

UTILIZATION OF Sn/Nb₂O₅ COMPOSITE FOR THE REMOVAL OF METHYLENE BLUE

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In this work, the oxidation of methylene blue textile dye in the presence of hydrogen peroxide, using niobium oxide impregnated with different proportions of tin (1, 5 and 10% in mass) as catalyst was studied. The materials were characterized by TPR, XPS, XRD and FTIR. The oxidation tests monitored by ESI-MS showed that the composite containing the higher amount of tin was the most efficient in the removal of the dye. The XRD, XPS, and TPR data presented evidence of the formation of the tin-niobium oxide composite containing Sn⁰ and supported SnO₂.

Keywords: niobium oxide; tin; organic dye.

INTRODUCTION

Industrial activity causes numerous environmental problems; water contamination by organic molecules is a good example. The growing development of the textile industry is a great contributor, because a large part of these pollutants is dye generated by this type of industry.

Due to their own nature, the dyes are easily detected by the naked eye, being visible in some cases at concentrations as low as 1 mg L⁻¹. That behavior presents advantages and disadvantages, because a small amount thrown in aquatic effluents can cause an accentuated change of coloration in the rivers, but can also be easily detected by environmental control authorities.¹ As a result, much effort has been made to degrade and even remove these dyes which constitute an environmental problem and a serious problem faced by modern society.²

Catalytic processes have been applied to the solution of several environmental problems, because it provides faster, low cost reactions, with higher selectivity. The interest in materials containing niobium oxides (Nb₂O₅) has been increasing in recent years due to the fact that this material can be applied in diverse fields of study,³ being used as a catalyst and as a catalytic support. The use of niobium oxide in Brazil becomes appealing due to its natural abundance in the country.^{4,5}

In the search for new materials with catalytic properties, the interest in the study of the effects of oxide supported metals has been increasing. The metal-oxide interaction induces important modifications in the adsorption and catalysis properties of the metal in different reactions.⁶ Furthermore, its use is justified by its having a larger area of contact between the metal and the organic molecule, which is not observed using the metal alone.

The introduction of transition metals, such as tin, on the surface of different supports results in high activity and selectivity for catalysis.⁷ The presence of metal dispersed on the surface acts as centers that present Lewis acid characteristics, which are desired as a reinforcer of the catalytic activity. In the investigation of surface catalytic properties, the acidity/basicity stands out, because it promotes alterations in the adsorption capacity, related to the properties of the exposed sites.⁸

In that context, the objective of this work was the preparation of tin on niobium oxide composites. Those materials were thermally treated for the formation of Sn⁰ (metallic tin) seeking their use as catalysts for H₂O₂ decomposition and methylene blue dye oxidation.

EXPERIMENTAL

Synthesis of catalyst Sn/Nb₂O₅

Different amounts of tin nitrate (1, 5 and 10% in mass) were incorporate with 2 g of niobium oxide, leading to samples containing different levels of the metal. The niobium oxide was put in contact with the tin nitrate solution and the volume was completed with water to 100 mL, soon afterwards, the material was kept under constant agitation a 100 ± 1 °C until dry. The produced solid was taken to an oven for complete drying of the material, and then calcinated, in air, at 500 °C for 3 h. For the obtaining of the metallic tin on the niobium oxide surface, the materials were treated with N₂/H₂ (5%) at temperatures predetermined by temperature-programmed reduction analyses (TPR).

Characterization of catalysts

The materials were characterized by X Ray diffraction in a Rigaku Geigerflex equipment, CuKα radiation (λ = 1.54056 Å) with 40 kV and 35 mA, infrared (FT-IR) spectroscopy, Digilab Excalibur, FTS 3000 series, scanning electron microscopy (SEM), LEO EVO 40XVP, UV-Vis spectroscopy, (Shimadzu-UV-1601 PC) and X Ray photoelectron spectroscopy (XPS), Kratos Analytical XSAM 800 cpi ESCA equipped with a Mg anode (Mg Kα radiation, 1253.6 eV) and spherical analyzer operating at 15 kV and 15 mA. The reduction profile of the materials was studied by Temperature-programmed reduction (TPR) in a Quantachrome ChemBet 3000.

