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Lanthanides Effects on TiO₂ Photocatalysts

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Abstract

Semiconductors have been evaluated to heterogeneous photocatalysis degradation of recalcitrant contaminants in aqueous media due to the capacity of mineralizing these compounds under UV or visible light irradiation. However, this process has the inherent feature of photogenerated charges recombination and the high bandgap energy of the electronic structure of some semiconductors that can reduce the formation of reactive oxygen species, which are responsible for the compound degradation. In this context, structural modifications in semiconductors have been proposed to enhance the photocatalytic activity, such as doping processes with elements that are capable of generating superficial defects that capture the formed electrons, avoiding the recombination, or increasing the density of -OH groups or water molecules on the surface of the catalyst, which can enhance the formation of hydroxyl radicals. Therefore, this brief review is proposed to show the role of lanthanides in the TiO₂ doping and the synthesis method applied, as well as the results discussed in the literature.

Keywords: photocatalyst, lanthanides, TiO₂, doping, optical properties

1. Introduction

Photocatalysis applied in gas or aqueous media involves the reactive oxygen species (ROS) formation, mainly hydroxyl radical ($\bullet\text{OH}$), superoxide ($\bullet\text{O}_2^-$), and singlet oxygen ($^1\text{O}_2$), which are generated by the oxidation of water molecules or capture of electrons by oxygen.

These species are very effective oxidant agents, and they are capable of degrading recalcitrant compounds due to the high potential of oxidation. These ROS are produced on the semiconductors' surface, such as titanium dioxide (TiO_2), which is considered the most promising material because it is inexpensive, nontoxic, chemically and thermally stable, abundant, and environmentally friendly. However, this semiconductor only will produce these species when it receives a minimum energy amount, called the bandgap energy (E_g), which is capable to remove an electron from the valence band (VB) and transfer it to the conduction band (CB), thus creating the electron-hole pair. For TiO_2 , this minimum energy is supplied by photons with frequency in the ultraviolet light region, which possess wavelengths below 400 nm [1–6].

Despite the ability of photocatalytic processes to degrade several compounds by the use of hydroxyl radicals, their use is still not widespread, with scarce industrial applications. This is due to some inherent features of the catalysts employed, such as the recombination of photo-generated charges, which reduces the formation of radicals and, consequently, the efficiency of photocatalytic degradation. Therefore, plenty of studies have been performed to overcome this drawback, like surface modifications that allow the capture of the generated electrons and avoid the recombination. Furthermore, the bandgap energy required for the formation of the electron/vacancy pair, which for TiO_2 is equal to 3.2 eV, restricts this catalyst to the use of a light source that has wavelengths in the ultraviolet region (≈ 390 nm). Therefore, only 5% of sunlight can be used in photocatalysis that applies this semiconductor, which makes the process more expensive. In this way, superficial modification through metal and nonmetal doping is fundamental to overcome these drawbacks [7–10].

Among the possible dopants, rare earths have been investigated for their ability to increase photocatalytic activity, possibly by reducing bandgap energy due to the introduction of orbitals between the conduction and valence bands, generating impurity energy levels in the semiconductor elements. These states are generated from the 4f level, which are electron deficient. Another hypothesis for this increase in contaminant degradability is that the adsorption of these lanthanides on the surface of the semiconductors generates an imbalance of surface charges, which can produce surface defects and vacancies of oxygen and titanium. These two propositions lead to states that serve as electron scavengers and reduce the recombination of photogenerated charges, increasing the probability of $\bullet\text{OH}$ formation. Moreover, the lanthanides adsorbed on the surface may act as traps to water molecule and $-\text{OH}$ (hydroxyl anion) groups, which increase their density on the photocatalyst surface and can promote more intense formation of hydroxyl radicals. Another important feature related to the use of these compounds is that they serve as a Lewis base, which could concentrate the contaminants dispersed in aqueous medium on the semiconductor surface enhancing the electron transfer for the direct degradation of the contaminant or increasing the probability of interaction between the molecules and the radicals formed [11–15].

The mechanisms of lanthanides doping on TiO_2 proposed by different researchers have not been the same, with two ways most discussed. Rare earths can be included in the TiO_2 lattice by direct linking or substitution producing $\text{a}\equiv\text{Ti}-\text{O}-\text{Ln}-\text{O}-\text{Ti}\equiv$ arrangement, which cause distortions/defects in the lattice due to the mismatch of ionic radius of Ln^{3+} and Ti^{4+} . On the

other hand, some doping methods do not supply enough energy to promote the ions substitution in the lattice, and the lanthanides are located in the TiO₂ surface or boundaries of the semiconductor particles, creating Ti–O–Ln bonds [16–20].

