

Photocatalytic Degradation of Organic Compound in Water using Synthetic Niobia: Experimental and Theoretical Studies

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Abstract The present work describes novel materials based on niobia oxides destined to oxidize an organic compound in aqueous medium via heterogeneous photocatalysis. The organic compound decomposition study was realized with a typical basic dye, methylene blue. The analysis of the products, with electrospray ionization mass spectrometry (ESI-MS), showed that the dye was successively oxidized in different intermediate compounds. These results strongly suggest that the oxidation of the organic dye involves oxidizing species mainly generated after previous treatment with H₂O₂.

Keywords Synthetic niobia · Oxidation · Photocatalysis · ESI-MS

1 Introduction

In the last decades an increasing interest in Niobium containing materials has arose mainly due to their application in different technological fields. However, Nb compounds are not completely understood like other industrially attractive elements. Niobium-based catalysts are efficient in a large number of applications such as pollution control, selective oxidation, hydrogenation and dehydrogenation, hydration, and dehydration, photochemistry, electrochemistry, and polymerization [1–4].

Brazil is the leading Niobium producer with 60% of the world production, justifying increasing interest in using

such source as starting material for different processes. Recent studies have shown the efficiency of Nb-based catalysts in the oxidation of organic compounds in aqueous solution [5, 6]. In heterogeneous catalysis, main applications involve Nb compounds as promoters of, and support for, other metals mainly due to the increase of catalytic activity and stability of the catalyst. Generally, the most common catalyst systems are with silica, alumina, and zeolites [7–10]. Alternatively, photo-catalysts can be prepared with Niobium oxide added to titanium oxide [8]. A direct use of Niobium oxide as the singular catalyst is scarce in literature, at least to our knowledge [11, 12].

Thus, the aims of this work were to synthesize, and to evaluate a pure niobium oxide and one modified with hydrogen peroxide in the oxidation of a model molecule, methylene blue in the presence of UV radiation. Moreover, a degradation mechanism is proposed based on electrospray ionization mass spectrometry (ESI-MS) and Density functional theory (DFT) calculations.

2 Materials and Methods

2.1 Synthesis and Characterization

Niobia was prepared by slow dropping of an 1 mol L⁻¹ NaOH solution in a 500 mL Teflon beaker containing 100 mL 0.26 mol L⁻¹ solution of NH₄NbO(C₂O₄)(H₂O)](H₂O)_n, kindly donated by CBMM—Companhia Brasileira de Metalurgia e Mineração (Araxá, state of Minas Gerais) at 70 °C under vigorous stirring. The solids obtained were washed with distilled water until neutral pH.

Treatment with hydrogen peroxide was performed treating the previously synthesized niobium oxide (300 mg) with 8 mL of aqueous hydrogen peroxide 30%

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(v/v) and 80 mL of water for 30 and 60 min. After these contact times the solids were washed with distilled water and oven-dried for 12 h at 60 °C.

XPS was performed by using Mg K α radiation (1,253.6 eV) and VG hemispherical electron-energy analyser using a pass energy of 20 eV. The chamber pressure during the measurement was around 10⁻⁹ Torr. The binding energies were corrected for the charging effect by assuming a constant binding energy for the adventitious O1s peak. UVvis spectroscopy with diffuse reflectance geometry was carried out in a Cary 5E spectrometer from 200 to 800 nm.

2.2 Oxidation of Methylene Blue

Ten milliliters of a 50 mg L⁻¹ methylene blue solution at pH 6.0 was mixed with 10 mg of the catalyst and irradiated with ultraviolet light. Reactions were monitored by UV–vis spectroscopy (Shimadzu-UV-1601 PC) at 665 nm with circulating water through a temperature controlled bath kept at 25 ± 1 °C.

2.3 Studies by ESI-MS

In an attempt to identify the intermediate formation, the methylene blue decomposition was also monitored with the positive ion mode ESI-MS of an Agilent MS-ion trap mass spectrometer. The reaction samples were analyzed by introducing aliquots into the ESI source with a syringe pump at a flow rate of 5 mL min⁻¹. The spectra were obtained as an average of 50 scans of 0.2 s. Typical ESI conditions were as follows: heated capillary temperature 1,508 °C; sheath gas (N₂) at a flow rate of 20 units (ca. 4 L min⁻¹); spray voltage 4 kV; capillary voltage 25 V; tube lens offset voltage 25 V.

