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**High efficiency photocatalytic degradation of Ambroxol over Mn doped TiO₂:
Experimental designs, identification of transformation products,
mineralization and mechanism**

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Abstract

Ambroxol (AMB) is a drug commonly used for chronic bronchitis prevention. Once released in surface water, this recalcitrant chemical becomes a hazardous pollutant. Here, we investigated the ability of 1% Mn-doped TiO₂ (Mn-TiO₂) to mineralize AMB by photocatalysis. We studied the morphology, and the physical and electrochemical properties of Mn-TiO₂ using X-ray diffraction, Scanning electron microscopy, Transmission electron microscopy, X-ray fluorescence, BET method, UV-visible, and electrochemical study and optimized the AMB degrading experimental conditions through response surface methodology (RSM). Mn-TiO₂ at the dose of 0.625 g.L⁻¹ allowed the complete photodegradation of AMB (30 ppm) at pH 7 under UVA light irradiation for 30 min while total mineralization in CO₂ (> 96%) was achieved after 24 h of irradiation. Mn-TiO₂ was 1.6-time more efficient than TiO₂ Degussa P25. Product studies were also carried out by liquid

chromatography coupled to electrospray high resolution mass spectrometry. Twenty-one photodegradation products were detected and identified. In addition, ionic chromatography analyses revealed the release of Br^- , NH_4^+ , and NO_3^- at respectively 97, 63 and 35% of the total Br, and N initially present in AMB. Finally, the reusability of the photocatalyst was also tested. After four cycles, the almost complete photodegradation of AMB was achieved showing that Mn-TiO₂ was highly stable. This work brings new physical characteristics on Mn-TiO₂ photocatalyst. Moreover, it is the first study investigating the photocatalytic degradation of recalcitrant AMB drug.

Keywords: Doped semi-conductor, emerging contaminant, Anti-mucolytic, Response surface methodology, Photoproducts, Reusability.

1. Introduction

In recent years, numerous studies have indicated the presence of a new class of molecules in the aquatic environment, known as "emerging pollutants" (Bagheri et al., 2021; Salazar et al., 2020a; Tobajas et al., 2017a). The extent of their threat toward human life, fauna and flora has not yet been completely elucidated, and their recent detection in water, even at very low amounts (Salazar et al., 2020a), has caused toxicity to plants, animals and humans (Abbas et al., 2018; Iqbal, 2016), and represents a new kind of concern that has no regulatory status. The creation of productive strategies for the degradation of this type of pollutants has become an urgent question and a subject of high priority for the researchers. (Salazar et al., 2020b; Tobajas et al., 2017b).

Monitoring of these sources has revealed that these pollutants are related to drugs, pesticides, personal care products, etc. (Yang et al., 2017), which contaminate natural resources such as urban areas, lakes and rivers. Additionally, several pharmaceutical products are not adsorbed significantly in the subsoil because of their polar nature and therefore can infiltrate into groundwater. It is one of the main resources that these pollutants end up in drinking water, which decreases its quality, thus causing waterborne infections (Sousa et al., 2018).

Chronic obstructive pulmonary disease affects approximately 64 million people worldwide, and mortality rates should increase. Estimates for 2030, published by the World Health Organization, predict that chronic obstructive pulmonary disease will become the third leading cause of death worldwide. This inevitably leads to an increase in the consumption of medications, which in turn increases concern about their presence in the aquatic environment and about their potential adverse effects on non-target populations. AMB (trans-4-[(2-amino-3,5-dibromobenzyl) amino] cyclohexanol) is an active ingredient used in the chronic bronchitis prevention (Xu et al., 2015); for complications, such as bronchopulmonary diseases in new borns, hyaline membrane diseases and in antioxidant therapies. Various analytical techniques have been reported for AMB titration in both biological and pharmaceutical samples using liquid chromatography , gas chromatography (Yang et al., 2021), chromatography with amperometric detection (Erady et al., 2019), UV spectrophotometry (Yang et al., 2021) and voltammetry (Zhu et al., 2021). In contrast, little is known regarding its environmental behavior, its degradation (Brüggemann et al., 2003), interaction with other environmental media and extraction method from wastewaters (Beckers et al., 2018; Brüggemann et al., 2003; Zhang et al., 2020). AMB is a biologically recalcitrant substance that for the most part is not degradable in

wastewater treatment plants (Zhang et al., 2020). Due to its persistence, it is important to use other treatments to ensure its elimination from water (Beckers et al., 2018).

Consequently, the main challenge is to improve processing technologies towards new methods that are less harmful, durable, cost effective and non-corrosive to equipment (Bagheri et al., 2021). In this respect, the photocatalysis is an efficient advanced oxidation process (AOP) which offers different advantages such as n ability to apply under ambient temperature and pressure, use to treat emerging pollutants and to achieve their mineralization to the ubiquitous substances like H_2O and CO_2 (Tab et al., 2020). In this respect, TiO_2 is extensively used (Belabed et al., 2014) in many applications, including paints (Fonseca et al., 2021), toothpastes (Liu et al., 2019), UV protection (Xu et al., 2020), photovoltaics, gas sensors as well as electro- and photochromism materials (Li et al., 2017). Moreover, TiO_2 is nontoxic, inexpensive, chemically stable over the entire pH range, and exhibits excellent performance for removing pollution from both water and air under UV light, which accounts for only 5% of the solar radiation (Carvalho et al., 2019; Güy and Özacar, 2016; Khan et al., 2020; Yanalak et al., 2020). However, as dopants, transition metals significantly improve the photocatalytic performance of TiO_2 , limit the recombination of charge carriers and shift the spectral photoresponse toward the visible region (Gu et al., 2020). Several dopants, such as Mn (Ahmed, 2016; Prashad Ojha et al., 2020), Fe (Wang et al., 2009), Ni (Dong et al., 2018), Co (Qian et al., 2019), Cr (Santara et al., 2016) and V (Rossi et al., 2018), have been attempted. According to a theoretical study, most 3d elements tend to induce surface states within the TiO_2 band gap by inserting semiconductors with intermediate bands (Das and Makal, 2020). Therefore, doping is an attractive approach to provide visible light sensitization centres through the formation of band-gap states. Mn has the highest potential for allowing wide

optical absorption in the visible and infrared regions of solar radiation. As a result of the modification of the optical properties, there is adequate charge carrier mobility because the intermediate bands due to Mn doping have a significant band bending. This behavior enables the transmission of visible photons from the valence band (VB) to the conduction band (CB). To our knowledge, neither the structural, morphological, optical and electrochemical properties of Mn-TiO₂ nor its application in photocatalysis have been studied previously.