Different methods are currently used for doping, like solvothermal, microemulsion, electrospinning, cathodic sputtering, hydrothermal, microwave, sonochemical, and sol–gel, which is the most usual process. However, these methods usually employ reactants such as tetrabutoxide and titanium isopropoxide, which are aggressive to the environment, besides using severe conditions of temperature and pressure. Therefore, the methodology using ultrasound appears as an alternative to avoid the application of secondary reactants and extreme conditions [21–25].

Lanthanides have particular features when compared with other metal oxides dopants, because they inhibit the transition from the anatase phase to the rutile phase, reduce the crystalline size, can easily react with the functional groups of Lewis bases to mineralize organic compounds, and bring luminescent properties to the titanium dioxide [19, 26, 27].

Thus, titanium dioxide doped with lanthanides, which avoid the recombination mechanisms, has been studied in the sense of optimizing the capacity of radical formation due to the increased numbers of defects and oxygen vacancies on the surface of the lattice to trap e⁻/h⁺ pairs and reduce the recombination, besides that increase the density of –OH groups or water molecules attached to the surface of the catalyst. However, the excess of these dopants reduces the photocatalytic capacity of the semiconductor, possibly due to the excess of vacancies generated, which act as recombination centers instead of electrons scavenger [28–30].

2. TiO₂

The crystalline structures of titanium dioxide are anatase, rutile, and brookite, which is difficult to be synthesized in laboratory. Therefore, the first two lattices are the most prominent in researches. All crystal lattices are composed of TiO₆ octahedra, but with distinct connections between these structures, since anatase has four connections between the edges, brookite has three connections, and rutile has only two. This structure confers to rutile a greater thermodynamic stability among the other polymorphs, as established by the third Pauling rule [31–33].

There is a great interest in the application of titanium dioxide as a photocatalyst because this compound is nontoxic, economical, chemically inert, and photostable to corrosion, besides high thermal stability, intense photocatalytic activity, and strong oxidant power. However, not all crystalline structures have the same efficiency in the absorption of light for catalysis; for example, although rutile is the polymorph thermodynamically more stable, its photocatalytic activity is lower than anatase, possibly due to the high temperature required for its preparation, which causes an increase in particle size, a high rate of electron/vacancy recombination that reduces the number of hydroxyl groups on the surface, and lower electron mobility in relation to anatase [34–37].

However, the rutile phase has a bandgap equal to 3.0 eV, having the ability to absorb radiation in the visible light spectrum, while the anatase has a bandgap of approximately 3.2 eV. Therefore, the interaction of these two crystalline structures often has better photocatalytic results than when they are purely applied, which is possibly due to the visible light absorption by the rutile, which serves as a photosensitizer for the anatase phase. An example of this phase interaction is the commercial P25® titanium dioxide from Degussa Evonik, which has a composition of 80% anatase and 20% rutile, exhibiting high photocatalytic activity [32, 38, 39].

Regarding to the electronic structure, this catalyst can be considered a semiconductor with indirect bandgap for anatase phase, meaning that the valence and conduction bands of this lattice do not have the same maximum and minimum momentum, respectively. This condition leads to a recombination of the electron/vacancy pair that only occurs if assisted by a phonon, resulting in a longer lifetime of this electron generated. Furthermore, TiO_2 is an n-type semiconductor; in other words it has a greater density of electrons than vacancies produced by oxygen, because they are compensated by the presence of Ti^{3+} , which brings the Fermi level closer to the conduction band [40–42].

Bandgap energy for the structure with the highest photocatalytic activity is approximately 3.2 eV, and the valence band, formed mainly by the 2p orbital of the oxygen, has an energy level of approximately 2.60 V, which is more positive than the oxidation potential of water to hydroxyl radicals ($E_0 = 2.27$ V). In the case of the conduction band, which is constituted mainly by titanium 3d orbitals, the energy level is equal to -0.51 V, with a value that is negatively greater than the oxygen reduction potential of the superoxide radical ($E_0 = -0.33$ V). As depicted in **Figure 1**, with these conditions titanium dioxide can degrade organic compounds through activation by UV light, which makes it a prominent catalyst [13, 32, 43–45].

