed on the photocatalyst may increase the sensitization of the photocatalyst under visible
5 light irradiation [40].

6 Based on the above findings and considering previous reports on the excited-state redox
7 properties of methylene blue adsorbed on the surface of a TiO_2 semiconductor [41], the reaction with
8 a photocatalyst irradiated under visible light may involve several mechanisms of degradation.
9 However, the most important is the photosensitized reaction [40,42] where light is absorbed by the
10 dye. The transfer of charge from the excited dye molecule to the semiconductor conduction band
11 results in the formation of an unstable dye radical and an active species on the surface of the
12 semiconductor that attacks the destabilized dye molecule.

13 A trend between the adsorption capacity and the photocatalytic activity was clearly observed,
14 as shown in Fig. 7. Under UV light irradiation, the lower the adsorption of MB, the greater the
15 photocatalytic activity. Conversely, under visible light irradiation, the higher the adsorption of MB,
16 the greater the photocatalytic activity. The high surface area and the change in the surface charge of
17 the materials provided by the hydrothermal method increased the adsorption of the dye and influenced
18 the mechanism of degradation. The dye on the particle surface assists the photosensitized reaction
19 under visible light, while under UV light such effect was not observed since the dye molecules
20 competed for the active sites on the surface of the photocatalyst decreasing the rate of formation of
21 OH radicals and therefore the degradation of MB.

22 The relation between adsorption and photocatalytic activity is very important to determine
23 the mechanism of organic compound degradation by photocatalysts doped with Ce or Nd. The
24 photocatalytic degradation of methylene blue using TiO_2 is widely studied and described in the
25 literature. It can be expressed by the general reaction (Eq. 6):

A detailed degradation pathway of MB by photocatalytic reaction and the identification of intermediate products has been reported by Houas et al (2001) and Dulian et al. (2019) [43,44]. Following MB adsorption on the semiconductor surface, the reaction of adsorbed molecule with HO• radicals leads to the formation of intermediate compounds (4-dimethylamino-phenol, aromatic sulphonic acids and phenol, among others). These intermediate compounds seem to be similar using different photocatalysts [45-47], suggesting that the adsorptive, optical properties, and amount of reactive oxygen species formed by light activation are fundamental to explain the photoactivity of the semiconductor. The resulting molecules undergo further reactions involving photogenerated radicals until the formation of simple inorganic molecules.

Fig. 7. Relationship between the kinetic constants under UV light and the adsorption capacity for the photocatalysts doped with Ce and Nd under (a) UV and (b) visible light.

For the photocatalysts doped with the metals there is an ideal concentration of dopant of 0.5% (by mass), at which they reach the highest photocatalytic activity under visible light, along with the best physical characteristics according to characterizations, including smaller band gap and larger surface area. Therefore, a suitable Ce or Nd content could preserve the large surface area of TiO₂

during the synthesis. Other authors also support our findings of 0.5% as an optimal Ce/Nd doping level [48,49]. Thus, the photoactivity of TiO_2 -P25, TiO_2 -450, 0.5Ce- TiO_2 -450 and 0.5Nd- TiO_2 -450 photocatalysts was further investigated in experiments performed in the absence of the dark equilibration adsorption phase.

3.8 Photocatalytic activity of TiO_2 photocatalysts in a single-step test: photodegradation of MB

The photocatalytic experiments performed after completion of the adsorption step of MB revealed that doping with cerium and neodymium increased the photocatalytic activity of the photocatalysts only under visible light, while under UV light TiO_2 -P25 remained the most active sample. Single-step experiments were further performed (Fig.8) to investigate the simultaneous effect of adsorption and reaction. In such experiments, the steps of adsorption and reaction take place simultaneously in the absence of the dark equilibration adsorption phase. These experimental conditions are more common during the photocatalytic oxidation of industrial effluents, where the photocatalyst is added to the liquid effluent to be treated and promptly activated by artificial or solar light to perform the degradation of the dissolved contaminants. Thus, adsorption and photodegradation occur at the same time.

Fig. 8. Single-step test for photodegradation of MB by photolysis, TiO₂-450, 0.5Ce-TiO₂-450 and 0.5Nd-TiO₂-450 under (a) UV light and (b) visible light (C₀=20 mg L⁻¹; C_{cat}=0.5 g L⁻¹).