The main target of this paper was to characterize Mn-TiO₂ as a photocatalyst and to evaluate its performance for the AMB mineralization. This work was the first detailed investigation of the photocatalytic AMB degradation. Photolysis and adsorption of AMB were studied and a multivariate analysis was conducted; In addition, a statistical model was developed in order to simultaneously optimize three factors namely, the catalyst dose, AMB concentration and pH. Powerful analytical techniques such as ultra high performance liquid chromatography (UHPLC)-electrospray ionization (ESI)- high resolution mass spectrometry (HRMS) and ionic chromatography were used to identify intermediates and propose the mechanism of degradation as well as the degree of mineralization during photodegradation. The reusability of Mn-TiO₂ and the mechanism of the photocatalytic degradation were also investigated.

2. Experimental

2.1 Materials and reagents

AMB (Fig. 1 and Table 1) was purchased from Pharmalliance Industry (Algiers) under hydrochloride form and used without any further treatment. Acetonitrile HPLC grade (CH₃ CN, ≥ 99.9%), sodium dihydrogen phosphate anhydrous (NaH₂ PO₄ ,

99.99%), sodium laureth sulfate ($\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OSO}_3\text{Na}$, $\geq 99\%$) and formic acid (CH_2O_2 , 98-100%) potassium hydroxide (KOH, $\sim 45\%$ (T)) and methanesulfonic acid ($\text{CH}_4\text{O}_3\text{S}$, $\geq 99\%$) reagent grade were purchased from Sigma-Aldrich. All solutions were prepared in purified water using a RIOS 5 reverse osmosis and synergy (Millipore) device (resistivity $18\text{ M}\Omega\cdot\text{cm}$, $\text{DOC} < 0.1\text{ mg}\cdot\text{L}^{-1}$). Titanium dioxide powders were obtained from different providers: Eroxide P90 (TiO_2 , $\geq 99.5\%$) and Degussa P25 (TiO_2 , $\geq 99.5\%$) from Evonik, Hombikat UV100 (TiO_2 , 99%) from Sachtleben, anatase (TiO_2 , 99.7%), rutile (TiO_2 , 99.5%) and Mn- TiO_2 (TiO_2 , $\geq 97\%$) from Sigma-Aldrich. Sodium sulfate anhydrous (Na_2SO_4 , $\geq 99\%$), sulfuric acid (H_2SO_4 , 95.0-98.0%) and sodium hydroxide (NaOH, $\geq 98\%$), all these reagents were of analytical grade and purchased from Sigma-Aldrich.

2.2 Characterization of the Mn- TiO_2 catalyst

The X-ray diffraction (XRD), using a Siemens D5000 diffractometer, was conducted to confirm the single phase and to evaluate the mean crystal size (D) of the Mn- TiO_2 nanoparticles. The measurements were performed at room temperature with a Cu $K\alpha$ radiation source ($\lambda = 0.15406\text{ nm}$) operated at 40 kV and an emission current of 30 mA. The crystallites size (D) was evaluated from the broadening (β , rad.) of the strongest XRD peak (101):

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where K (= 0.89) is the shape factor and λ the wavelength of the Cu $K\alpha$ radiation. Scanning electron microscopy (SEM, Hirox SEM SH-4000MB) and transmission electron microscopy (TEM, Hitachi H-7650) equipped with an energy dispersive spectroscopy (EDS) detector were employed to identify the relief and grain dimensions. In regard to the SEM analysis, the sample (Mn- TiO_2) was deposited on a

conductive carbon adhesive. For the TEM observation, the powder was dispersed in deionized water and sonicated for 15 min. Next, 10 μL of the sonicated suspension was deposited on carbon-formvar copper grids and left to dry overnight at room temperature.

The distribution and average size of Mn-TiO₂ particles were determined using Image J software, with a total of 100 particles. The corresponding histogram was obtained with the software Origin 2019. EDS was used for conducting the elemental percentage analysis. The X-ray fluorescence (XRF) spectroscopy was conducted with a Panalytical Axios sequential spectrophotometer, and a rhodium tube was fitted as the source of radiation to achieve complete Mn photocatalyst loading. Pressed pellets were used to perform the XRF measurements, and the sample included 10 wt.% wax. The BET method was employed to calculate the specific surface area using an ASAP2010 Micrometrics instrument and N₂ gas as adsorbent. The UV-visible spectrum of Mn-TiO₂ was recorded with a Varian Cary 500 spectrophotometer attached to an integrating sphere. A PGZ301 potentiostat was used for the electrochemical study, performed in a three-electrode cell containing Na₂SO₄ solution (10⁻¹ mol.L⁻¹) as support electrolyte with the working electrode (Mn-TiO₂), an auxiliary Pt electrode and a saturated calomel electrode (SCE) as the reference. The intensity-potential J(E) characteristics were plotted at room temperature at a scanning rate of 10 mV.s⁻¹.

2.3 Photocatalytic degradation experiments

The experiments were performed under UVA irradiation; the source was provided by a fluorescent tube (Philips HPK 15 W) emitting in the near UV region (maximum: 365 nm). Mn-TiO₂ powder and 15 mL of AMB solution were introduced in the cylindrical Pyrex reactor (13.5 cm height and 1.9 cm internal diameter) that was

thermoregulated at 25 °C by water circulation in a water jacket to preclude vaporization. The suspension was agitated in the dark for 2 h to reach adsorption equilibrium and illuminated under UVA for 30 min. The degradation was studied under various conditions by varying the pH of the solution, the initial AMB concentration (C_0) and the Mn-TiO₂ dose. H₂SO₄ and NaOH (0.1 mol.L⁻¹) were used for adjusting the pH. Aliquots were regularly withdrawn, vigorously centrifuged (3000 rpm, 5 min) and filtered through a 0.45 µm filter (Waters, Millipore) before analyses.