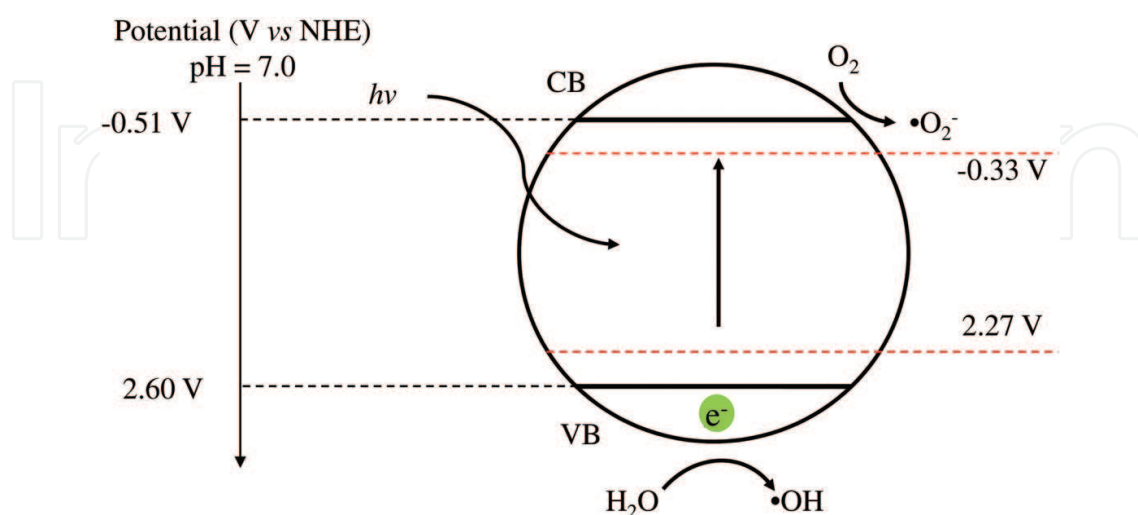


Figure 1. Redox potential of conduction and valence bands and the radical formation.

3. Lanthanides

The rare earths (RE) are a group of elements with physicochemical properties that are very similar, which is constituted by lanthanides (lanthanum to lutetium), scandium, and yttrium, totalizing 17 elements of the periodic table. This series can be separated into light rare earths that comprise low atomic mass elements (lanthanum to europium) and heavy rare earths, which are constituted from lutetium to gadolinium, besides yttrium [19, 46].

These elements have shown great potential for industrial applications because of their unique magnetic, optical, and/or redox properties, with important uses in the field of catalysis, high temperature superconductors, hybrid cars, permanent magnets, nuclear magnetic resonance, rechargeable batteries, manufacture of glass and ceramic materials, shift reagents, etc. The electronic configuration of these chemical elements assure these properties due to the distribution of the electrons with the complete levels until 5, such as xenon, but with the level *f*, it was incomplete and protected by orbitals 6 *s* and/or 5*d*, except for of the scandium and yttrium. Thus, the representation of the electronic configuration is described as [Xe] 4f^{*n*}6s² or [Xe] 4f^{*n*}5d¹6s² for lanthanides (Ln), which usually have an oxidation state equal to 3+ (Ln³⁺) [47–51].

The orbitals 4*f* that were partially completed are responsible for the optical properties of rare earths, since different arrangements of these orbitals generate different levels of energy, allowing the absorption in a broad spectrum of light radiation, which can vary from ultraviolet to visible. Moreover, the luminescence of some rare earth ions arises from the *f-f* electronic transitions within their partially filled 4*f* orbitals that can occur by electric or magnetic dipole [52, 53].

Another advantage of this configuration is that these orbitals are sterically shielded from the surrounding microenvironment by the filled 5*s* and 5*p* orbitals, meaning that there are almost no perturbations of these transitions by other bonding elements, which assure that the optical properties do not undergo sudden changes [48, 54, 55].

4. Surface modification by lanthanides

The surface modification of semiconductors that occurs by the addition of tiny and controlled impurities is denominated doping, and this process is applied to achieve distinct electronic properties from those raw materials. Metal doping has a main feature, the bandgap reduction, which optimizes the ability of a semiconductor to absorb wavelengths with less energy, reduce recombination of the vacancy/electron pairs, and modify the adsorptive capacity of the surface of this photocatalyst. Bandgap reduction occurs possibly due to the formation of energy levels between the conduction and valence bands, such as when transition metals are used, because these incorporate levels 3*d* in the TiO₂ lattice, which leads to the formation of electronic levels occupied near to the conduction band. However, visible light absorption by

semiconductor doped with noble metals, such as gold and silver, may be associated with the surface resonance effect of Plasmon, which is described as an oscillation of the electrons on the surface of these metals, which cause a separation of charge carriers [13, 44, 56].