The results of such experiments shown in Fig. 8 and Table 4 demonstrate that under UV or visible light, the photocatalysts 0.5Ce-TiO₂-450 and 0.5Nd-TiO₂-450 are the most active photocatalysts of those prepared in this study, although they reach the same final percentage of degradation in 90 min of reaction.

Table 4. Pseudo-first-order kinetic constants for methylene blue photodegradation in a single-step test under UV and visible light using different photocatalysts.

Photocatalysts	Under UV light		Under visible light	
	k x 10 ² (min ⁻¹)	R ²	k x 10 ² (min ⁻¹)	R ²
Photolysis	0.09 ± 0.010	0.93	0.12 ± 0.03	0.89
TiO ₂ -P25	12.71 ± 0.19	0.99	0.46 ± 0.02	0.99
TiO ₂ -450	11.56 ± 1.20	0.97	12.36 ± 1.26	0.97
0.5Ce-TiO ₂ -450	24.18 ± 2.77	0.96	16.31 ± 1.32	0.98
0.5Nd-TiO ₂ -450	19.55 ± 3.37	0.92	18.07 ± 2.61	0.94

The first-order rate constants reported in Table 4 show that under UV and visible light, the 0.5Ce-TiO₂-450 and 0.5Nd-TiO₂-450 photocatalysts significantly increase the rate of degradation of MB beyond the values reported in Table 4, in more than 5 times. This result could not be observed in the experiments shown in Fig. 6, in which the adsorption and photocatalytic oxidation steps were carried out separately. The results also show a decrease of the oxidation rates by TiO₂ P25, suggesting that a diffusion limited regime may be reached under an excess of hydroxyl radicals formation and a deficiency of MB molecules on the TiO₂ surface.

Doping by these rare earth metals increased the photocatalytic activity of TiO_2 under UV light beyond the values shown in Table 4. It also confirms that the relation between adsorption and photocatalytic activity can be crucial to reveal the controlling mechanism for either an increase or a decrease of the photocatalytic activity under UV and visible light irradiation.

3.9 Photocatalytic activity of TiO_2 photocatalysts in a single-step test: photodegradation of the colored effluent (CE)

The adsorption results at equilibrium under darkness shown in Fig. 9, reveal that the both the undoped and doped hydrothermally treated photocatalysts had the same capacity to adsorb CE (approximately 20%), while the untreated catalyst, $\text{TiO}_2\text{-P25}$, adsorbed 60% of CE. This difference can be attributed to the higher affinity between the compound and the photocatalyst, in addition to the pH of the solution.

Fig. 9. (a) Amount of CE adsorbed and photodegraded under UV and visible light and (b) Pseudo-first-order kinetic constant in a single-step test under UV and visible light for $\text{TiO}_2\text{-450}$, $0.5\text{Ce-TiO}_2\text{-450}$ and $0.5\text{Nd-TiO}_2\text{-450}$ ($t_{\text{reaction}}=4$ h; $C_{\text{cat}}=0.5$ g L^{-1}).

The photolysis of CE (Fig. 9a) under UV or visible light irradiation was negligible (<10%). As expected, the degradation of CE was significantly higher in the presence of photocatalyst. Doping

the TiO₂-450 hydrothermally treated sampled with either Ce or Nd increased the degradation of CE under UV light by 8 % to reaching 50% after 4 h of reaction (Fig. 9a). Several factors influence the photocatalytic degradation of textile dyes, such as the initial concentration of each dye and the pH [21, 50]. Under UV light, the doped photocatalysts increased by 30% the rate of degradation of the effluent compared to the undoped TiO₂ sample (0.0035 to 0.005 min⁻¹). On the other hand, under visible light, the photocatalysts doped and undoped reached only 15% of degradation in 4 h of reaction with very similar pseudo-first-order kinetic constant (0.0015 min⁻¹).

The TiO₂-P25 photocatalyst showed the highest activity (0.043 min⁻¹) under UV and visible light, with the highest adsorption capacity being observed for the CE (60 %), in the tests carried out in a single step. This finding, along with the difference in the results obtained in the tests with MB and CE, shows that there is a very important relation between adsorption and photodegradation: a higher amount of dye adsorption being associated with greater photodegradation. In addition, when less effluent was adsorbed there was a lower rate of degradation.

Overall, the photodegradation rate for CE was lower than that for the pure dye (MB), due to the presence of other species in the synthetic effluent.