2.4 Analytical determination

2.4.1 HPLC-UV

The concentration of AMB was determined using a Shimadzu 8040 HPLC system consisting of LC-20AD-XR binary pumps, an SIL-20ACXR autosampler, a SPD-M30A diode array detector, a DGU-20A3 degasser, a CTO-20AC column furnace, an FCV-20AH2 and laboratory solutions Shimadzu software. Analytical separation was performed using a Nucleodur 100-3 C₁₈ end-capped column (125 mm×4.0 mm, 3 µm particle size). The mobile phase was a mixture of (A) 50 mmol.L⁻¹ NaH₂ PO₄ , 5 mmol.L⁻¹ CH₃(CH₂)₁₀CH₂(OCH₂CH₂)_nOSO₃Na and (B) CH₃ CN. The gradient program started with 15% B from 0 to 5 min, 38% B from 5 to 10 min and 45% B from 10 to 17 min at a flow rate of 0.75 mL.min⁻¹. The detection wavelength, injection volume and column oven temperature were 248 nm, 20 µL and 30 °C, respectively.

2.4.2 Ionic Chromatography

205 A ThermoScientific Dionex ICS-5000 instrument equipped with a conductometer
206 detector was employed for ion analysis. A Thermo Scientific Dionex Ion Pac AS11
207 HC (50 mm×4 mm) column and KOH, as eluent, were used to analyze the anions at
208 0.25 mL.min⁻¹ and 30 °C. For the NH₄⁺ analysis, a Thermo Scientific Dionex Ion Pac
209 CS16 HC column (50 mm×3 mm) and CH₄O₃S as eluent were used at a flow rate of
210 0.36 mL.min⁻¹ and 40 °C.

211 **2.4.3 UHPLC-ESI-HRMS**

212 HRMS was performed on an Orbitrap Q-Exactive (Thermoscientific) coupled to an
213 UHPLC instrument Ultimate 3000 RSLC (Thermoscientific). The mass spectrometer
214 with heated ESI was operated in both positive and negative ESI modes with a spray
215 voltage of 3 kV for both modes. The column was a Waters analytical column (2.1
216 mm×100 mm, 1.7 µm particle size) and the column oven temperature was regulated at
217 30 °C. The aqueous phase (A) was a mixture of 0.1% CH₂ O₂ - CH₃ CN as the
218 organic phase (B). The separation was realized with a gradient program that consisted
219 of 5% and 99% of the mobile phase B from 0-7.5 and 7.5-8.5 min, respectively. The
220 injection volume was 5 µL, and the flow speed was fixed at 0.450 mL.min⁻¹. The
221 system was monitored by the Xcalibur 2.2 Thermo Fisher Scientific software.

222 **2.4.4 TOC analysis**

223 A Shimadzu 5050 TOC analyzer was used to monitor the mineralization of AMB. The
224 percentage of mineralization was calculated using the following equation:

$$225 \quad \text{Mineralization} = \frac{(OC_0 - OC_t)}{OC_0} \times 100$$

226 (2)

227 where OC₀ is the organic carbon present in the solution at the initial time and OC_t at
228 time t. OC is obtained by subtracting the inorganic carbon from the total carbon.

229 **2.5 Multivariate experimental design**

Based on the method of single factor analysis, preliminary tests were initially conducted to determine the ranges of the most prominent experimental parameters influencing the AMB photodegradation. RSM was used to analyze the interactions among the AMB concentration, Mn-TiO₂ dose and pH during photodegradation and to study their simultaneous effects. To assess the combined influence of the independent variables (AMB concentration, Mn-TiO₂ dose and pH) on two responses using 15 sets of experiments, the Box-Behnken method of experiments was adopted. The response factor (Y) corresponding to AMB depletion (percent) after irradiation for 30 min, as shown in Table 2, displays the ranges and levels of the independent variables.

The Box-Behnken design was used because it is very effective and does not have any point created by the upper and lower limits of the variables at the vertices of the cubic region. It has been commonly used to optimize different physical, chemical and biological processes that have used RSM (Zhang Junwei et al., 2010). To obtain the experimental matrix and to draw the response surface, the JMP8 (Statistical Discovery™ from SAS) statistical program was used.

3. Results and discussion

3.1 Comparison of the photocatalytic activities of Mn-TiO₂ and other photocatalysts

The photocatalytic activity of Mn-TiO₂ was compared to that of other TiO₂ types, namely, P25, UV100, P90, rutile and anatase, by measuring the loss of AMB against the irradiation time under UVA light (Fig. 2). Mn-TiO₂ exhibits the highest of photodegradation with an abatement of 99% after 30 min of irradiation, followed by P25, P90, anatase, UV100 and rutile with 60, 51, 46, 38 and 12% abatement,

respectively. The degradation rate was thus 1.65 times faster with Mn-TiO₂ than with P25 under UVA light. Previous studies on synthesized Mn-TiO₂ photocatalysts showed photocatalytic activities, two times higher than TiO₂ P25 (Park et al., 2012). Moreover, Mn-TiO₂ is also photoactive under visible light (Oseghe et al., 2015). This could be explained by the fact that doping improved the optical and photoelectrical properties of TiO₂. Indeed, doping led to a redshift of Mn-TiO₂ absorption toward the visible region (Oseghe et al., 2015). The high performance of both commercial and synthesized Mn-TiO₂ (Park et al., 2012) could be explained by the existence of sub-band-gap states for effective excitation under irradiation by low energy photons, thus extending the lifetime of charge carriers by providing a longer diffusion length before the recombination of (e-/h⁺) pairs (Oseghe et al., 2015). No detailed studies were carried out for the selected catalyst (Mn-TiO₂); thus, we conducted several characterizations to understand its performance.