Another advantage of metal doping is the decrease in photogenerated charges recombination, which is due to the Schottky barrier formation in the interface of semiconductor and metal. The electrons formed migrate, and they are captured by the metal particles, which become active sites for oxygen reduction. This barrier is formed by the electronic binding between the lanthanides and titanium dioxide, allowing the mobility of electrons formed in the semiconductor valence band to the metal, until equilibrium occurs between the Fermi levels [57, 58].

The rare earths when applied in TiO_2 doping have shown one or both features above discussed, mainly due to the presence of incomplete 4f levels, surface defects, and oxygen vacancies. The first ones reduce the TiO_2 bandgap due to the appearance of orbitals between the conduction and valence bands, which generates impure energy levels. This reduction provides an electron transfer from VB until the orbital created and/or from this to the CB requires less energy. In addition, these orbitals *f* have the ability to produce complexes with several Lewis bases, increasing the concentration of these species on the surface of the catalyst and, consequently, the photocatalytic activity. Moreover, these orbitals have the ability to trap the photogenerated electrons due to their incomplete levels, which avoids the recombination of the charge carriers [11–15].

Another advantage of lanthanides is the ability of some ions of these elements (Ln^{3+}) to generate surface defects and titanium and oxygen vacancies. This occurs possibly because some lanthanides ions have an atomic radius higher than Ti^{4+} (0.68 Å), such as La^{3+} (1.15 Å) and Sm^{3+} (1.24 Å). In these cases, Ln^{3+} is not able to replace the titanium ions in the semiconductor lattice, and these ions only are adsorbed on the surface, forming Ti-O-Ln^{3+} bonds. This fact leads to an imbalance in the surface charges of the TiO_2 crystal structure. Since titanium atom has a Pauling electronegativity value (1.54) higher than those presented by lanthanum (1.10) and samarium atoms (1.17), a transfer of electrons occur from these lanthanides to the titanium, which is converted from Ti^{4+} to Ti^{3+} . The excess of negative charge disturbs the electronegativity, and it is necessary remove an ion of O^{2-} for every two Ti^{3+} ions produced, which causes the formation of oxygen and titanium vacancies, generating a surface defect. Furthermore, the presence of lanthanides, dispersed as interstitial impurities on the TiO_2 lattice causes surface defects. The presence of these vacancies and defects causes the capture of electrons produced on the surface of the photocatalyst and decreases the recombination of photogenerated charge carriers. However, an excess of lanthanides on the photocatalyst surface can lead to a high density of defects and vacancies, which creates recombination centers [30, 59–64].

Rare earth application as dopant also can increase the surface area of the catalyst because it reduces the growth of the crystal structure. Besides, these elements can increase the thermal stability, since they interfere in the conversion of the anatase phase to rutile during the calcination of the doped semiconductors [12, 25, 65].

Lanthanides have been applied as TiO_2 dopants in many researches, highlighting yttrium, cerium, neodymium, praseodymium, europium, samarium, and lanthanum, with promising

photocatalytic activity responses, such as studies performed by Liu et al. [66] which evaluated the cerium doping on titanium dioxide using chemical coprecipitation method, with molar ratio from 0.5 to 2.5% of cerium in relation to the semiconductor to evaluate the degradation of methylene blue 2,3-dichlorophenol and benzene, under visible and UV light. The best results occur when the RE concentration was equal to 0.50% (mol•mol⁻¹). Xue et al. [67] evaluated the effects of cerium doping into TiO₂ nanotubes by chemical impregnation and ultrasound. The molar ratio applied was 0.1–1.0% of the lanthanide in relation to the semiconductor, with subsequent calcination of all samples at 673 K. The results obtained in the degradation of glyphosate under UV light showed that the molar ratio equal 0.15% optimizes the photocatalysis.

Cerium doping was also recently evaluated by Pei et al. [68] in the titanium dioxide nanorods formation. The inclusion of cerium in the semiconductor occurred by hydrothermal method. The inclusion of this element changed the semiconductor wavelength absorption to 480 nm, with bandgap energy equal to 2.65 eV, meaning that photocatalysis can occur in visible light.

