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Photocatalytic properties of WO_3 nanoparticles obtained by precipitation in presence of urea as complexing agent

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WO₃ nanoparticles were synthesized by a precipitation method in presence of urea at different calcination temperatures. The characterization of the WO₃ samples was carried out by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), adsorption–desorption N₂ isotherms (BET), and diffuse reflectance spectroscopy (DRS). During the precipitation process, the presence of urea led to the formation of WO₃ nanoparticles with rectangular and ovoid shapes as a function of calcination temperature. The photocatalytic activity of WO₃ samples was evaluated in the degradation of rhodamine B (rhB), indigo carmine (IC) and congo red (CR) molecules in aqueous solution under UV and visible-light radiation. The best results were obtained with the sample synthesized at 500 °C due to a contribution of factors such as morphology, surface area and the degree of aggregation of their particles. The photocatalytic activity for the degradation degrees after 96 h of irradiation were 29% for rhB and 86% for IC.

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1. Introduction

Heterogeneous photocatalysis has proved to be a useful tool for the degradation of water pollutants over the last years. As such, it is been recognized as a green technology for the treatment of all kinds of contaminants, especially for the removal of organic dyes with complex molecular structure, which are usually present in wastewater from the textile industry [1]. This type of industry consumes large amounts of different dyes, which are lost in quantities of up to 15% during the dyeing process and disposed of in the textile effluents, leading to a substantial contamination of water [2]. Organic dyes found in textile effluents are a serious ecological problem, since even a small amount of them in water can cause a significant coloring and they can be toxic to aquatic as well as human life [3]. Hence, their removal from wastewater is of fundamental importance for the environment [4].

The high photocatalytic activity under UV radiation, low cost, and stability to corrosion processes of the anatase polymorph of TiO₂ has positioned this material as the photocatalyst par excellence for commercial applications [5]. However, its relative wide energy band gap (E_g) of 3.2 eV limits further applications of the material in the visible-light region (λ > 390 nm). In the search of semiconductor materials with photocatalytic activity under

visible-light irradiation, important efforts have been carried out in the last decade. For example, the TiO_2 anatase polymorph has been doped with nitrogen in order to increase its absorption in the visible range [6]. In another approach, several authors have proposed alternative oxides than traditional TiO_2 with high photocatalytic activity under visible-light irradiation such as $In_{1-x}Ni_xTaO_4$ [7], $CaIn_2O_4$ [8], $InVO_4$ [9], and $BiVO_4$ [10].

In view of the economical use of visible-light radiation and because of its predominance in the solar spectrum, the development of photocatalysts with high activity under visible-light radiation is desirable. In this sense, tungsten trioxide (WO₃) is a visible-light responsive photocatalyst that absorbs radiation in the region up to 480 nm [11], which makes it an attractive candidate for photocatalytic applications. Additionally, WO₃ is a material with high stability in aqueous solution under acidic conditions, and it is an inexpensive material with an E_g between 2.4 and 2.8 eV [12–14].

The WO₃ oxide has already been tested as a photocatalyst for the degradation of the azo dyes acid orange 7 and direct blue 1 [15]. Furthermore, composite nanoparticles of WO₃/TiO₂ were employed as a photocatalyst in order to degrade methylene blue [16]. Although WO₃ can act as a photocatalyst in the degradation processes of the organic dyes cited above, this oxide has received little attention when it comes to the purification of water polluted with organic dyes.

Recently, we reported the photocatalytic activity of WO_3 nanoparticles synthesized by simple precipitation method in the degradation processes of rhodamine B (rhB), indigo carmine (IC)

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Fig. 1. Molecular structure of: (a) rhodamine B, (b) indigo carmine and (c) congo red.

and congo red (CR) [17]. Given that photocatalytic activity of the samples was closely related with the morphology they presented, in this work we proposed a method to modify the morphology of WO₃ nanoparticles obtained by precipitation. In this case, the influence of urea when is used as additive during the precipitation process was revised. In the same way, the formation of •OH radicals was determined when an aqueous dispersion of WO₃ oxide was exposed to UV–vis light radiation.