Catalytic tests

Oxidation of methylene blue dye

The catalytic properties of the materials were tested through the degradation of the methylene blue textile dye, model organic molecule. The oxidation tests were done using a 9.9 mL solution of methylene blue at a concentration of 25 mg L⁻¹, 0.1 mL of 30% H₂O₂ solution and 10 mg of the Sn/Nb₂O₅ composite, under constant agitation at 100 rpm.

The degradation was monitored by UV-visible spectroscopy (Shimadzu-UV-1601 PC) in the maximum absorption wavelength of methylene blue: 645 nm. The degradation products were analyzed by ESI-MS (Agilent-1100). The sample was inserted in the apparatus

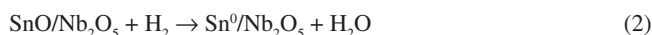
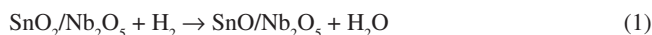
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by infusion at a flow of 5 $\mu\text{L min}^{-1}$, with charge control in the quadrupole (ICC) set to 30,000 and positive mode. The drying gas (N₂) temperature was 325 °C with a flow rate of 4 L min^{-1} , with an ion extraction potential of -3500 V.

RESULTS AND DISCUSSION

Characterization of the catalysts

For the determination of the treatment temperature for obtaining metallic tin on niobium oxide, the material impregnated with SnO₂ after being calcinated, was characterized by TPR. The programmed temperature reduction profiles for the SnO₂ sample on niobium oxide (SnO₂/Nb₂O₅, 10% tin in mass) and of the support are shown in Figure 1. The observed reactions were described by the Equations 1 and 2:⁹



The peak centered approximately at 427 °C, shown in Figure 1, corresponds to the reduction of Sn⁴⁺ to Sn²⁺ as schematized in Equation 1. The reduction of the active phase for Sn⁰ occurs at approximately 619 °C, as shown in Equation 2, indicating the treatment temperature for obtaining the material containing metallic tin. The samples containing 1 and 5% tin on niobium oxides presented reduction profiles similar to those observed in Figure 1. Moreover, the reduction of the Nb₂O₅ support, could be observed close to 900 °C, as reported in the literature.³

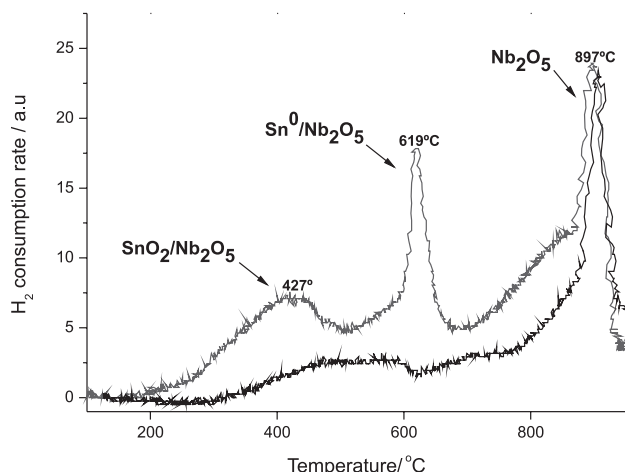


Figure 1. TPR profiles of SnO₂/Nb₂O₅ precursor and of Nb₂O₅ support

In Figure 2 the X-ray diffractograms of the Sn/Nb₂O₅ samples (1, 5 and 10% in mass) are shown.

Due to the reflections presented by the DRX analyses it can be noted that the reverse-oxidation of part of the metallic phase probably occurred, because the presence of SnO₂/Nb₂O₅ and SnO/Nb₂O₅ as well as Sn⁰/Nb₂O₅ composites were evident.¹⁰⁻¹² These results could be confirmed by the XPS analysis, Figure 3.