3.2 Mn-TiO₂ characterization

The XRD analysis was used to characterize the crystal structure, and the corresponding pattern is shown in Fig. S1. According to JCPDS No. 65-5714, the characteristic peaks at 29.47, 43.18, 44.18, 45.10, 56.41, 63.49, 64.93, 73.6, 74.32, 81.96, 83.89, 88.74, 90.29, 91.32, 97.56, 99.47, 100.17 and 100.82° are assigned to the anatase-phase TiO₂ (space group I4₁/amd) correspond to the reflections from (101), (103), (004), (112), (200), (105), (211), (213), (204), (116), (220), (107), (215), (301), (008), (303), (224), (312) crystal planes of the tetragonal TiO₂ structure. The respective measured *d*-spacings are: 3.51, 2.43, 2.37, 2.33, 1.89, 1.70, 1.66, 1.49, 1.48, 1.36, 1.33, 1.28, 1.26, 1.25, 1.19, 1.17, 1.16 and 1.15 Å.

On the other hand, the particle size of the catalyst (*D*= 37 nm) was calculated from the full width at half maximum by using the acquired data from the XRD pattern. The

broadening of the peaks suggests a smaller size of Mn-TiO₂ crystals, which is also confirmed by the SEM and TEM images. The mean particle size correlates well with the BET and TEM analysis (Table S1) which also evaluate the structural morphology of nanocatalyst along with determination of size of its particles.

The SEM micrographs (Fig. 3a and b) revealed that the particles have nanoscale sizes and seem spherical in general. To better explore the particle size distribution and to study the morphology of the photocatalyst, TEM was also performed. Fig. 3c and d clearly show that Mn-TiO₂ was formed from crystallites with spherical and uniform forms in agreement with the results obtained for the Mn-TiO₂ nanoparticles (Prashad Ojha et al., 2020). The nanospheres were homogeneously dispersed with no segregation phenomenon (Fig. 3c and d). The dark areas of the TEM images could be explained by the high electron density (Molnárová et al., 2020). The crystallite size distribution (histogram, Fig. 4a) was plotted from TEM analysis images, and a mean size of 30 nm was calculated with diameters in the range (25-35 nm) for more than 50% of the particles. Moreover, these acquired results are in good agreement with the BET analysis. The Energy-dispersive X-ray (EDS) spectrum accompanied by the relative weight (%) and atomic (%) of elements were studied to assess the elemental composition of the photocatalyst. Based on the EDS analysis, Table S1 shows the elemental composition of the catalyst. As presented in Fig. 4b, all elements exist by their signals, including Ti, O and Mn. The elemental analysis confirmed that 1% Mn was introduced and revealed that Mn²⁺ ions were inserted in the Ti⁴⁺ sub-lattice owing to their ionic radii, 0.061 and 0.090 nm, respectively. Finally, the difference in the atomic ratio may be based on the local analysis with the EDS technique.

The XRF analysis allowed us to deduce the elemental composition i.e. the mass concentrations of elements. The XRF analysis provided the total Mn loading on the

photocatalyst (Table S2). Both the EDS and XRF analyses clearly show that TiO₂ are successfully doped by the hetero-valent ion Mn²⁺.

According to the supplier, the surface area of Mn-TiO₂ could be > 14 m².g⁻¹. From our BET analysis, it was deduced that the exact specific surface area was 37 m².g⁻¹ (Fig. S2), an attractive property for photocatalysis. Comparing this specific surface area (37 m².g⁻¹) to those of other TiO₂ (Table S1), Mn-TiO₂ had the smallest value, which revealed that it was not the only factor influencing the photoactivity.

The diffuse reflectance was used to investigate the optical properties of Mn-TiO₂. The diffuse reflectance spectrum is shown in Fig. S3. The band gap value is 2.88 eV (= 1240/λ). Using the diffuse reflectance data, the gap E_g (Eq. 3) was obtained with a direct transition, and its value was reliably determined from the well-known formula:

$$(\alpha h \nu)^m = \text{Constant} \times (h\nu - E_g) \quad (3)$$

where α and ν are the optical absorption coefficient and the light frequency, the exponent m provides information about the transition type. Compared to pure TiO₂ anatase in the literature, the spectral photoresponse is shifted toward longer λ values. This result could be due to the appearance of electronic states within the band gap (sub-band-gap states) explained by the gap decrease due to the quantum effect (H. Y. Liu et al., 2020). Consequently, the distance of charge transfer between the valence or conduction band of TiO₂ and Mn-3d electrons is shortened, leading to a visible light absorption response.

To our knowledge, only few papers have reported on the photo-electrochemistry of Mn-TiO₂ (Ning et al., 2016); thus, an in-depth electrochemical study was undertaken. The current density-potential J(E) characteristics were plotted in the range of -1 to 1 V_{RHE} in Na₂SO₄ solution (pH ~ 7) at a scan rate of 10 mV.s⁻¹ to elucidate the

interfacial reactions and to delimit the electrochemical stability (Fig. 5a). The experiments were performed once the open-circuit potential stabilized. The photocurrent (J_{ph}) starts to flow at a potential of $E_{on} \sim 0.01 V_{RHE}$ (Fig. 5a) and increases in the anodic direction, indicating the *n*-type nature of Mn-TiO₂. However, the recombination of electron/hole (e^-/h^+) pairs at the trapping levels and/or grain boundaries was evidenced by the lack of current saturation. The capacitance potential (C^{-2} -E) plot (Fig. 5c) provides an accurate flat-band potential of $E_{fb} = -0.84 V_{RHE}$ and an electron concentration $N_D = 1.9 \pm 0.1 \times 10^{16} \text{ cm}^{-3}$ from the intersection of the potential axis at infinite capacity ($C^{-2} = 0$) and the slope of the linear part:

$$C^{-2} = \pm \frac{(2/S^2 e \epsilon \epsilon_0 N_D) \{E - E_{fb}\}}{(4)}$$

where ϵ_0 is the permittivity of vacuum, ϵ ($= 98$) the permittivity of Mn-TiO₂ (B. Liu et al., 2013), e the electron charge and S the geometric surface area of Mn-TiO₂. The *n*-type behavior of Mn-TiO₂ is supported by the positive slope of the (C^{-2} - E) plot.