2. Experimental

2.1. Synthesis of samples

WO₃ nanoparticles were synthesized by precipitation method in the presence of urea. For this purpose, 0.00107 mol of ammonium tungstate hydrate (H₄₂N₁₀O₄₂W₁₂·xH₂O) were dissolved by magnetic stirring at 80 °C in 100 mL of a nitric acid solution (10% v/v, HNO₃). Then 0.0646 mol of urea (NH₂CONH₂) were added to the solution under continuous stirring and maintaining a constant temperature until the formation of a yellow-green solid precipitated. This material was used as a precursor for the WO₃ nanoparticles. The precursor obtained was decomposed by thermal treatments at 450, 500 and 600 °C (heating rate 10 °C min⁻¹) during different periods of time in order to obtain the monoclinic crystalline structure of the WO₃ oxide. These samples will be identified hereafter as W450, W500 and W600, respectively. For comparative purposes, WO3 nanoparticles were obtained by the same experimental procedure but without the addition of urea. This reference sample will be identified as WR400.

2.2. Characterization of samples

Structural characterization of the WO₃ samples was carried out by powder X-ray powder diffraction using a Bruker D8 advanced diffractometer with CuK α radiation (λ = 1.5418 Å) coupled with a Vantec high speed detector and Ni filters. X-ray diffraction data of the samples was collected in the 2 θ range of 10–70° with a scan rate of 0.05° s⁻¹. The morphology and particle size of the prepared WO₃ samples were investigated by scanning electron microscopy (FEI Nova 200 NanoSEM) and transmission electron microscopy (JEOL 2010 instrument with an accelerating voltage of 200 kV). UV–vis diffuse reflectance absorption spectrums of the samples were obtained by using a UV–vis spectrophotometer (PerkinElmer Lambda 35) equipped with an integrating sphere and by using BaTiO₃ as reference. The E_g value was determined with the following relationship:

$$\alpha = \frac{A(h\nu - E_{\rm g})^n}{h\nu} \tag{1}$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g the energy band gap, A and n are constants, and n has a value of n = 1/2 for materials with direct transition. To calculate the E_g from the UV–vis spectrum, a straight line was extrapolated following the slope of the line to the x-axis, where $\alpha = 0$, and, consequently, $E_g = h\nu$. The Brunauer–Emmett–Teller (BET) surface area of the photocatalysts was determined by adsorption–desorption N₂ isotherms by means of a Micromeritics Tristar 3000 surface area and pore size analyzer. The isotherms were evaluated at $-196 \,^{\circ}$ C after a pretreatment of the sample at 100 $^{\circ}$ C during 2 h.

2.3. Photocatalytic experiments

The photochemical reactor employed was a homemade device consisting of a borosilicate glass beaker embedded in a water jacket to maintain the reaction temperature at 25 ± 1 °C. A Xe lamp of 10,000 K with a luminous flux of 2100 lm was used as the visible-light source. The emission spectrum of the Xe lamp was measured on a UV–vis spectrophotometer. After filtration by the borosilicate container, a contribution of UV radiation ($\lambda > 315$ nm) with an intensity of 1380 µW cm⁻² was still observed. Additionally, some experiments were also performed with a UV source of 365 nm. In order to have comparative results, a UV lamp with a radiation intensity of 1250 µW cm⁻² was selected for these specific experiments.

The photocatalytic activity of WO₃ nanoparticles was evaluated in the reaction of degradation of rhodamine B (rhB, CAS 81-88-9), indigo carmine (IC, CAS 860-22-0), and congo red (CR, CAS 573-58-0) in aqueous solution. The molecular structure of these organic dyes is showed in Fig. 1. In a glass beaker, 220 mL of an organic dye solution containing 220 mg of photocatalyst were put in an ultrasonic bath to eliminate aggregates. By considering the molar extinction coefficient of each dye, the initial concentrations were determined to be 5, 30 and 20 mg L^{-1} , respectively. In order to ensure that the adsorption-desorption equilibrium of the dye on the catalyst surface had been reached, the solution was kept in the dark for 1 h. After this time, the light source was turned on. During the reaction, samples were taken from the reactor at different time intervals and then analyzed following the procedures established in a previous work [18]. The dye mineralization degree was monitored by analyzing the total organic carbon content (TOC) in



Fig. 2. XRD patterns of WO_3 powders obtained at different calcinations temperatures.

the solutions with different irradiation times. Performing a typical experiment, 200 mL of the corresponding dye solution (50 mg L^{-1} for rhB and 100 mg L⁻¹ for IC) containing 200 mg of photocatalyst were employed. The irradiated samples were analyzed in a Shimadzu VSCN8 TOC analyzer.