3.10 Toxicity analysis of CE after photodegradation

The acute toxicity of the treated colored effluent was evaluated to determine the toxicity of a partially treated effluent. This was determined by bioluminescence assays of the marine bacterium *Vibrio fischeri* exposed to the untreated and partially treated samples at different times. The inhibition of bioluminescence is greater in presence of toxic components in the colored wastewater. The results shown in Fig. 10 illustrate that for TiO₂-P25 the toxicity of the sample decreased up to 90 min of treatment under UV light irradiation, but at 120 min the toxicity significantly increased, possibly due to the formation of a toxic by-product. TiO₂-P25 was evaluated for only 120 min because at this time the color of the sample was totally removed.

The undoped catalyst (TiO_2 -450) did not modify the toxicity of the sample and the inhibition remained at 64 % for up to 240 min of reaction. The photocatalysts doped with Ce and Nd presented different initial behaviors but achieved the same inhibition after 240 min of reaction, considerably reducing it by up to 45%. Thus, a 30% improvement in the reduction of toxicity was observed for the photocatalysts 0.5Ce- TiO_2 -450 and 0.5Nd- TiO_2 -450 when compared to TiO_2 -450.

Although a longer reaction time was required, it may be concluded that the doped photocatalysts are more efficient in terms of both the degradation capacity (Fig. 9) and reducing the effluent toxicity after photocatalytic treatment.

Fig. 10. Percentage inhibition of bioluminescence of the bacteria *Vibrio fischeri* as a function of time of CE photodegradation by photocatalysts under UV light ($t_{\text{reaction}}=4$ h; $C_{\text{cat}}=0.5$ g L^{-1}).

4. Conclusions

In this study we have shown that hydrothermal treatment of TiO₂ P25 and further doping with Ce or Nd alters the physical and chemical characteristics of TiO₂. It increases the thermal stability of the catalyst, decreases the crystallite size, impact the morphology of the material, increases the BET surface area, modifies the band gap, increases the absorption of photons in the visible region and alters the surface charge of the materials in aqueous dispersion.

The increase in the surface area after doping through the hydrothermal method provided a greater capacity to adsorb methylene blue dye. However, this adversely impacted the photocatalytic degradation of MB under UV light due to a competition between the dye and H₂O/OH⁻ adsorption, and decreasing the number of •OH radicals formed. In contrast, under visible light irradiation, the increased adsorption rate of MB enhances the photocatalytic activity due to the photosensitization effect which becomes important in the degradation of the dye.

It was demonstrated that two separate steps (dark adsorption and photocatalytic reaction) or one step (simultaneous adsorption and reaction) may produce significant different results for the degradation of methylene blue, the rate being controlled by the competitive adsorption of the reacting organics and the H₂O/OH⁻ species. The pre-adsorbed colored compounds prevent the efficient of light absorption and electron/hole formation. The reaction being driven by the radical oxygen species (ROS) formed on the catalyst surface.

The photodegradation of a synthetic wastewater containing dyes (CE) was favored by the hydrothermally treated TiO₂ photocatalysts doped with cerium or neodymium, and this resulted in a reduction in the effluent toxicity after treatment. The results obtained in the degradation of CE by TiO₂-P25 strengthen the hypothesis that the rate of degradation of effluent is controlled by the rate of adsorption and the rate of reaction with the ROS formed by photocatalysis.

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References

- [1] M. Shirzad-Siboni, M. Samarghandi, J.-K. Yang, S.-M. Lee, Photocatalytic Removal of Reactive Black-5 Dye from Aqueous Solution by UV Irradiation in Aqueous TiO₂: Equilibrium and Kinetics Study, *J. Adv. Oxid. Technol.* 14 (2011) 302-307.
- [2] R. Khlifi, L. Belbahri, S. Woodward, M. Ellouz, A. Dhouib, S. Sayadi, T. Mechichi, Decolourization and detoxification of textile industry wastewater by the laccase-mediator system, *J. Hazard. Mater.* 175 (2010) 802-808.
- [3] P. Sun, L. Liu, S. Cui, J. Liu, Synthesis, characterization of Ce-doped TiO₂ nanotubes with high visible light photocatalytic activity, *Catal. Lett.* 144 (2014) 2107-2113.
- [4] F. Cheng, S. M. Sajedin, S. M. Kelly, A. F. Lee, A. Kornherr, UV-stable paper coated with APTES-modified P25 TiO₂ nanoparticles, *Carbohydr. Polym.* 114 (2014) 246-252.
- [5] J. Xiao, Y. Xie, H. Cao, F. Nawaz, S. Zhang, Y. Wang, Disparate roles of doped metal ions in promoting surface oxidation of TiO₂ photocatalysis, *J. Photoch. Photobio. A* 315 (2016) 59-66.
- [6] J. Park, K. Choi, J. Lee, C. Hwang, D. Choi, J. Lee, Fabrication and characterization of metal-doped TiO₂ nanofibers for photocatalytic reactions, *Mater. Lett.* 97 (2013) 64-66.
- [7] S. M. Adyani, M. Ghorbani, A comparative study of physicochemical and photocatalytic properties of visible light responsive Fe, Gd and P single and tri-doped TiO₂ nanomaterials, *J. Rare Earth. In Press* (2017) 1-15.