The mean crystalline size for the different tin phases and for the best peaks of each tin phase, in this case SnO₂ ($2\theta = 26.95^\circ$) and Sn⁰ ($2\theta = 63.67^\circ$) were calculated through the Scherrer equation: $d = k\lambda/\beta\cos\theta$, in which d represents the mean diameter of the particles, k is the Scherrer constant, which depends on the morphology of the crystals, λ is the radiation length used, in this case $\text{Co K}\alpha$

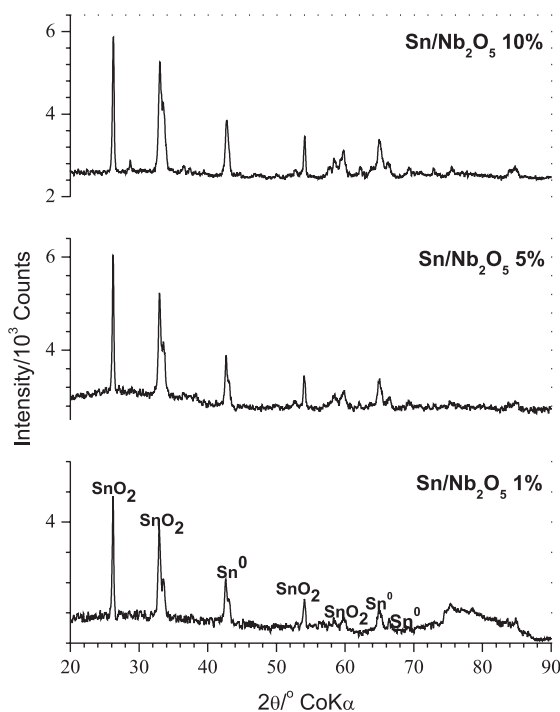


Figure 2. X-ray diffractogram of SnO₂/Nb₂O₅, SnO/Nb₂O₅ and Sn⁰/Nb₂O₅ composites

(1.5418 Å) and β corresponds to the value of the maximum width at half the height of the reflection of interest. In Table 1 the results for the mean particle size of the tin dioxide and the metallic tin are presented.

Table 1. Mean diameter of the materials present on the surface of Nb₂O₅

Material	Particle size (nm)
SnO ₂ /Nb ₂ O ₅	0.64
Sn ⁰ /Nb ₂ O ₅	0.81

Reflections referring to niobium oxide were not observed, suggesting the occurrence of an amorphous material.¹³

The tin phases were also characterized by XPS. In Figure 3, the spectrum obtained for the Sn⁰/Nb₂O₅-5% composite is presented.

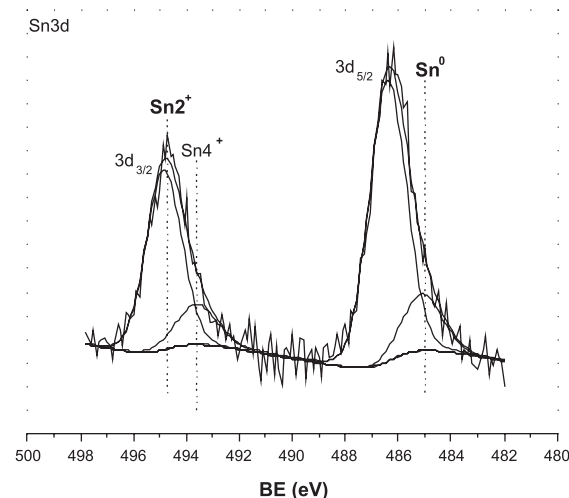


Figure 3. XPS spectrum of SnO₂/Nb₂O₅ and Sn⁰/Nb₂O₅

By XPS analysis, the presence of the reduced species Sn^0 (BE = 485.1 eV) and the oxidized state Sn^{2+} (BE = 494.8) and Sn^{4+} (BE = 493.7 eV),¹⁴ can be verified.

The vibrational spectra in the infrared region for the niobium oxide, before and after heat treatment, are shown in Figure 4.