The generation of •OH radicals during the photocatalytic reaction was investigated by the photoluminescence method. Terephthalic acid was used to readily react with •OH to form highly fluorescent product, 2-hydroxyterephthalic acid, which can be detected by fluorescence spectrum (excitation wavelength: 312 nm, fluorescence peak: 426 nm) [19]. For this purpose, 220 mg of photocatalyst were dispersed in a solution formed by terephthalic acid ($5 \times 10^{-4} \text{ mol L}^{-1}$) and NaOH ($2 \times 10^{-3} \text{ mol L}^{-1}$). The dispersion formed was irradiated for different amounts of time. From the fluorescence intensity, the amount of •OH radical could be estimated. The •OH-trapping photoluminescence spectrums were performed in a PerkinElmer precisely LS 55 luminescence spectrophotometer.

3. Results and discussions

3.1. Characterization of samples

The powder used as a precursor to obtain the WO₃ samples presented a greenish tinge. The crystalline structure of WO₃ was found to form starting at 450 °C, below this temperature the material was amorphous without diffraction lines. The X-ray diffraction patterns of the W450, W500 and W600 samples obtained by thermal treatments are shown in Fig. 2. For the three samples, all diffraction lines were correctly assigned to the monoclinic polymorph of WO₃ according to the JCPDS Card No. 01-083-0950. On the other hand, as shown in Fig. 2, in absence of urea the crystalline structure of WO₃ is formed by a thermal treatment at temperatures as low as 400 °C (WR-400). This indicates that the presence of urea during Table 1

Physical properties of the WO_3 samples synthesized under different experimental conditions.

WO ₃ sample	$E_{\rm g}~({\rm eV})$	BET surface area (m ² g ⁻¹)
WR400	2.59	16.45
W450	2.68	10.43
W500	2.67	6.10
W600	2.65	3.15
Commercial	2.62	3.32

the precipitation process seems to slow down the crystallization process.

A study of the morphology and particle size of WO₃ nanoparticles was performed by SEM and TEM analyses. Fig. 3 shows selected TEM micrographs of WO₃ synthesized at different calcination temperatures. In the first case, the morphology of the particles of the W450 sample was characterized by rectangular and oval shapes with variable sizes ranging from 10 to 50 nm, as showed in Fig. 3a. A similar morphology and particle size was observed for the W500 sample, but with a predominance of the oval particles over the rectangular ones (Fig. 3b). This behavior was accentuated for W600, where only ovoid particles were present. These particles presented a major thickness, compared with the previously observed at lower temperatures, as shown in Fig. 3c. The ovoid morphology of the WO₃ nanoparticles can be associated with the presence of the organic additive during the precipitation process. A TEM analysis for the WR400 sample revealed a material with a high heterogeneity in the shape of its particles, which exhibited morphologies of square and rectangular plates, see Fig. 3d. As the calcination temperature was increased for WR400, i.e. 500 and 600 °C, the morphology of the nanoparticles shifted towards a prevalence of the rectangular plate shape [17]. This situation confirms the effect of urea in the morphology of the samples. For comparative purposes, Fig. 3e shows a TEM micrograph of a WO₃ commercial sample (99.9%, Aldrich) where bigger particles with a size of approximately 100 nm are observed. The morphology of the commercial sample resembles the shape of the particles obtained by precipitation with urea in this work.

Fig. 4 shows the detailed SEM micrograph of the W450, W500 and W600 samples. Here, is possible to appreciate that the morphology of the particles in these samples consisted of large agglomerates of the smaller size particles observed by the TEM technique, as shown in Fig. 4a–c. In general, a natural tendency to form larger agglomerates of particles was observed at lower temperatures. Fig. 4d and e shows that the particles of WR400 and commercial oxides have the tendency to form even larger agglomerates. This is relevant because, under our experimental conditions, a good material dispersion in aqueous solution allows a major area of material exposed to the radiation lamp.

Table 1 shows the corresponding energy band gap values of the samples obtained, which are found to agree with the previously reported for WO₃ [12]. The BET surface area of WO₃ samples is reported also in Table 1. It was found that when the calcination temperature of the samples increases, the BET surface area decreased, as was expected due to the sinterization of the samples at higher temperatures. In this case, the WR400 reference sample showed the highest surface area value.

3.2. Photocatalytic activity

The photocatalytic activity of the WO₃ nanoparticles was evaluated for the degradation of rhB, IC and CR molecules in aqueous solution under Xe lamp radiation. Fig. 5 shows the data corresponding to the temporal degradation of rhB when the different synthesized WO₃ samples were used as photocatalysts. All the WO₃ samples tested were able to bleach the rhB solution, however, there



Fig. 3. TEM analysis of the morphology of the WO₃ nanoparticles synthesized by precipitation in the presence of urea: (a) $450 \degree C$, (b) $500 \degree C$, (c) $600 \degree C$, (d) by simple precipitation $400 \degree C$, and (e) commercial WO₃.