In regard to the quantification of the electrical contributions at the Mn-TiO₂/electrolyte interface, electrochemical impedance spectroscopy (EIS) was performed. The EIS data of the Mn-TiO₂/Na₂SO₄ junction were obtained at the open-circuit potential (Fig. 5d). The semicircle at high frequencies is assigned to the bulk effect whose center is positioned below the real axis. The depletion angle accounted for the non-ideal component of the capacity attributed to the sub-band-gap states and rugosity of the electrode, which introduce a constant phase element (CPE):

$$Z_{CPE} = Q^{-1} / (j\omega)^k \quad (5)$$

where Q is independent of the frequency, j the complex number ($j^2 = -1$), ω the angular frequency, and k the homogeneity factor ($0 < k \leq 1$). The displacement from

the origin is equal to the electrolyte resistance ($R_{el} = 105 \Omega \cdot \text{cm}^2$) due mainly to the molar conductivity of the most mobile ion H^+ ($350 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$).

3.3 Adsorption of AMB on Mn-TiO₂

Fig. S4a shows the amounts of AMB adsorbed per gram of Mn-TiO₂ (Q_t) vs. the contact time, the equilibrium was reached after 2 h of stirring. The adsorption can be described by the Freundlich model (Eq. 6) (Bekkouche et al., 2012; Ghosh et al., 2019; Malakootian et al., 2020; Pal et al., 2016)

$$Q_e = K_F C_e^{1/n} \quad (6)$$

The linearization of Eq. (6) indicates the relationship between $\ln Q_e$ and $\ln C_e$ (Eq. 7).

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

where $Q_e = (C_0 - C_e) \times V/m$ represents the adsorbed quantity of AMB per unit of mass of Mn-TiO₂ ($\text{mg} \cdot \text{g}^{-1}$), C_e the AMB concentration at equilibrium ($\text{mg} \cdot \text{L}^{-1}$) and K_F is the Freundlich coefficient. The coefficient n is related to the adsorption mechanism.

Fig. S4b shows that good linearity is obtained by plotting $\ln Q_e$ against $\ln C_e$. The constants K_F and $1/n$ deduced from the intercept and the slope are listed in Table S3.

K_F is equal to 0.54 and $n = 4.24$. The value $1/n < 1$ corresponds to a L-shape that refers to a decrease in the site availability as the concentration of the drug increases. As shown in Table S3, the adsorption coverage and the adsorption constant of AMB on Mn-TiO₂ are small compared to those of other phenolic derivatives on other TiO₂ photocatalysts (Bekkouche et al., 2012; Pal et al., 2016). This result could be explained by the weak interaction AMB (adsorbate)-Mn-TiO₂ (adsorbent) (Bekkouche et al., 2012; Pal et al., 2016).

3.4 Kinetics of photocatalytic degradation

Fig. S5a compares the loss of AMB vs. time in the absence of Mn-TiO₂ (photolysis), in the presence of Mn-TiO₂ (adsorption) and in the presence of Mn-TiO₂ upon irradiation (photocatalysis). While the AMB concentration remains almost unchanged after 30 min of irradiation (< 3% degradation) in photolysis and decreases by 10% through the dark adsorption, a complete degradation (> 95%) is achieved by photocatalysis. For most organic compounds (Arshad et al., 2020; Ghenaatgar et al., 2019), the photodegradation rate follows a pseudo-first order (Fig. S5b) model and can be linearized as (8):

$$\ln \frac{C_t}{C_0} = -k_{app} \times t \quad (8)$$

where k_{app} (min⁻¹) is the apparent first-order rate constant and C_t and C_0 are the AMB concentrations at time t and after dark adsorption, respectively. Fig 10b confirms the pseudo-first-order kinetics for AMB with a high correlation coefficient R^2 (> 0.995).

3.5 Construction of the polynomial expression and 3D response surface

3.5.1 Statistical analysis

A three-variable Box-Behnken design was used to optimize the AMB photocatalytic degradation on Mn-TiO₂. This design was chosen owing to its productivity and involves only a limited number of experiments. The spherical design contains all points that lie on a two-square root radius sphere. There are no points on the vertices of the cubic area generated by the lower and upper limits of every variable (Ray et al., 2009). The polynomial equation of the empirical second order was generated for AMB elimination % (Table 2) as the response variable with three independent variables:

$$\begin{aligned}
& Y = 97.92 + 3.10X_1 - 19.55X_2 + 1.23X_3 + 2.99X_1X_2 + 1.26X_1X_3 + 0.47X_2X_3 - \\
& 3.92X_1^2 - 16.3X_2^2 - 4.24X_3^2 \\
& (9)
\end{aligned}$$

where Y represents the AMB removal (%) and X_1 , X_2 and X_3 are the coded values of the Mn-TiO₂ dose, initial AMB concentration and pH respectively. Using variance analysis, the experimental data were analyzed for AMB removal from a statistical point of view. The ANOVA for the responses of the second-order quadratic polynomial indicated that this model was very significant, as the F-value for the 1044.693 model and the corresponding *p*-value was small (< 0.0001). This result indicated that, regardless of noise, there is only 0.01% probability of the variable F-value occurring. The lack of fit should be negligible for this model to be widely used for producing predictions. The determination of the coefficient was explained as the ratio of the variation, which showed that the total variation could be used as a measurement of the model degree of fitting. The expected R^2 value (= 0.998) is in good agreement with the corresponding modified R^2 value (= 0.996). The R^2 value must be close to 1 for the best fitting of the experimental results. The smaller the R^2 value is, the lower the model adaptation to the experimental data. The R^2 values showed that the quadratic polynomial (Mona et al., 2011) was used to forecast the experimental degradation of AMB. The AMB removal was plotted against the corresponding observed values in Fig. S6.