- [8] L. Lin, H. Wang, H. Luo, P. Xu, Enhanced photocatalysis using side-glowing optical fibers coated with Fe-doped TiO₂ nanocomposite thin films, *J. Photoch. Photobio. A* 307-308 (2015) 88-98.
- [9] L. M. Santos, W. A. Machado, M. D. França, K. A. Borges, R. M. Paniago, A. O. T. Patrocinio, A. E. H. Machado, Structural characterization of Ag-doped TiO₂ with enhanced photocatalytic activity, *RSC Adv.* 5 (2015) 103752-103759.
- [10] M. S. Hassan, T. Amna, O.-B. Yang, H.-C. Kim, M.-S. Khil, TiO₂ fibers doped with rare earth elements and their photocatalytic activity, *Ceram. Int.* 38 (2012) 5925-5930.
- [11] J. Reszczyńska, T. Grzyb, Z. Wei, M. Klein, E. Kowalska, B. Ohtani, A. Zaleska-Medynska, Photocatalytic activity and luminescence properties of RE³⁺-TiO₂ nanocrystals prepared by sol-gel and hydrothermal methods, *Appl. Catal. B-Environ.* 181 (2016) 825–837.
- [12] N. Haque, A. Hughes, S. Lim, C. Vernon, Rare earth elements: Overview of mining, mineralogy, uses, sustainability and environmental impact, *Resour.* 3 (2014) 614-635.
- [13] L. Matejová, K. Kocí, M. Reli, L. Capek, A. Hospodková, P. Peikertová, Z. Matej, L. Obalová, A. Wach, P. Kustrowski, A. Kotarba, Preparation, characterization and photocatalytic properties of cerium doped TiO₂: On the effect of Ce loading on the photocatalytic reduction of carbon dioxide, *Appl. Catal. B-Environ.* 152-153 (2014) 172-183.
- [14] J. Thomas, S. Radhika, M. Yoon, Nd³⁺-doped TiO₂ nanoparticles incorporated with heteropoly phosphotungstic acid: A novel solar photocatalyst for degradation of 4-chlorophenol in water, *J. Mol. Catal. A-Chem.* 411 (2016) 146-156.
- [15] H. Gao, B. Qiao, T.-J. Wang, D. Wang, Y. Jin, Cerium oxide coating of titanium dioxide pigment to decrease its photocatalytic activity, *Ind. Eng. Chem. Res.* 53 (2014) 189-197.
- [16] Y. Ono, H. Fujii, Low-temperature synthesis of cerium oxide nanorods and their suppressive effect on photocatalysis of titanium dioxide. *Ceram. Int.* 41 (2015) 15231-15234.
- [17] A. Bokare, M. Pai, A. A. Athawale, Surface modified Nd doped TiO₂ nanoparticles as photocatalysts in UV and solar light irradiation, *Sol. Energy* 91 (2013) 111-119.