50 nm

were differences in the rate at which this was achieved. The sample with the best photocatalytic activity was W500, which bleached the rhB solution after 210 min of lamp radiation. Different factors can contribute to the high photocatalytic activity observed in W500.

At first instance, a minor aggregation of the particles of W500 and W600 with respect to W450 was observed. As mentioned before, this promotes a better dispersion of the photocatalyst during the photocatalytic experiment. Regarding the surface area, W500 has a



Fig. 4. SEM analysis of the morphology of the WO₃ samples synthesized by precipitation in the presence of urea: (a) 450 °C, (b) 500 °C, (c) 600 °C, (d) by simple precipitation 400 °C, and (e) commercial WO₃.



Fig. 5. Evolution of the rhB concentration during its photocatalytic degradation $(5 \, \text{mg} \, \text{L}^{-1})$ by WO₃ nanoparticles using a Xe lamp as source of radiation, pH_o 6.0. The concentration of rhB was determined through its absorption band maximum (554 nm).

higher exposed surface, compared to W600. On the other hand, WR400 had the highest surface area among all the synthesized samples but, at the same time, it tended to form the largest agglomerates. Additionally, the better photocatalytic activity observed for W500 can be associated with its higher crystallinity with respect to W450. As it is well known, the crystalline defects act as recombination centers of the electron–hole pair. As a conclusion, it is possible to think that the degradation rate of the organic dye is the result of the contribution of all factors mentioned. The photocatalytic activity for the degradation of rhB followed the sequence W500 > W600 > commercial > W450 > WR400.

The temporal evolution of spectrum changes during the rhB photodegradation process by W500 is shown as Supplementary data in S1. The main rhB absorption band located at 554 nm is due to the presence of four ethylated groups on the dye molecule. The irradiation of the W500/rhB dispersion with Xe lamp produced a gradual depletion of the absorbance value. This depletion takes place almost without a shift of the dye absorption band, revealing some features of the pathway followed during the rhB photodegradation can occur by two competitive mechanisms: by attacking •OH radicals on the aromatic chromophore ring, leading to the degradation



Fig. 6. Evolution of the IC concentration during its photocatalytic degradation (30 mg L^{-1}) by WO₃ nanoparticles using a Xe lamp as source of radiation, pH₀ 6.0. The concentration of IC was determined through its absorption band maximum (610 nm).

of the rhB structure and reduction of the absorption band without a wavelength shift (pathway 1) or by a successive de-ethylation from the aromatic rings, causing significant blue wavelength shifts according to the formation of the different de-ethylated rhodamine intermediates (pathway 2) [20–22]. According to the spectrum changes observed in S1, it seems clear that the mechanism concerning the rhB photodegradation occurs by the attack of the aromatic chromophore ring, and predominates over the de-ethylated processes.

Fig. 6 shows the high photocatalytic activity of the WO₃ samples for the degradation process of IC, which was even higher than that observed with rhB. Note that the initial IC concentration used in these experiments was 6 times higher than the one employed for rhB due to their respective molar extinction coefficients. Once again, in all cases the samples were able to bleach the IC solution. In fact, this process was completed after only 150 min of radiation for the samples calcined at higher temperatures (W500 and W600). The sequence of the photocatalytic activities of the WO₃ samples was W500 > W600 > W450 > WR400 > commercial.

The temporal evolution of spectrum changes during the IC photodegradation process by W500 followed a similar behavior that observed for rhB, see data Supplementary S2. The depletion in the absorbance value without a shift of the dye absorption band revealed a possible direct attack of the aromatic chromophore ring of IC by radicals formed.

Fig. 7 shows the data of the temporal degradation of CR when WO_3 samples were used as photocatalysts. In general, after 300 min of light radiation the CR solutions remained colored. The difficulty to degrade CR is associated with the presence of the two azo (-N=N-) groups in its molecular structure, see Fig. 1. The recalcitrant nature of the azo dyes is due to the high energy necessary to break the azo bond. Due to this result, additional experiments with CR were not carried out.