2.4 Computational Methods

The calculations were carried out with the *Gaussian98* package [11]. All the transition states, intermediates and precursors involved were calculated. Each conformer was fully optimized by DFT. The energy profile at selected DFT geometries along the reaction pathway was computed at B3LYP level of theory using the 6-31+G (d,p) basis set. This computational procedure has been employed previously on similar systems with success [12]. Furthermore, after each optimization, the nature of each stationary point was established by calculating and diagonalizing the Hessian matrix (force constant matrix). The unique imaginary frequency associated with the transition vector (TV) [12], i.e., the eigenvector associated with the unique negative eigenvalue of the force constant matrix, was characterized. The solvent effect was evaluated with utilization of

polarized continuum model (PCM) solvation calculations, initially proposed by Barone et al. [13]. Electronic transition energies were computed by CISD calculation at Hartree–Fock level employing 6-31+G (d,p) basis. All UV calculations were carried out using *Gaussian98* [11].

3 Results and Discussion

3.1 Methylene Blue Oxidation: Discoloration Study

Photocatalytic oxidation of methylene blue onto niobias was followed by UV–vis spectroscopy. No significant discoloration was observed with only ultraviolet light and no catalyst. Similar results were observed when catalyst was loaded but no incident ultraviolet light (Fig. 1a). On the other hand, niobia previously activated with hydrogen peroxide for the period of 60 min promoted total dye solution discoloration after 60 min of reaction time.

Successive cycles of discoloration of methylene blue were studied with pure niobia, and niobia treated with hydrogen peroxide for 30 and 60 min. Absorbance was measured after 90 min of reaction time of each cycle (Fig. 1b). Niobia treated with hydrogen peroxide for 60 min presented high activity even after four consecutive reaction cycles. Such behavior could be explained by hydroxyls coordinated on the catalyst surface [6]. These hydroxyls would be more reactive and their catalytic activity could be explained by (1) direct oxidation through attack of the aromatic rings; (2) decreasing the band gap, and/or (3) avoiding the recombination of electron-hole pair, giving a more reactive catalyst. For all the experiments a linear behavior was observed (Fig. 2). Although the discoloration is very complex process, this linear behavior suggests that under the conditions employed the reaction can be approximate to a pseudo-zero order kinetics. The discoloration rate constants were obtained by the slope of the discoloration plots.

3.2 Methylene Blue Oxidation: Identification of Intermediates

Discoloration measured by UV–vis spectroscopy does not give any information about any reaction intermediates of methylene blue oxidation reaction. Such identification could be achieved by using mass spectroscopy with electrospray ionization. Identification of intermediates was studied obtaining spectra after 60 and 150 min of pure niobia (Fig. 3a) and niobia treated with hydrogen peroxide for 60 min (Fig. 3b).

Spectrum of methylene blue dye indicated only one peak at m/z = 284 due to its cationic structure. For different reaction times, total mineralization was not achieved since