- 1 [18] M. S. Beegam, S. B. Narendranath, P. Periyat, Tuning of selective solar photocatalysis by Mn^{2+}
2 decorated nanocrystalline mesoporous TiO_2 , *Sol. Energy* 158 (2017) 774-781.
- 3 [19] W. Zhou, Y. He, Ho/TiO_2 nanowires heterogeneous catalyst with enhanced photocatalytic
4 properties by hydrothermal synthesis method, *Chem. Eng. J.* 179 (2011) 412-416.
- 5 [20] H. Cai, X. Chen, Q. Li, B. He, Q. Tang, Enhanced photocatalytic activity from Gd. La codoped
6 TiO_2 nanotube array photocatalysts under visible-light irradiation, *Appl. Surf. Sci.* 284 (2013) 837-
7 842.
- 8 [21] M. Farrokhi, S-C. Hosseini, J-K. Yang, M. Shirzad-Siboni, Application of $\text{ZnO-Fe}_3\text{O}_4$
9 nanocomposite on the removal of azo dye from aqueous solutions: kinetics and equilibrium studies,
10 *Water Air. Soil. Pollut.* 225 (2014) 1-12.
- 11 [22] ISO, Water Quality: Determination of the Inhibitory Effect of Water Samples on the Light
12 Emission of *Vibrio fischeri* (Luminescent Bacteria Test), ISO 11348-1, 2 and 3, International
13 Standardization Organization, Geneva, Switzerland, 1998.
- 14 [23] C. Wang, Y. Ao, P. Wang, J. Hou, J. Qian, Preparation, characterization and photocatalytic
15 activity of the neodymium-doped TiO_2 hollow spheres, *Appl. Surf. Sci.* 257 (2010) 227-231.
- 16 [24] M. Meksi, H. Kochkar, G. Berhault, C. Guillard, Effect of cerium content and post-thermal
17 treatment on doped anisotropic TiO_2 nanomaterials and kinetic study of the photodegradation of
18 formic acid, *J. Mol. Catal. A-Chem.* 409 (2015) 162-170.
- 19 [25] K. Chen, S. Xie, E. Iglesia, A. T. Bell, Structure and properties of zirconia-supported
20 molybdenum oxide catalysts for oxidative dehydrogenation of propane, *J. Catal.* 189 (2000) 421-
21 430.
- 22 [26] H. Abdullah, M. R. Khan, M. Pudukudy, Z. Yaakob, N. A. Ismail, $\text{CeO}_2\text{-TiO}_2$ as a visible light
23 active catalyst for the photoreduction of CO_2 to methanol, *J. Rare Earth.* 33 (2015) 1155-1161.
- 24 [27] G. Xiao, J. Zhou, X. Huang, X. Liao, B. Shi, Facile synthesis of mesoporous sulfated Ce/TiO_2
25 nanofiber solid superacid with nanocrystalline frameworks by using collagen fibers as a biotemplate
26 and its application in esterification, *RSC Adv.* 4 (2014) 4010-4019.

- [28] B. Trujillo-Navarrete, M. P. Haro-Vázquez, R. M. Félix-Vavarro, F. Paraguay-Delgado, H. Alvarez-Huerta, S. Pérez-Sicairos, E. A. Reynoso-Soto, Effect of Nd³⁺ doping on structure, microstructure, lattice distortion and electronic properties of TiO₂ nanoparticles, *J. Rare Earth.* 35 (2017) 259-270.
- [29] L. P. D'Souza, R. Shwetharani, V. Amoli, C. A. N. Fernando, A. K. Sinha, R. G. Balakrishna, Photoexcitation of neodymium doped TiO₂ for improved performance in dye-sensitized solar cells, *Mater. Des.* 104 (2016) 346-354.
- [30] G. Magesh, B. Viswanathan, R. P. Viswanath, T. K. Varadarajan, Photocatalytic behavior of CeO₂-TiO₂ system for the degradation of methylene blue, *Indian J. Chem.* 48A (2009) 480-488.
- [31] N. Aman, P.K. Sataphathy, T. Mishra, M. Mahato, N.N. Das, Synthesis and photocatalytic activity of mesoporous cerium doped TiO₂ as visible light sensitive photocatalyst, *Mater. Res. Bull.* 47 (2012) 179-183.
- [32] D. Sun, K. Wang, Z. XU, R. LI, Synthesis and photocatalytic activity of sulfate modified Nd-doped TiO₂ under visible light irradiation, *J. Rare Earth* 33 (2015) 491-497.
- [33] N.R. Khalid, E. Ahmed, Z. Hong, M. Ahmad, Synthesis and photocatalytic properties of visible light responsive La/TiO₂-graphene composites, *Appl. Surf. Sci.* 263 (2012) 254-259.
- [34] Q. Wang, S. Xu, F. Shen, Preparation and characterization of TiO₂ photocatalysts co-doped with iron (III) and lanthanum for the degradation of organic pollutants, *Appl. Surf. Sci.* 257 (2011) 7671-7677.
- [35] D.J. Park, T. Sekino, S. Tsukuda, S-I. Tanaka, Synthesis of Sm-doped TiO₂ nanotubes and analysis of their methylene blue-removal properties under dark and UV-irradiated conditions 39 (2013) 1581-1591.
- [36] Q. Xiao, Z. Si, J.Zhang, C. Xiao, X. Tan, Photoinduced hydroxyl radical and photocatalytic activity of samarium-doped TiO₂ nanocrystalline, *J. Hazard. Mat.* 150 (2008) 62-67.