In the event of AMB degradation, the independent variables of the quadratic polynomial X_1 and X_2 , the interaction of the Mn-TiO₂ dose (X_1)/AMB concentration C_0 (X_2), X_1X_2 and the quadratic terms X_1^2 , X_2^2 and X_3^2 are very significant, as their *p*-values are smaller than 0.001.

From the regression coefficients, the order for which the independent variables influenced AMB degradation is as follows: initial AMB concentration (X_2) > Mn-TiO₂ dose (X_1) > pH (X_3). The positive effects of X_1 and X_3 are very low compared to the negative effect of X_2 , which agree with the reports of the preliminary experiments. Thus, the AMB concentration (C_0) is the dominant factor influencing the AMB photodegradation on Mn-TiO₂. This result is found to efficiently generate oxidizing species such as hydroxyl radicals ($\bullet$ OH).

3.3.2 Response surface methodology

Using RSM, the effects of independent variables (the Mn-TiO₂ dose, AMB concentration and pH) and their interaction on AMB degradation were graphically illustrated by three-dimensional response surface plots and two-dimensional contour plots. The responses were provided, and the optimal photodegradation percentage was studied (Zhang Junwei et al., 2010). The interaction effect of the dose of Mn-TiO₂ and concentration C_0 on the degradation rate is shown in Fig. 6a. which shows that the degradation percentage of AMB diminished with increasing concentration C_0 . As shown from the contour diagram (Fig. 6b), a maximal photodegradation was observed in the concentration range (10 – 30 ppm). The AMB photodegradation increased with an increasing the Mn-TiO₂ amount until an optimal value of 0.7 g.L⁻¹, after which it remained almost constant, regardless of the dose of the photocatalyst. According to the contour plots, the maximum photodegradation occurred in the region (0.6 - 1 g.L⁻¹). Fig. 6c shows the influence of the concentration C_0 (AMB) and pH on the photodegradation kinetics. According to Fig. 6d and as expected, the photodegradation increased slightly with pH regardless of the concentration of AMB, and the maximum region occurred in the pH region (6-8). Likewise, the augmentation in initial AMB concentration indicated a diminution in the photodegradation rate.

Moreover, the maximum domain is in the range (10–30 ppm), which is feasible at higher AMB concentrations. The effects of the pH and Mn-TiO₂ dose on the rate of AMB removal are shown in Fig. 6e. One can see that the photodegradation rate slightly increased with increasing pH up to pH 8 and then slowly decreased at high catalyst doses. From the contour plot (Fig. 6f), the maximum domain was in the range (0.6 - 0.9 g.L⁻¹) of the Mn-TiO₂ dose and pH of 7-8.

3.5.3. Optimization of the independent variables and the validation experiment

Any reaction system needs to be optimized using various analytical techniques and design methodologies to achieve optimal operating conditions and yield the best result. In this study, efforts have been focused on maximizing the AMB concentration C₀ to keep the pH as close as possible to a natural pH and to limit the amount of catalyst used. A Mn-TiO₂ dose of 0.7 g.L⁻¹, an AMB concentration of 37.7 ppm and a pH of 7.7 for the aqueous suspension were found to be optimal for the photodegradation under the mentioned constraints. According to these conditions, the RSM predicted the photodegradation rate of AMB of 90%. The results clearly indicated the efficient utilization of RSM to optimize the photocatalytic degradation on Mn-TiO₂ (Moztahida and Lee, 2020). Given these conditions, the model provided a photodegradation abatement of 89%. The results showed the efficiency of the RSM (Moztahida and Lee, 2020) for determining the optimal parameters of AMB degradation on Mn-TiO₂ under UVA light.

To verify and validate the model accuracy, AMB photodegradation was performed in batch mode under optimal conditions. From the validation experiments, the photodegradation reached 89%, a result in perfect accordance with the predicted results. Consequently, the successful calculation of the optimum point was

demonstrated by RSM. This technique could be employed for the optimization of the photocatalytic degradation of AMB in the presence of Mn-TiO₂.

3.6 Photocatalytic activity of Mn-TiO₂ under optimized conditions

3.6.1 Involvement of hydroxyl radicals in the reaction

AMB can be oxidized by valence band h^+ or by $\bullet$ OH radicals, a degradation by poorly oxidant $O_2^{\bullet-}$ appearing very unlikely. Indeed, aromatic pollutants are generally reactive with both species, and the addition of alcohols at moderate concentration is a way to selectively inhibit the free $\bullet$ OH-mediated processes (Amine-Khoja et al, 2005). Ethanol (10^{-2} - 10^{-1} mol.L⁻¹) was used to quench these species and added to the mixture containing AMB and Mn-TiO₂. Fig S7 shows that ethanol inhibited the photocatalytic degradation of AMB by 54 % at 10^{-2} mol.L⁻¹ and by 90-95% at 5.10^{-2} mol.L⁻¹ and above. If we make the hypothesis that until 10^{-2} mol.L⁻¹ ethanol only scavenged free $\bullet$ OH, then one can conclude that AMB was mainly oxidized by $\bullet$ OH whereas h^+ only played a secondary role in the reaction. The significant contribution of $\bullet$ OH to the reaction here using Mn-TiO₂ was previously reported with TiO₂ Wackherr (Soji et al., 2011). but not observed with TiO₂ Degussa P25 (Soji et al., 2011). A plausible explanation of this result may come from the different compositions of the catalysts, as both TiO₂ Wackherr and Mn-TiO₂ crystallizes exclusively in the anatase variety, whereas TiO₂ Degussa P25 consists of 85% anatase and 15% rutile (Vione et al., 2005). This may suggest that the presence of the rutile phase affected the contribution of h^+ in the photocatalytic process. Nevertheless, the connection between the degradation pathways and crystalline phase needs supplementary studies.