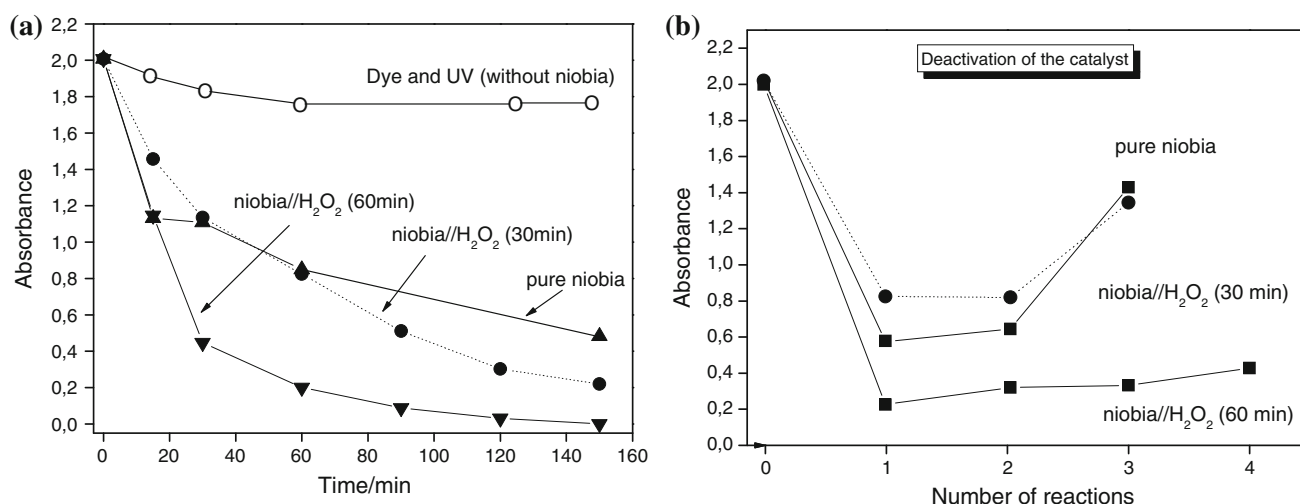


Fig. 1 Discoloration of methylene blue dye with pure and H₂O₂-treated niobias (a) and reaction cycle (b) monitored by UV-visible spectrometry

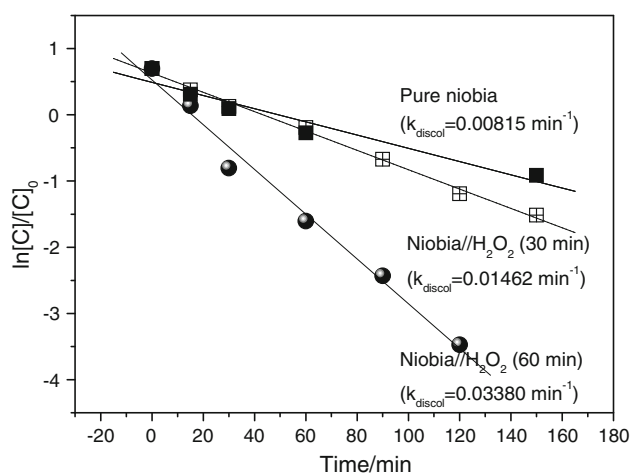


Fig. 2 Discoloration rate constants k_{discol} for the oxidation of methylene blue dye in the presence of niobias

reaction intermediates could be observed in the spectra. However, the peak at $m/z = 284$ had its intensity decreased more prominently in the reaction with niobia pre-treated with hydrogen peroxide (Fig. 3b) compared to pure niobia (Fig. 3a). This is in agreement with the high catalytic behavior discussed previously for this sample (Fig. 1).

Moreover, spectrum of niobia treated with H₂O₂ indicated an intense peak at $m/z = 270$ suggesting the beginning of dye structure degradation. Also after 150 min of reaction the characteristic dye peak practically disappeared at the expense of an increase in the intensity of peaks at $m/z = 300$, 316 and 326 probably due to successive hydroxylation of the aromatic ring, according to Oliveira et al. [6]. Peaks at $m/z = 230$ and 258 are indicative of ring rupture and a subsequent possible total mineralization.

3.3 Reaction Mechanism

Schemes of the photo-activation of niobias are shown in Fig. 4. It can be observed that there is a proposal mechanism of ·OH radical formation by ultraviolet light action on semiconductor material mainly after the H₂O₂ treatment. The intermediate structures are reported in Fig. 5. The calculation of the Gibbs free energy for the stability of the intermediates was performed by the method implemented in the *Gaussian98* package [11]. The resulting energies values are shown in Table 1. Previous works [6, 14] put in evidence that the intense fragment corresponding to $m/z = 300$ (Fig. 2) result from the hydroxylation in the aromatic ring. According to data listed in Table 1, it can be observed that the hydroxyl group at C2 position is about +3.30, +6.65, +7.86 and +8.68 kcal mol⁻¹ more stable than the alternative C3, C5, N and S, respectively.