Neodymium (Nd) has attracted interest as a semiconductor dopant because of its ability to absorb and emit wavelengths in the range from UV to IR radiation, besides the usual features of RE, such as discussed above. Du et al. [69] used this element in the titanium dioxide film doping by sol–gel method. In this research, the photocatalytic effects of the mass ratios of neodymium (0.1 and 0.9%) after calcination at 823 K for 2 h were evaluated. The obtained films were used in the degradation of methylene blue under UV light, with efficiency upper of 92% in the removal of this dye when using a mass ratio of 0.10%. Possibly, this increment occurs due to a reduction in bandgap energy, since analysis showed an increase in the visible light wavelengths absorption by the doped semiconductor. Another important research was done by Thomas et al. [70] who applied molar ratios equal to 0.30, 0.50, and 0.70% of neodymium to doping titanium dioxide via sol-gel method. It evaluated the insertion of a third component, phosphotungstic acid, in the degradation of methylene blue and 4-chlorophenol under visible light. The results obtained showed an increase in the degradation in relation to the pure semiconductor, with the best result when the molar ratio was equal to 0.50%.

Another element evaluated for titanium dioxide doping is praseodymium, classified as a light rare earth with molar mass equal to 140.9 g•mol⁻¹. Liang et al. [71] evaluated the degradation of the reactive yellow dye 4 under UV and visible radiation using TiO₂ doped with different ionic ratios of praseodymium (0.50–1.80%), which was included in the crystal lattice by sol–gel method, with calcination at 773 K for 2 h. The photodegradation results demonstrated that Ln³⁺:TiO₂ equal to 1.0 and 1.5% optimizes the photocatalytic capacity of the semiconductor in degrading the contaminant under UV and visible light, respectively. This increase in the catalytic activity of praseodymium doped semiconductors was also confirmed according to research published by Kralova et al. [72], which demonstrated that titanium dioxide doped with 0.3 mol% of praseodymium at different temperatures (723, 823 and 923 K) and calcination times (4, 8 and 12 h) promotes a reduction in bandgap energy (from 3.20 to 3.14 eV) when the photocatalyst was calcined at 723 K for 8 h. The efficiency increase in the degradation of an organochlorine pesticide under UV light (LED) possibly is related to milder temperatures joined with intermediate times, which ensure a diffusion of the lanthanide without changes in the crystalline phase.

The studies performed by Leal et al. [73] are prominent due to the extensive evaluation about lanthanides doping of TiO_2 lattices. The light lanthanide series (La-Eu), besides gadolinium, were evaluated for the degradation of orange and violet methyl by UV light. The pH values (3.1 and 5.6) and the mass fraction of $\text{Ln}^{3+}:\text{TiO}_2$ (0.1 and 0.3%) were used as parameters for the experiments, with semiconductor doping by the sol-gel method and calcination at 773 K for 2 h. The results showed an increase (approximately 37%) in the degradation of the compounds when the doped semiconductors were applied instead of pure TiO_2 . Therefore, this research provides an overview of the potential application of these lanthanides to degrade different compounds under different process conditions.

Reszcyńska et al. [74] also evaluated the effects of the application of yttrium, praseodymium, erbium, and europium in the photodegradation efficiency of phenol, under visible and UV light. Furthermore, hydrothermal and sol-gel methods for semiconductor doping were compared in relation to photocatalytic activity response. It used the molar ratios of 0.25 and 0.50% of Ln^{3+} in relation to titanium dioxide. The results showed an increase in phenol degradation under visible light for doped photocatalysts when compared to pure TiO_2 . When UV light was applied as radiation source only, the hydrothermal process showed better results than the pure semiconductor. However, if the decomposition efficiencies of the contaminant are compared, it is remarkable that the hydrothermal process overcomes the sol-gel method in most cases. This possibly is related to the high surface area, low crystallite dimensions, and higher density of $-\text{OH}$ obtained in the first method employed. In addition, the lower concentration of rare earths in doping showed the best degradation results of the molecule evaluated.

Lanthanum (La) doping has an extensive discussion about the mechanisms, which are well-known. However, different methods, as well as the optimized rare earth amount for each of these methods, are still evaluated, without being exhausted. Among the researches carried out, Li et al. [75] evaluated different amounts (0–0.50%) of lanthanum in the TiO_2 doping, which are impregnated in the semiconductor by sol-gel method, with subsequent calcination (973–1173 K). The best response in methyl orange photodegradation occurred when the concentration of lanthanum was 0.05% with a calcination temperature at 973 K.