3.6.2 Photoproducts studies

3.6.2.1 Identification of the AMB transformation products (TPs)

One of the goals in this work was to optimize the photocatalytic degradation of AMB based on the kinetic parameters, but the identification of TPs was also of high importance because in some cases, the degradation products are more hazardous than the parent compound (Bansal and Sud, 2013). To consider this issue, UHPLC-HRMS analyses were carried out. Solutions withdrawn after 10 min (30% of AMB conversion), 30 min (95% of AMB conversion) and 4 h of irradiation were analyzed and 21 TPs were detected, as listed in Table S4. Table S4 indicates in which ESI mode, positive or negative, the TPs were detected, along with the experimental and theoretical m/z values of the detected ions, error in ppm, chemical formula of the neutral TP and possible structure. The tolerance error value of m/z was 5 ppm.

AMB had a molecular ion cluster of $m/z = 376.9860/378.9825/380.9800$ with an isotope distribution of 1:2:1, in accordance with the two isotopes of Br (78.9178 and 80.9157) with natural abundances of 50.5 and 49.5%. TP1, TP2 and TP3 showed the same three ion clusters with $m/z = 392.9788/ 394.9782/ 396.9762$, $m/z = 377.9620/ 379.9658/ 381.9598$ and $m/z = 263.8754/ 265.8644/ 267.8629$, respectively. These samples had therefore kept the two Br atoms. TP1 gained one O atom compared to AMB, while in TP2, NH_2 was replaced by OH, and TP3 was formed following cleavage of the aliphatic substituent. Given their two ion clusters with $m/z = 315.0689/ 317.0669$ and $m/z = 313.0542/ 315.0520$, and their isotope distribution of 1:1, TP4 and TP5 were identified as monobrominated derivatives. Based on the probable chemical formulas $\text{C}_{13}\text{H}_{19}\text{O}_2\text{N}_2\text{Br}$ and $\text{C}_{13}\text{H}_{17}\text{O}_2\text{N}_2\text{Br}$, one could conclude that TP4 was generated after the loss of Br and the gain of OH and TP5 after the loss of Br and 2 H atoms and the gain of OH. The other TPs detected were all debrominated. TP6 with $m/z = 267.1335$ corresponded to $\text{C}_{13}\text{H}_{18}\text{O}_4\text{N}_2$, which

indicates the replacement of two Br atoms by two OH groups and the addition of one O atom.

Photoproducts TP7 to TP12 showed m/z values between 186.1126 and 114.0913 and contained between 9 and 6 C atoms and 11 to 17 H atoms; thus, these TPs could be assigned to aminocyclohexanol ($C_6H_{11}ON$) derivatives formed following the detachment of the aromatic ring. TP11 might correspond to aminocyclohexanol, and TP12 to aminocyclohexanone. With $C_9H_{17}O_3N$, $C_8H_{15}O_3N$ and $C_7H_{13}O_3N$, TP7, TP8 and TP9 differed by CH_2 and could be assigned to aminocyclohexanols with $-(CH_2)_2-CO_2H$, $-CH_2-CO_2H$ and CO_2H substituents on NH. TP13 and TP14 with $m/z = 134.1174$ and 128.0340 likely had chemical formulas of $C_6H_{15}NO_2$ and $C_5H_7NO_3$ and were formed by opening the cyclohexane ring. The other TPs with m/z ranging from 128.0340 to 59.0127 contained between 6 and 2 C atoms and corresponded to small molecules often detected after photodegradation of aromatic compounds (Y. Liu et al., 2013).

For comparison, UHPLC-HRMS analyses of AMB irradiated in the presence of TiO_2 Degussa P25 were carried out. They were also carried out at two conversion extents: 30 and 95%. TP1-TP14 were detected as for Mn- TiO_2 , and two new degradation products were detected in ESI^+ . With $m/z = 374.9702$, 376.9682 , 378.9661 and $m/z = 372.9544$, 374.9522 , 376.9501 , these compounds correspond to $C_{13}H_{16}ON_2Br_2$ and $C_{13}H_{14}ON_2Br_2$ for the neutral molecules and thus to the elimination of 2 and 4 H atoms respectively.

3.6.2.2 Mineralization process

CO_2 results from the ultimate photodegradation of organic compounds in photocatalysis, and its monitoring provides information about the real efficiency of

the photocatalytic process. The profile of CO₂ formation under irradiation is shown Fig. S8. After 30 min of irradiation corresponding to complete AMB loss, approximately 5% of the initial organic carbon was converted into CO₂, meaning that at this stage, AMB was essentially transformed into intermediary products. Total mineralization (> 96%) was achieved after 24 h of irradiation. Moreover, AMB contains two Br atoms and two amino groups; hence, Br⁻, NH₄⁺ and/or NO₃⁻ ions might also be generated during degradation (Ganzenko et al., 2020). The formation of these three ions was monitored by ionic chromatography. Data are presented in Fig. S8. after 12 h of irradiation. After 12 h of irradiation, at least 97% of the Br atoms were released in solution as Br⁻ and the concentration of NH₄⁺ reached a plateau at 63% of the total N initially present in AMB, while the concentration of NO₃⁻ was at 15% and increased progressively until 35% at 24 h. Further oxidation of NH₄⁺ into NO₃⁻ appeared possible. These data showed that Mn-TiO₂ was efficient as a photocatalyst in the elimination and full mineralization of AMB.

3.6.2.3 Photodegradation mechanism of AMB

The main degradation pathways under Mn-TiO₂ are summarized in Scheme 1. Based on the TP structures, it can be supposed that the attack of AMB by •OH initially led to the replacement of Br by OH (Xu et al., 2011) and of NH₂ by OH (Li et al., 2019), along with the oxidation of the aromatic ring or cyclohexanol ring and the cleavage of the C-C bond linking the aromatic to the aliphatic chain. The presence of three C atoms linked to N in TP7 showed that one of the C atoms came from the aromatic ring. TP7 was thus generated by cleavage of the aromatic ring. Further oxidations induced the cleavage of the aromatic and cyclohexanol rings to form small carboxylic acids and carbonyls before full mineralization.