In order to get deeper insight about the $m/z = 300$ signal, the Gibbs free energy for the stability of some possible isomers with $m/z = 300$ at DFT level was calculated (Fig. 5). From our data, we may note that the most stable fragment of the hydroxyl group is at C2 position. Further calculations revealed that the hydroxylation occurs at C2', which explains the resulting intense fragment corresponding to $m/z = 316$. Thus, compounds **II** and **III** (Fig. 5) are supposed to be stable and the reaction path may still involve other hydroxylations. From these results, the third hydroxylation would more likely occur at position 5 generating the signal with $m/z = 332$. This is a critical step, as it would simultaneously lead to the formation of hydroquinone or hydroquinone-like intermediates generated by the ·OH attack. This is an unstable key-intermediate that points out the quick and high probability of rupture of both chemical bonds C1–C2 and C5–C6 [6].

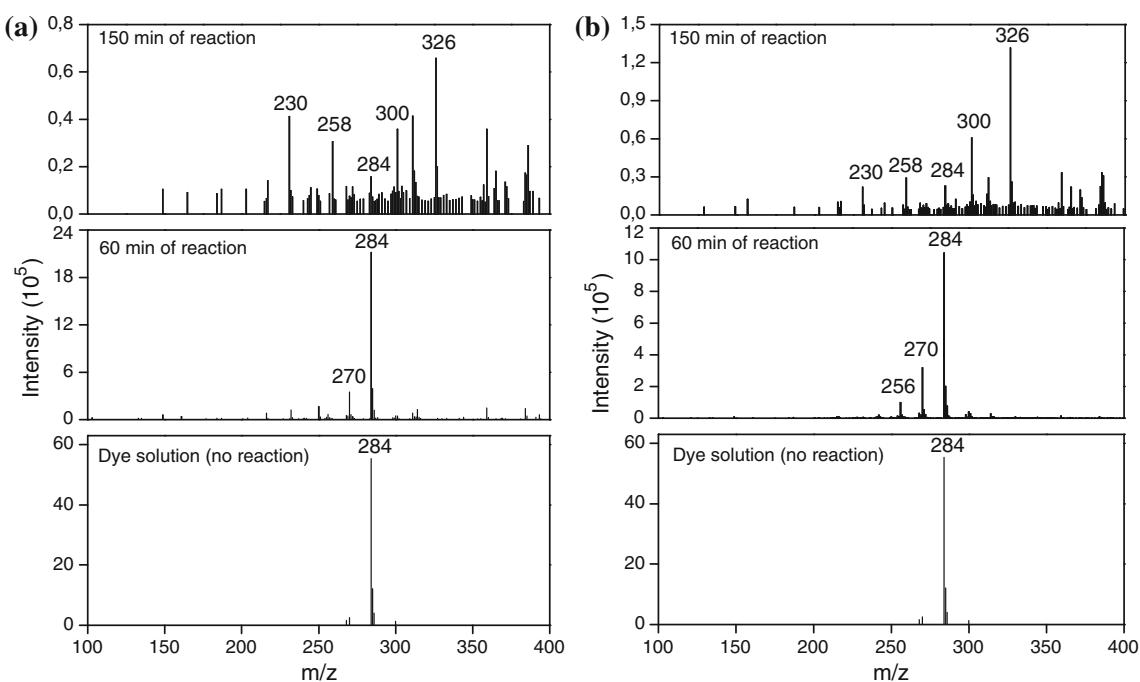
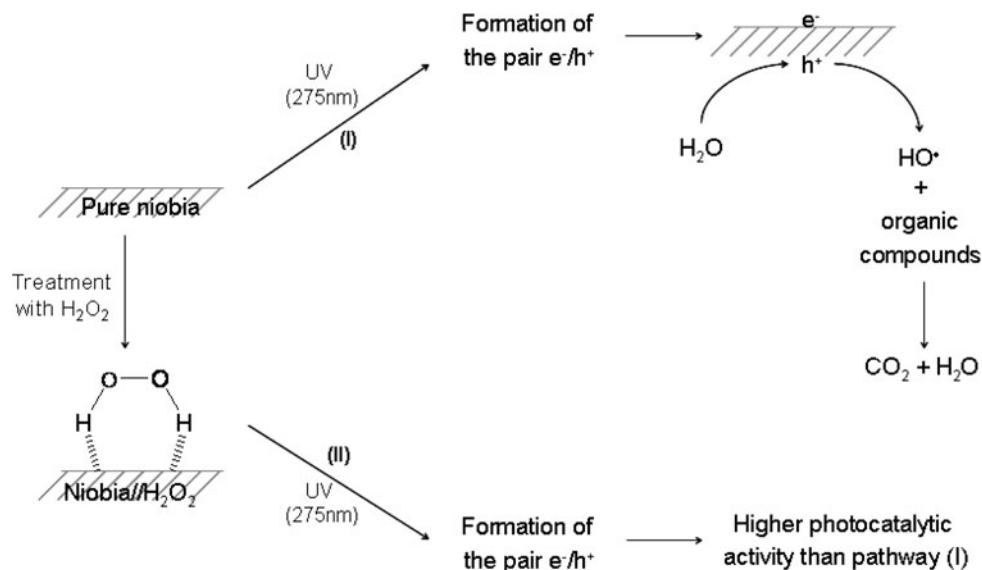