Jun et al. [76] analyzed the photocatalytic activity of TiO_2 doped with different concentrations of lanthanum (from 0 to 0.90% $\text{w}\cdot\text{w}^{-1}$) by sol-gel method followed by calcination at 823 K for 2 h. The results showed that mass ratio 0.30% (0.17% $\text{mol}\cdot\text{mol}^{-1}$) demonstrated the best results in methylene blue removal. It was proposed that the increase in photocatalytic efficiency is due to the formation of vacancies and defects from the presence of lanthanide on the TiO_2 surface. It was also possible to verify that an increase in lanthanum concentration causes a reduction in photocatalytic efficiency, possibly because La serves as a mediator in the interfacial charge transfer or as a recombination center.

Samarium (Sm) has been used to doping semiconductors because its presence causes significant improvements in the degradation of compounds, which leads the semiconductors to absorb wavelengths in the visible light spectrum, besides low cost of the compound when compared with others lanthanides. Tang et al. [77] doped titanium dioxide with different concentrations of samarium (0–2.16% $\text{mol}\cdot\text{mol}^{-1}$) by the sol-gel method followed by different calcination temperatures (623–1123 K). The pollutants evaluated were methanol and acetone,

with best results when the lowest concentrations of samarium (0.30 and 0.43%) were applied. The photocatalytic degradations achieved results of upper 90% when applied by UV light, which demonstrates that an increase in the amount of rare earths can lead these photocatalysts from electron traps to recombination centers.

Xiao et al. [78] demonstrated that methylene blue degradation under UV light showed best responses when the lowest samarium molar ratio was applied (0.50%). The sol-gel method was used for the inclusion of Sm in the TiO₂ lattice, and the samples were calcined for 2 h at 873 K.

4.1. Calcination temperature effects

Calcination is a vital step for doping, since it allows the activation and/or fixation of the dopant in the semiconductor crystal structure, besides the removal of impurities and the increase in the density of vacancies due to the removal of oxygen from the photocatalyst lattice, in addition to promoting an increase in crystallization. However, an excessive increase in the calcination temperature can lead to a particle aggregation and, consequently, reduction of the surface area, besides the conversion of the anatase phase to rutile, which can affect the photocatalytic activity. Therefore, the calcination temperature control is essential to assure high photocatalytic activity [75, 79–81].

Usually anatase to rutile phase transformation occurs at temperatures between 500 and 750°C, as soon as there is an increase in the crystalline size of anatase when the calcination temperature enhances. However, the lanthanides doping shift the phase transformation to higher temperatures (above 700°C) and suppress the anatase crystalline growth between 500 and 700°C [82–86].

Chen et al. [87] evaluated the effect of rare earth doping (0.20, 0.50, 1.0, and 2.0% mol) by hydrothermal method and the calcination temperature (673, 773, 873 and 1073 K). The results obtained showed that the best photocatalytic activity was achieved when the temperature of calcination was 773 K for 2 h, with a crystallite size equal to 15 nm. It was possible to verify that an increase of the temperature reduces the surface area of the crystal structures formed.

Cruz et al. [88] published a research about titanium dioxide doped with samarium via sol-gel method, in which the photocatalytic degradation of a herbicide under UV light was investigated. The parameters evaluated were the calcination temperature and the samarium concentration, with the best efficiency in herbicide degradation when the samples were calcined at 773 K for 4 h. Similar results were obtained by Yang et al. [76], which showed that the degradation of the methylene blue by TiO₂ doped with neodymium and fluorine via sol-gel method was optimized when the temperature and time of calcination were equal to 773 K and 3 h, respectively.

Li et al. [89] also evaluate the effect of temperature on the photocatalytic activity of titanium dioxide doped with europium via hydrothermal method. It used calcination temperatures between 573 and 1173 K. The temperature at 773 K, with a calcination time of 4 h, improves the degradability of the contaminant, probably because of the increase in crystallization and reduction of defects, which improve the ability to absorb visible light wavelengths.

5. Conclusion

The degradation of recalcitrant compounds using semiconductors doped with lanthanides, in aqueous media, is a promising area due to the increasing incidence of these compounds in water media due to the inefficiency of current processes in eliminating such molecules. Doping semiconductors with lanthanides has been an efficient strategy to generate defects in the surfaces of the materials. These defects act as active sites that capture the electrons and prevent recombination events or increase the density of hydroxyl groups and increase the amount of water molecules bound on the surface of photocatalytic materials. All these mechanisms increase the efficiency of the photodegradation processes. However, the excess of these dopants reduces the photocatalytic capacity of the semiconductor, possibly due to the excess of vacancies generated, which act as recombination centers instead of electrons scavenger.

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Conflict of interest

There are no conflicts to declare.

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