To determine if the mineralization of organic dyes is feasible by WO₃ under the Xe lamp radiation, experiments to determine the variation of total organic carbon were performed in the course of the photocatalytic reaction for the degradation of rhB and IC, as is shown in Fig. 8. These experiments were carried out with the photocatalyst synthesized at 500 °C, i.e. W500. To achieve a greater accuracy in the quantification concerning the experiment with rhB, the initial concentration was modified to 50 mg L⁻¹. This data showed that the complete mineralization of rhB by the WO₃ photocatalyst is not feasible (29% after 96 h). The bleaching of the dye solution is just associated with the inactivation of the chromophore groups in the molecular structure of rhB. A different



Fig. 7. Evolution of the CR concentration during its photocatalytic degradation (20 mg L^{-1}) by WO₃ nanoparticles using a Xe lamp as source of radiation, pH_o 6.0. The concentration of CR was determined through its absorption band maximum (498 nm).

situation was observed in the degradation of IC where after 96 h of radiation a mineralization degree of 86% was reached for a solution of IC (100 mg L⁻¹). This data confirms the high photocatalytic activity of WO₃ for the degradation process of IC. The observed difference in the mineralization degree of rhB and IC can be associated with the recalcitrant behavior of the products formed during the photodegradation of rhB, as was previously reported [23,24].

In the same way, the origin of this important difference can be related to the mechanism that operates in each dye's photodegradation process. In order to elucidate this point, some experiments were performed varying the source of radiation. The degradation of rhB and IC by the action of a photocatalyst can take place by two ways. The first of which is by a true photocatalytic process, where radiation on the photocatalyst promotes an electron from its valence band to the conduction band, and then the electron-hole pair is formed. The second possibility is through a photosensitization process, where the radiation excites an electron from the dye and then, it is injected to the conduction band of the semiconductor oxide. In both processes, a series of consecutive reactions leads to the eventual mineralization of organic dyes to CO₂ and H₂O. In order to elucidate which mechanism is involved, some experiments were performed varying the source of radiation. The photocatalytic degradation of rhB over the WO₃ photocatalyst was performed, but now the photocatalyst/dye dispersion was irradiated with UV light (365 nm). As it can be seen in Fig. 9a, the photocatalytic activity of W500 decreased considerably, and after 150 min of UV-radiation



Fig. 8. Changes in the TOC during the mineralization of rhB and IC using a Xe lamp as source of radiation, $pH_{\rm o}$ 6.0.

only 12% of the dye solution was bleached. In the same period, the solution was bleached in a 95% when it was irradiated with the Xe lamp. This experiment revealed that the degradation of rhB by WO₃ seems to occur predominantly through the photosensitization of the organic dye by the action of visible-light radiation. Fig. 9b shows a similar experiment but in this case an IC solution was irradiated with the UV source in the presence of W500. Although the photocatalytic activity decreased when the dispersion was irradiated with UV-radiation a considerable activity was still observed in this experiment. This situation suggests that the two possible mechanisms of dye degradation take place simultaneously, i.e. true photocatalysis and the photosensitization process. As was previously mentioned, the mineralization degrees achieved after 96 h of Xe lamp radiation were 29% for rhB and 86% for IC. This behavior can be explained on the basis of the proposed photocatalytic degradation mechanism of rhB. By taking into account that the photosensitization process is the predominant degradation mechanism, the presence of rhB promotes degradation by this mechanism. When the solution is bleached, the photosensitization process is avoided and the mineralization of rhB is considerably inhibited. On the other hand, for IC the temporal TOC value decreases considerably during the experiment. Due to the fact that the IC degradation occurs by simultaneous photosensitization and true photocatalysis processes, the bleaching of the solution does not affect considerably the mineralization process.

In order to investigate the participation of $^{\circ}$ OH radicals in the course of the photocatalytic degradation of organic dyes in presence of WO₃, a test with terephthalic acid was performed. This test is recognized as an efficient method to determine the formation of $^{\circ}$ OH radicals when a semiconductor is exposed to a radiation source. Due to the formation of a unique product during the reaction of terephthalic acid with $^{\circ}$ OH radicals, the 2-hydroxyterephthalic acid, and its photoluminescence properties, an estimated of the $^{\circ}$ OH radical concentration can be calculated from the photoluminescence spectrum of the product formed. Fig. 10 shows the $^{\circ}$ OH-trapping



Fig. 9. Evolution of the (a) rhB and (b) IC concentration during its photocatalytic degradation by WO₃ nanoparticles under UV and vis irradiation.