Fig. 3 ESI mass spectra in the positive ion mode for monitoring the oxidation of methylene blue dye in water by the pure niobia (a) and niobia treated with hydrogen peroxide for 60 min (b) via photocatalysis at different reactions times

Fig. 4 Mechanisms of photo-activation of pure and H_2O_2 -treated niobias



These calculations show good agreement with the experimental data (Fig. 3). Surprisingly, the fragmentation pathway is quite similar to that described in our previous study [14]. This could strongly suggest that the reaction with niobia catalyst initializes by the activation of H_2O_2 to produce an $\cdot\text{OH}$ radical.

In order to shed more light on the overall reaction mechanism model in the photocatalysis, molecular orbital calculations for pure niobia were performed and after treatment with H_2O_2 (niobia/ H_2O_2) by the algorithm

implemented in the *Gaussian98* package with the CIS technique [8]. This method is a powerful tool for the computation of UV parameters. These peroxy species are potentially oxygen donors to organic substrates in the liquid phase. The pure niobia and niobia/ H_2O_2 exhibit absorption bands at 217.9 and 250.12 nm, respectively (Fig. 6). A strong band at 217.9 nm for pure niobia is red-shifted after the treatment with hydrogen peroxide, which generates a decrease in the band gap from 5.69 to 4.97 eV. These theoretical values are qualitatively in good