- [37] I. S. Grover, S. Singh, B. Pal, The preparation, surface structure, zeta potential, surface charge density and photocatalytic activity of TiO₂ nanostructures of different shapes, *Appl. Surf. Sci.* 280 (2013) 366-372.
- [38] N. Arjmandi, W. V. Roy, L. Lagae, G. Borghs, Measuring the electric charge and zeta potencial of nanometer-sized objects using pyramidal-shaped nanopores, *Anal. Chem.* 84 (2012) 8490- 8496.
- [39] C. Belver, J. Bedia, M. A. Álvarez-Montero, J. J. Rodriguez, Solar photocatalytic purification of water with Ce-doped TiO₂/clay heterostructures, *Catal. Today* 266 (2016) 36-45.
- [40] P. W. Koh, M. H. M. Hatta, S. T. Ong, L. Yuiati, S. L. Lee, Photocatalytic degradation of photosensitizing and non-photosensitizing dyes over chromium doped titania photocatalysts under visible light, *J. Photoch. Photobio. A* 323 (2017) 215-223.
- [41] A. Rapsomanikis, A. Apostolopoulou, E. Stathatos, P. Lianos, Cerium-modified TiO₂ nanocrystalline films for visible light photocatalytic activity, *J. Photoch. Photobio. A* 280 (2014) 46–53.
- [42] G. B. Vieira, H. J. José, M. Peterson, V. Z. Baldissarelli, P. Alvarez, R. F. P. M. Moreira, CeO₂/TiO₂ nanostructures enhance adsorption and photocatalytic degradation of organic compounds in aqueous suspension, *J. Photoch. Photobio. A* 353 (2018) 325-336.
- [43] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Herrmann, Photocatalytic degradation pathway of methylene blue in water, *Appl. Catal. B Environ.* 31 (2001), 145-157.
- [44] P. Dulian, W. Nachit, J. Jaglarz, P. Zięba, J. Kanak, W. Żukowski, Photocatalytic methylene blue degradation on multilayer transparent TiO₂ coatings, *Opt. Mater.* 90 (2019) 264-272.
- [45] S-K. Ray, D. Dhakal, Y. K. Kshetri, S. W. Lee, Cu- α -NiMoO₄ photocatalyst for degradation of Methylene blue with pathways and antibacterial performance, *J. Photochem. Photobio.* 348 (2017) 18-32.

- [46] C. H. Nguyen, C-C. Fu, R-S. Juang, Degradation of methylene blue and methyl orange by palladium-doped TiO₂ photocatalysis for water reuse: Efficiency and degradation pathways, J. Clean. Prod. 202 (2018) 413-427.
- [47] Z. Ma, L. Hu, X. Li, L. Deng, G. Fan, Y. He, A novel nano-sized MoS₂ decorated Bi₂O₃ heterojunction with enhanced photocatalytic performance for methylene blue and tetracycline degradation, Ceram. Int. 45 (2019) 15824-15833.
- [48] V. Gomez, A. M. Balu, J. C. Serrano-Ruiz, S. Irusta, D. D. Dionysioud, R. Luque, J. Santamaría, Microwave-assisted mild-temperature preparation of neodymium-doped titania for the improved photodegradation of water contaminants, Appl. Catal. A-Gen. 441-442 (2012) 47-53.
- [49] H. Liu, M. Wang, Y. Wang, Y. Liang, W. Cao, Y. Su, Ionic liquid-templated synthesis of mesoporous CeO₂-TiO₂ nanoparticles and their enhanced photocatalytic activities under UV or visible light, J. Photoch. Photobio. A 223 (2011) 157-164.
- [50] R. P. Barkul, M. K. Patil, S. M. Patil, V. S. Shevale, S. D. Delekar, Sunlight-assisted photocatalytic degradation of textile effluent and Rhodamine B by using doped TiO₂ nanoparticles, J. Photoch. Photobio. A 349 (2017) 138-147.