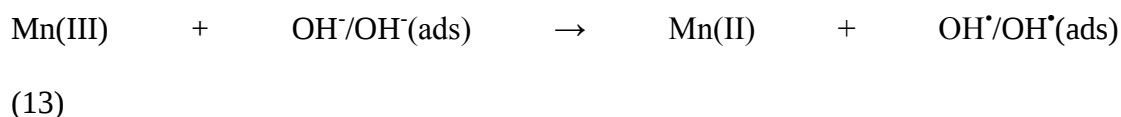
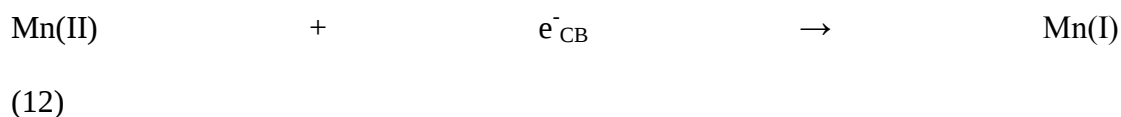
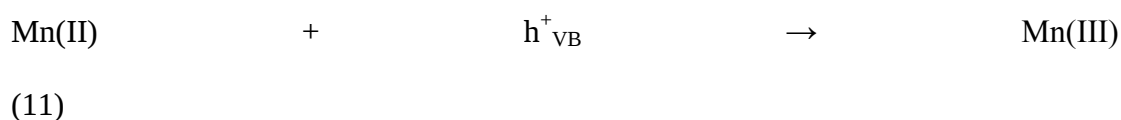
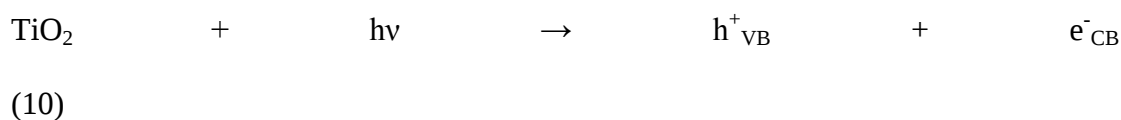
3.7 Reusability of the catalyst

From the economic and practical point of view, the recyclability and stability of the catalyst is one of the main concerns that has a high impact for its application during the degradation process (Ong et al., 2018). We thus studied the stability of Mn-TiO₂ by carrying out 4 successive photocatalytic cycles. Between each cycle, the suspension containing the photocatalyst was centrifuged, collected, thoroughly rinsed with deionized water and dried at 100 °C for 24 h. Moreover, the structure and composition of Mn-TiO₂ after reuse were reanalyzed by XRD, TEM and SEM to check the stability of the oxide. A very good efficiency was obtained even after 4 cycles, with each lasting 30 min. The photodegradation performance was nearly unchanged with an abatement close to 100% (Fig. 7a). These results imply that the intermediates were not adsorbed either on the surface or in the pores and channels of the catalyst. According to the XRD pattern (Fig. 7b), SEM image (Fig. 7c) and TEM analysis (Fig. 7d), there were no detectable changes in the structure and composition compared to the analysis performed before photocatalysis. Such results provided clear proof of the high photocatalytic performance and chemical stability of the used Mn-TiO₂.

3.8 Mechanism of $\cdot\text{OH}$ formation from the Mn-TiO₂ photocatalyst

Scheme 2 shows the proposed mechanism. Mn has modified the photoelectric properties of TiO₂ by producing an intermediate Mn 3d-O 2p energy level within its energy gap. Above the valence band edge in Mn-TiO₂, an intermediate energy level improves the separation of (e^-/h^+) pairs to facilitate the electron transfer and narrows the optical band gap to absorb more light by shifting the spectral photoresponse toward longer wavelengths. The half-filled electronic structure of Mn²⁺ enhances the photocatalytic activity because of its electronic configuration 3d⁵, which changes to d⁴ when accepting h⁺ and to d⁶ upon receiving electrons (Y. Liu et al., 2020). The energy

level of the couple $\text{Mn}^{2+}/\text{Mn}^{+}$ is below the conduction band edge, while that of $\text{Mn}^{2+}/\text{Mn}^{3+}$ is above the valence band of TiO_2 (Zhang et al., 2012). Consequently, Mn(II) can trap both h^{+} and electrons to assist the charge transfer process in TiO_2 (Eqs. (10) -(12)). Mn(III) is formed by oxidation of Mn(II) by h^{+} through a valence band process, and then free hydroxyl OH^{-} is quickly adsorbed and reacts with unstable Mn(III) to produce adsorbed $\bullet\text{OH}$ (Eq. (13)), which confirms that $\bullet\text{OH}$ plays the main role in the AMB degradation, a result in agreement with the effect of ethanol. These reactions contribute to the charge's separation, which improves the photocatalytic efficiency according to the following sequences:



4. Conclusion

In this work, a complete investigation was carried out for the characterization of Mn-TiO_2 and its application for the photodegradation of AMB, which has not been studied before. The optimization of parameters affecting the photodegradation process was conducted and the radicals, photoproducts, mineralization and stability of the material were evaluated. We have demonstrated that Mn-TiO_2 displayed a good photocatalytic activity and structural stability. The morphology, structural and optical

properties of the Mn-TiO₂ nanocomposite were investigated. The optimal parameters of the initial AMB concentration, Mn-TiO₂ dose and pH assessed by the response surface methodology and contour plots were 0.625 g.L⁻¹, 30 ppm, and 7 respectively. At these optimal parameters, a complete photodegradation was achieved after 30 min of irradiation. The degradation kinetic obeyed a pseudo-first-order model. A high determination coefficient ($R^2 = 0.998$ and $\text{Adj-}R^2 = 0.996$) was obtained by the variance analysis, thus ensuring a satisfactory adjustment of the second-order regression model with the experimental results. Trapping experiments have demonstrated that hydroxyl radicals were the main active oxidant species. The UHPLC-ESI-HRMS and ionic chromatography techniques showed that the photocatalytic process could be used for a complete mineralization. Finally, the reusability of the photocatalyst for 4 consecutive cycles was shown. Such results provided proof of the high photocatalytic performance and chemical stability of Mn-TiO₂ which is also attractive from an economic point of view. Studies on other heterojunctions or even other catalysts based on this material are in progress, and many applications are being targeted in addition to those in pollutant elimination (e.g., antibacterial activity and H₂ production and storage).

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