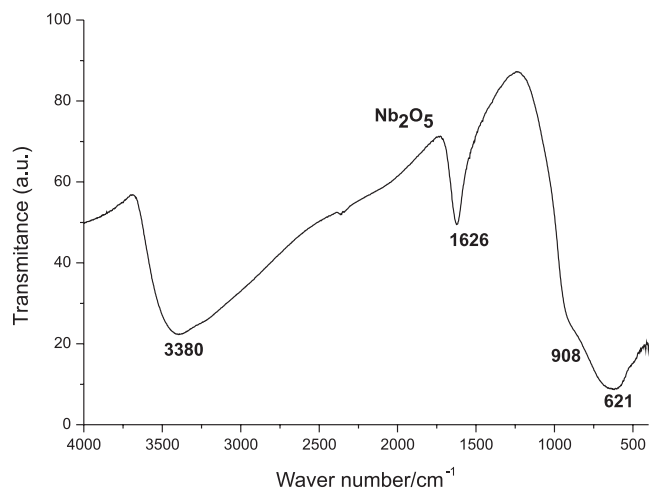


Figure 4. Vibrational spectrum in the infrared region for niobium oxide

The spectrum of Figure 4 presents bands characteristic of amorphous niobium oxide,¹⁵ characterized mainly by the bands centered at 621 and 908 cm^{-1} . Furthermore, it presents vibrations referring to OH surface groups and adsorbed H_2O at 1626 and 3380 cm^{-1} .

The spectra in the infrared region shown in Figure 1S, supplementary material, indicates tin presence on the surface of the niobium oxide represented by the peaks 807 and 873 cm^{-1} . The band centered at 560 cm^{-1} is associated with the Sn-O-Sn asymmetrical stretching.¹⁰

Decomposition of H_2O_2

The decomposition of H_2O_2 was carried out as the first evaluation of the catalytic activity presented by the material. In view of this, the pure niobium oxide and the materials obtained by the thermal reduction of the niobium oxide impregnated with different levels of tin were studied as catalysts in the decomposition of hydrogen peroxide.

Decomposition of H_2O_2 in aqueous solution and decomposition of H_2O_2 in the presence of MB

The decomposition capacity of H_2O_2 is indirectly measured by the volume of O_2 formed, given by the Equation 3:



The decomposition of H_2O_2 is accelerated as the tin level on the surface of the niobium oxide (Figure 5) increases until the tin level of 5%. Considering that the beginning of the reaction is of pseudo-first order kinetics in relation to H_2O_2 one has $V_{\text{decomp.}} = K_{\text{decomp.}} \cdot [\text{H}_2\text{O}_2]$ and the constants of velocity exhibited by the materials were 0.0006; 0.0017; 0.007 and 0.0001 min^{-1} , for the samples: pure niobium oxide, $\text{Sn}^0/\text{Nb}_2\text{O}_5$ -1%, $\text{Sn}^0/\text{Nb}_2\text{O}_5$ -5%, $\text{Sn}^0/\text{Nb}_2\text{O}_5$ -10%, respectively.

With these results, there is evidence that the presence of the metallic tin in the surface of the niobium oxide possesses an important function in the activation of the hydrogen peroxide. To try to elucidate the of H_2O_2 decomposition mechanism, the reaction was conducted in the presence of the organic compound methylene blue.

The decomposition of H_2O_2 in the presence of organic composition, species that with likeness for radicals, supplies information on the present mechanism in the oxidation with the composites and H_2O_2 .

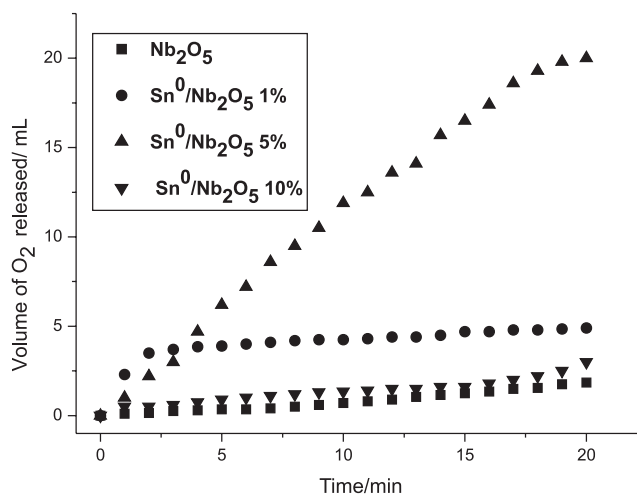


Figure 5. Profile of O_2 liberation by H_2O_2 decomposition for niobium oxide and the different materials