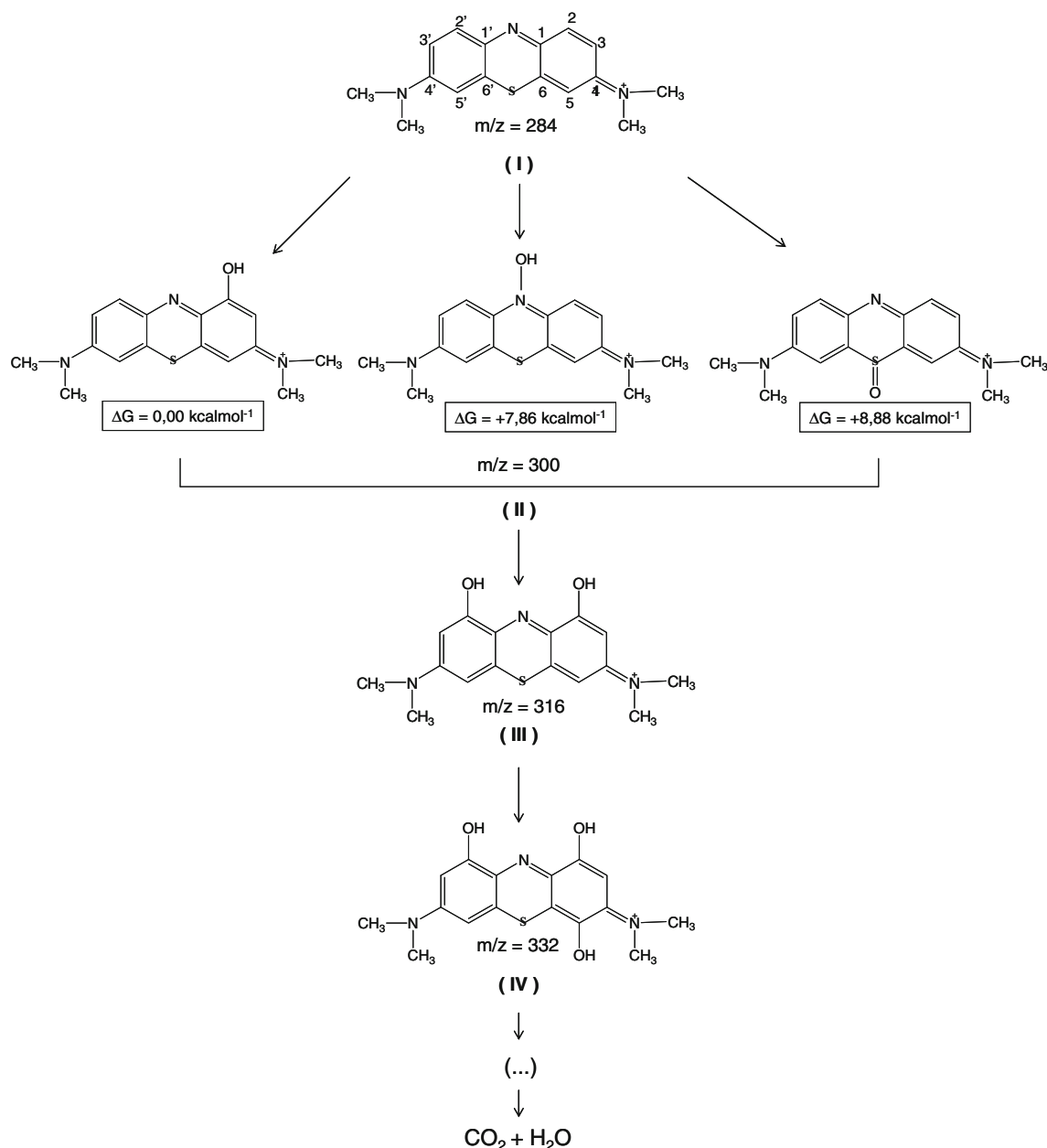


Fig. 5 Scheme with intermediates proposed for the oxidation of methylene blue dye ($m/z = 284$) by photocatalysis

agreement with the experimental results from UV–vis diffuse reflectance (see Sect. 3.4 for more details). This could, in principle, justify the catalytic efficiency of the pure niobia previously treated with H₂O₂ (niobia//H₂O₂).

3.4 Niobia Characterization

XRD patterns for the samples indicate, for this preparation procedure, that the materials are amorphous. These results are in very good agreement with other experimental studies [15]. UV–vis diffuse reflectance was used to determine the band gap of these materials (Fig. 7) in order to better

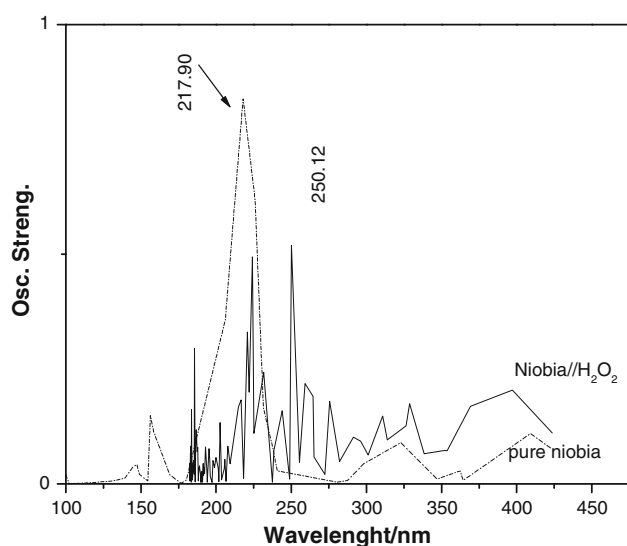
understand the differences of catalytic activities exhibited after hydrogen peroxide treatment.

The band gap peak due the electron-hole pair formation and catalyst activation was observed at 345 nm for pure niobia. On the other hand, a dislocation to lower energies is evident for the material treated with H₂O₂ (niobia//H₂O₂) with band gap at 375 nm. The energy required for the formation of electron-hole pair is lower, increasing the photocatalytic efficiency for the conversion of organic compound (Figs. 1, 2 and 3).