Fig. 10. •OH-trapping photoluminescence spectra of WO₃ (W500) and TiO₂ (P25) in a solution of terephthalic acid at room temperature (excitation at 312 nm, emission at 426 nm): (a) WO₃, UV-light radiation (365 nm), (b) WO₃, Xe lamp radiation, (c) TiO₂, UV-light radiation (365 nm) and (d) TiO₂, Xe lamp radiation.

photoluminescence spectrums of sample WO₃ (W500) in a terephthalic acid solution at room temperature under: (a) UV-light radiation (365 nm), and (b) Xe lamp radiation. In the same way, experiments with both radiation sources but now using TiO₂ P25 as photocatalyst were also performed, see Fig. 10c UV-light radiation and Fig. 10d Xe lamp radiation. In first instance, it is clear that the formation of •OH radicals is feasible when WO₃ is used as photocatalyst. The concentration of •OH radicals is notably increased when the dispersion was exposed to the Xe lamp radiation. Although both lamps have similar intensity of UV radiation, the emission spectrums of the lamps are necessary to characterize completely the radiation source. Nevertheless, an effective comparison can be realized if TiO₂ P25 is used as reference.

The formation of •OH radicals when the dispersion of TiO₂ was irradiated with UV was more than double in relation with the results obtained with the visible-light source. The chemical composition of TiO₂ P25 included the polymorphs anatase (80%) and rutile (20%), both polymorph oxides with band gaps > 3.1 eV and susceptible to be excited only by UV radiation under 390 nm [25]. The activity observed for the formation of •OH radicals under Xe lamp irradiation is due to the presence of UV radiation not filtered by the borosilicate container. On the other hand, the higher activity of WO₃ in the formation of •OH radicals when it is exposed to visiblelight source is indicative that this type of radiation has the main contribution to the photocatalytic process. This result is in agreement with the recent work of Kim et al. [26], where they relate the formation of •OH radicals when a dispersion of platinized WO₃ (Pt/WO₃) photocatalyst was exposed to visible-light radiation. The generation of •OH radicals in the dispersion of WO₃ (W500) would take place through two paths; one of them the reductive path, with the participation of electrons of the conduction band of WO₃:

$$2WO_3 + h\nu \to 2WO_3(h^+) + 2WO_3(e^-)$$
(2)

$$WO_3(e^-) + O_2 \rightarrow WO_3 + O_2^{\bullet -}$$
 (3)

$$WO_3(e^-) + O_2^{\bullet -} + H^+ \rightarrow WO_3 + HO_2^{\bullet}$$

$$\tag{4}$$

$$\mathrm{HO}_{2}^{\bullet} + \mathrm{H}^{+} \to \mathrm{H}_{2}\mathrm{O}_{2} \tag{5}$$

$$H_2O_2 + e^- \rightarrow \bullet OH + OH^- \tag{6}$$

or by direct oxidation of hydroxide ions by the holes of WO_3 generated in its valence band during the charge separation (oxidative path):

$$WO_3(h^+) + OH^- + H^+ \rightarrow WO_3 + {}^{\bullet}OH + H^+$$
 (7)

Both mechanisms can operate simultaneously in an aqueous dispersion of a semiconductor oxide. So, the generation of •OH radicals in aqueous dispersion of WO_3 is by a direct oxidation of hydroxide ions by the holes generated in the valence band of WO_3 during the charge separation process. In the same way, in a second mechanism •OH radicals can be also formed by a reductive path (Eqs. (2)–(6)).

4. Conclusions

WO₃ nanoparticles were prepared successfully by the precipitation method in the presence of urea at different calcination temperatures. The presence of urea during the precipitation process led to the formation of particles with rectangular and ovoid shapes. A high photocatalytic activity of the WO₃ nanoparticles synthesized was observed in the bleaching of rhB and IC aqueous solutions. Moreover, the mineralization of indigo carmine was also completed after 96 h of light radiation. In general, the best photocatalytic activity was obtained with the sample calcined at 500 °C. The reason behind its higher activity was associated with factors such as morphology, aggregation degree of its particles, and, to a lesser extent, surface area. Throughout the experiments with visand UV-radiation, it was possible to conclude that the degradation of rhB by WO₃ seems to occur predominantly through the photosensitization of the organic dye by the action of visible-light irradiation, whereas the degradation of IC simultaneously happens by photosensitization and true photocatalytic processes. Finally, the formation and participation of $^{\circ}$ OH radicals in the degradation of organic dyes when WO₃ is used as photocatalyst was confirmed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.03.034.

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