The results shown in Figure 2S, supplementary material, indicated an inhibition in the decomposition of the peroxide promoted by the addition of compounds which possess an affinity for hydroxylated radicals, that would be formed in the decomposition of the peroxide in a Fenton type system. It is inferred, with that, that those organic compounds participate in competitive processes during the decomposition of H_2O_2 , in which the intermediate compounds that promote the formation of O_2 react with the organic compound present, causing a decrease in the velocity constant by 0.0005; 0.0014; 0.006 and 0.0005 min^{-1} of Nb_2O_5 , $\text{Sn}^0/\text{Nb}_2\text{O}_5$ -1%, $\text{Sn}^0/\text{Nb}_2\text{O}_5$ -5% and $\text{Sn}^0/\text{Nb}_2\text{O}_5$ -10%, respectively.

Oxidation of the methylene blue dye

The oxidation of the organic dye methylene blue by the $\text{Sn}/\text{Nb}_2\text{O}_5$ type catalysts containing different tin levels can be observed in Figure 6. The oxide of pure niobium did not present dye removal capacity.

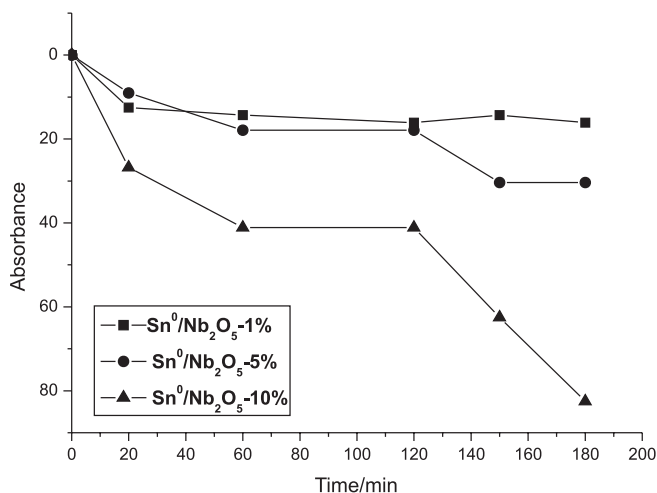


Figure 6. Removal of methylene blue dye monitored for Uv-Vis spectroscopy

It can be observed in Figure 6 that the sample containing 10% in mass of Sn in the surface of the niobium oxide presented higher discoloration capacity of the solution containing the of methylene blue dye during the whole interval of time studied. It is interesting to observe that the removal of the dye happens slowly up to 120 reaction min. After this time, an abrupt increase was observed in the discoloration until total removal of the dye from the aqueous medium.

Figure 3S, supplementary material, displays the ESI-MS study presenting hydroxylation signals and the break of the dye ring. Studies by electrospray coupled to a mass spectrometer of (ESI-MS) showed that up to 120 min only dye adsorption in the surface of the catalyst occurred, without oxidation intermediate formation. On the other hand, after 180 reaction min, the formation of hydroxylated intermediates with signals at $m/z = 301$ and 354 are presented, besides signals at $m/z = 250$ and 270 possibly due to the break of the dye aromatic ring, Figure 4S, supplementary material. The formation of these methylene blue dye oxidation intermediates is accompanied by the decrease of the signal $m/z = 284$ regarding the organic dye. It is important to point out that for the catalysts containing 1 or 5% of Sn⁰ the oxidation intermediate formation was not observed in the ESI-MS analyses, showing that the low removal of the dye by those materials, shown in Figure 6, occurred through adsorption processes.