The O1s region was investigated for pure niobia and niobia//H₂O₂ 60 (Fig. 8). The analysis of the corresponding

Table 1 Gibbs free energy of II and III intermediates using B3LYP/6-31+G (d,p)

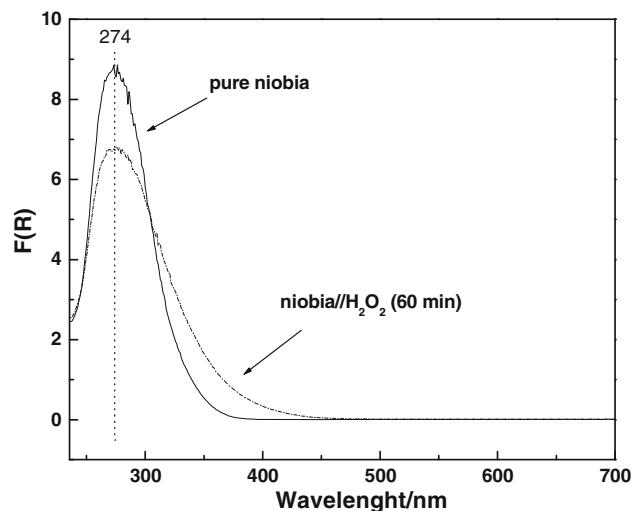
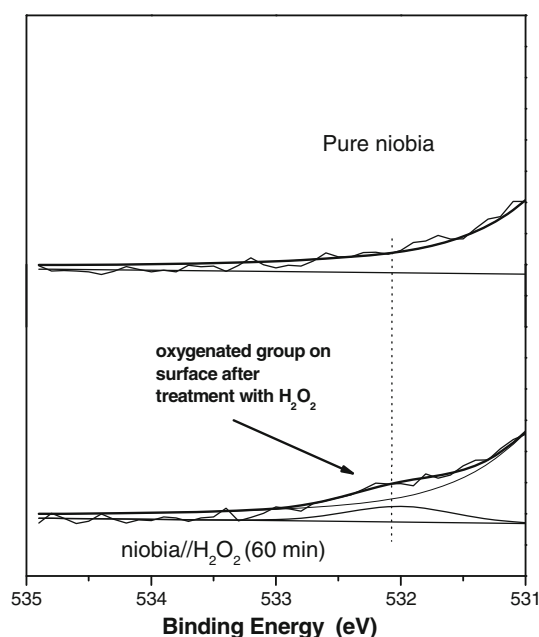
Intermediate	Hydroxyl position	ΔG (kcal mol ⁻¹)
II	2	0.00
	3	+3.30
	N	+7.86
	S	+8.68
	5	+6.65
III	2, 2'	0.00
	2, 5'	+34.69
	3, 2'	+11.73
	3, 3'	+14.26
	3, 5'	+3.25
	5, 5'	+21.22

**Fig. 6** UV theoretical spectra from CISD calculation for pure and H₂O₂-treated niobias

spectra showed the presence of two peaks at 529.9 and 532.1 eV for niobia//H₂O₂ 60. The main peak at 529.9 eV is related to the oxygen anions, O²⁻, bound to the metal cations in the lattice [15, 16]. The second peak at 532.1 eV could be attributed to the formation of oxygenated groups on the niobia surface as reported in the literature [6]. The better catalytic activity of the material after the previous treatment with H₂O₂ may be due to these oxygenated groups.

4 Conclusion

Synthetic niobia is a good catalyst in the oxidation of a model molecule of organic contaminants such as methylene blue dye under ultraviolet light. ESI-MS and

**Fig. 7** UV-reflectance spectra for the pure and H₂O₂-treated niobias**Fig. 8** XPS profiles of O1s region of pure and treated niobias

theoretical calculations indicated that an oxidation mechanism may occur by attack of the free radical ·OH over the molecule giving rise to hydroxylation products as principal byproduct but compounds resultant from the ring cleavage are also detected.

Theoretical data using CIS methodology indicate that a strong band at 263.1 nm for niobium complex is shifted as compared to peroxo niobium complex, which generates a decrease in the band gap, remaining still in the UV region. Our data put in evidence that the previous treatment with hydrogen peroxide might decrease the energy of the electron-hole pair formation increasing catalytic activity and also coordination of active hydroxyl groups.

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