Figure 4S, supplementary material, presents the possible structures responsible for the signals obtained in the ESI-MS spectra. The signal $m/z = 284$ (the dye structure) is hydroxylated, forming the structure with $m/z = 300$,¹⁶ and the signal $m/z = 354$, suggesting successive hydroxylations. It can be clearly noticed in Figure 7a, the spectrum with signal at $m/z = 301$ and the structure which represents a possible formation of the hydroxylated intermediate, presenting the value of 300. Studies of the mechanism involved seeking to propose the structure of the intermediate with signal $m/z = 301$ are being carried out. In Figure 4S the structures with $m/z = 270$ and 250 regarding the dye degradation are presented.

Reaction proposal involving the dye

The obtained results suggest that the tin impregnated in the structure of the niobium oxide favors the decomposition of the hydrogen peroxide, according to Equation 4.



According to Equation 5 that process is thermodynamically favorable.



Such a process is characterized by the reaction between the tin and the hydrogen peroxide leading to the formation of the •OH radical, with strong oxidizing capacity. The radical can undergo two processes: oxidize the organic compound or react with H₂O₂ to form the hydroperoxide radical, •OOH, that can regenerate the reactive site.

CONCLUSIONS

The obtained results showed that the system based on Sn/Nb₂O₅ containing 10% tin in mass presented good degradation capacity of the methylene blue textile dye. It is important to observe that the removal of the dye is accompanied by the formation of intermediate compounds, confirming the non-mineralization of the material.

The characterizations showed that part of Sn⁰ is oxidized after the reduction process with H₂ which can be compromising the •OH radical generation stage.

SUPPLEMENTARY MATERIAL

The supplementary material described below is available for free in <http://quimicanova.sbgq.org.br>, in the form of PDF file: Figure 1S. Vibrational spectrum in the infrared region for the materials containing SnO₂ and Sn⁰; Figure 2S. Profile of O₂ liberation catalysed by niobium oxide materials and composites in the presence of MB; Figure 3S. ESI-MS in the presence of H₂O₂ and of the composites; Figure 4S. Proposed scheme for the formation of possible oxidation intermediates of the methylene blue dye.

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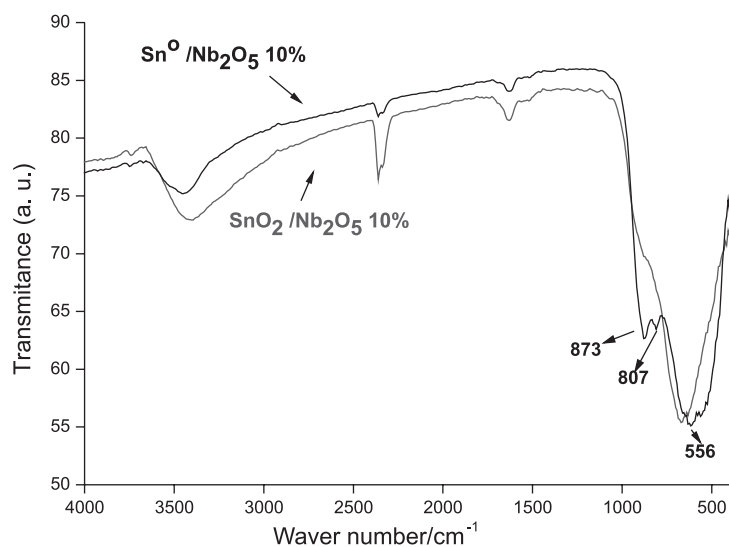


Figure 1S. Vibrational spectrum in the infrared region for the materials containing SnO₂ and Sn⁰

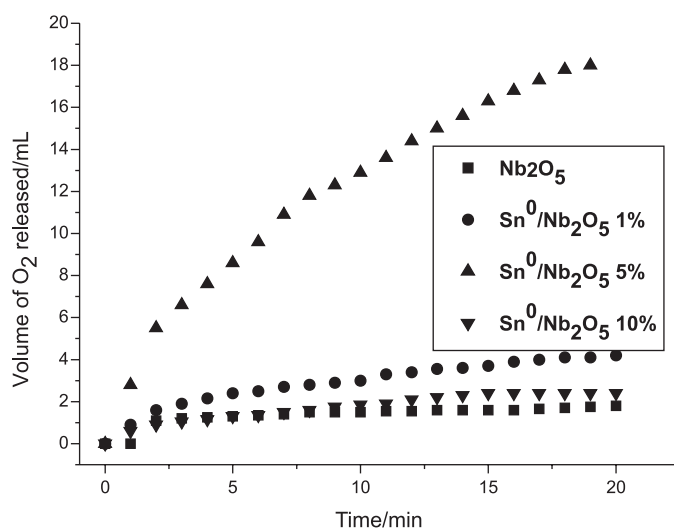


Figure 2S. Profile of O₂ liberation catalysed by niobium oxide materials and composites in the presence of MB

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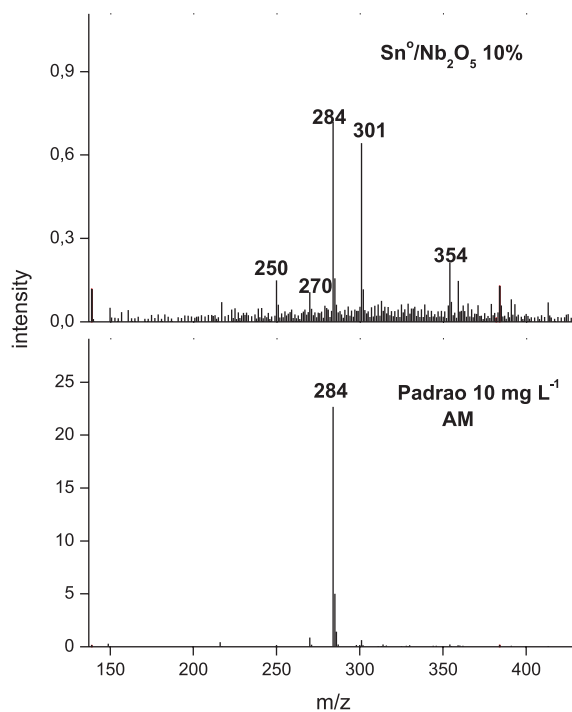


Figure 3S. ESI-MS in the presence of H₂O₂ and of the composites

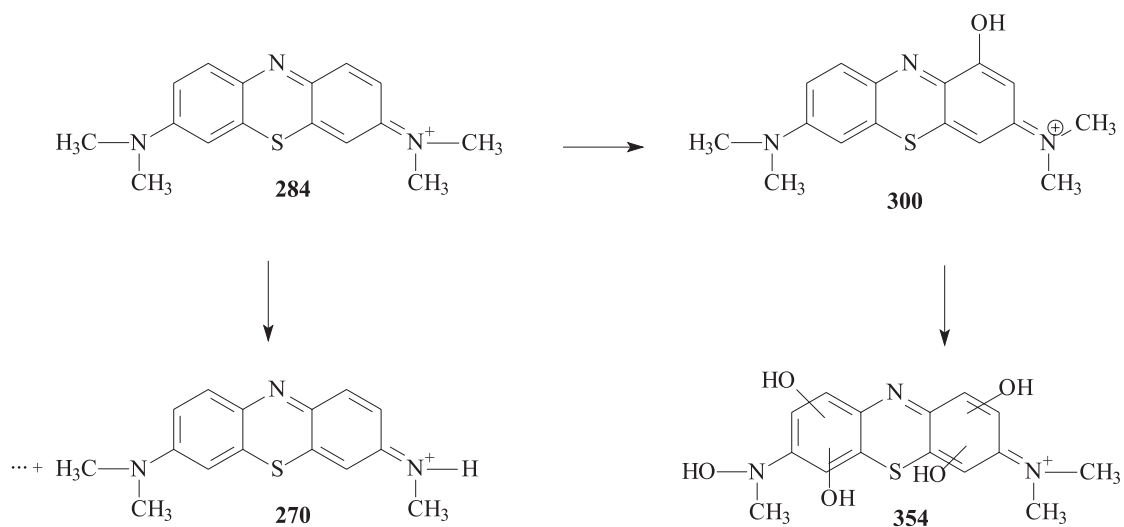


Figure 4S. Proposed scheme for the formation of possible oxidation intermediates of the methylene blue dye