Photocatalytic degradation pathway of methylene blue in water

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Abstract

The TiO\textsubscript{2}/UV photocatalytic degradation of methylene blue (MB) has been investigated in aqueous heterogeneous suspensions. In addition to a prompt removal of the color, TiO\textsubscript{2}/UV-based photocatalysis was simultaneously able to oxidize the dye, with an almost complete mineralization of carbon and of nitrogen and sulfur heteroatoms into CO\textsubscript{2}, NH\textsubscript{4}\textsuperscript{+}, NO\textsubscript{3}\textsuperscript{−} and SO\textsubscript{4}\textsubscript{2−}, respectively. A detailed degradation pathway has been determined by a careful identification of intermediate products, in particular aromatics, whose successive hydroxylations lead to the aromatic ring opening. These results suggest that TiO\textsubscript{2}/UV photocatalysis may be envisaged as a method for treatment of diluted waste waters in textile industries. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

About 15% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents [1]. The release of those colored waste waters in the ecosystem is a dramatic source of non-aesthetic pollution, eutrophication and perturbations in the aquatic life. As international environmental standards are becoming more stringent (ISO 14001, October 1996), technological systems for the removal of organic pollutants, such as dyes have been recently developed. Among them, physical methods, such as adsorption [2], biological methods (biodegradation) [3,4] and chemical methods (chlorination, ozonation [5]) are the most frequently used.

Among the new oxidation methods or advanced oxidation processes (AOP), heterogeneous photocatalysis appears as an emerging destructive technology leading to the total mineralization of most of the organic pollutants [6–12], following the usually proposed mechanism.

1. Absorption of efficient photons ($h\nu \geq E_G = 3.2$ eV) by titania

\begin{equation}
\text{(TiO}_2\text{)} + h\nu \rightarrow e^-_{CB} + h^+_{VB}
\end{equation}

2. Oxygen ionosorption (first step of oxygen reduction; oxygen’s oxidation degree passes from 0 to $-1/2$)

\begin{equation}
(O_2)_{ads} + e^-_{CB} \rightarrow O_2^-\text{•}
\end{equation}
3. Neutralization of OH\(^{-}\) groups by photoholes which produces OH\(^{\ddagger}\) radicals

\[
(H_2O \leftrightarrow H^+ + OH^-)_{ads} + h_{VB}^+ \rightarrow H^+ + OH^\ddagger (3)
\]

4. Neutralization of O\(_2\)^\(-\) by protons

\[
O_2^\circ^- + H^+ \rightarrow HO_2^\circ (4)
\]

5. Transient hydrogen peroxide formation and dismutation of oxygen

\[
2HO_2^\circ^- \rightarrow H_2O_2 + O_2 (5)
\]

6. Decomposition of H\(_2\)O\(_2\) and second reduction of oxygen

\[
H_2O_2 + e^- \rightarrow OH^- + OH^- (6)
\]

7. Oxidation of the organic reactant via successive attacks by OH\(^{\ddagger}\) radicals

\[
R + OH^\ddagger \rightarrow R^\ddagger + H_2O (7)
\]

8. Direct oxidation by reaction with holes

\[
R + h^+ \rightarrow R^\circ \rightarrow \text{degradation products} (8)
\]

As an example of the last process, holes can react directly with carboxylic acids generating CO\(_2\)

\[
RCOO^- + h^+ \rightarrow R^\ddagger + CO_2 (9)
\]

A quasi-exhaustive list of various families of organic pollutants which can be treated by photocatalysis has been given in [13]. In most cases, the degradation is conducted for dissolved compounds in water with UV-illuminated titania. The possible extents of the technique concern the irradiation source and the physical state of the pollutant. Recently, some works have reported the degradation of organic dyes induced by visible light by photosensitization [14–17]. The interest is to use solar visible light which is free and inexhaustible.

In the present article, it was attempted to establish the degradation pathway of a dye present in colored aqueous effluents from textile industries. The model dye chosen was methylene blue (MB). The kinetics of its disappearance was already studied in [18–38] but the detailed description of the main steps of the whole degradation process was not treated.

### 2. Experimental

#### 2.1. Materials

Methylene blue was supplied by a textile firm and used as received. Solutions were prepared using water from a Millipore Waters Milli Q purification unit. The photocatalyst was titania Degussa P-25 (anatase/rutile = 3:1; surface area = 50 m\(^2\) g\(^{-1}\), non-porous particles, mean size = 30 nm).

#### 2.2. Photoreactor and light source

Two types of Pyrex reactors open to air were utilized. Reactor 1 (90 ml) had a cylindrical shape with a bottom optical window whose section area was ca. 11 cm\(^2\), through which the suspension was irradiated. Constant agitation of the solution was insured by a magnetic stirrer working perpendicularly to the reactor basis. The UV-irradiation was provided by a high pressure mercury lamp (Philips HPK 125 W) and passed through a 2.2 cm thick circulating-water cuvette to remove the heating IR beams. This cuvette was mounted with either Pyrex filters (transmittance > 290 nm) or with Corning 0–52 cut-off filters transmitting wavelengths >340 nm. The intensity of the UV radiation reaching the reactor was measured with a radiometer and estimated to be 6.94 \times 10^{-7} and 2.39 \times 10^{-7} Einstein s\(^{-1}\) (mol of photons per second).

Reactor 2 (1 l) was equipped with a plunging tube containing the same Philips HPK 125 W lamp. This tube had a Pyrex cylindrical jacket in which water was circulated to avoid the heating of the solution. The intensity of the UV-radiation reaching the reactor (\(\lambda > 290 \text{ nm}\)) delivered an efficient photonic flux (i.e. absorbable by titania) equal to 6 \times 10^{-6} Einstein s\(^{-1}\) (mol of photons per second).

#### 2.3. Procedure

A volume of 20 ml of the aqueous solution of MB (\(C_0 = 72\ \mu\text{mol l}^{-1}\)) was introduced in reactor 1 with 50 mg of powder TiO\(_2\) (2.5 g l\(^{-1}\)). In reactor 2, 750 ml of solution and 375 mg of TiO\(_2\) were used. The degradations were carried out at 293 K and at three different pH values. The pH was adjusted either by using NaOH or HNO\(_3\). The suspension was first stirred in the dark for 60 min before irradiation. This was...
sufficient to reach an equilibrated adsorption as deduced from the steady-state concentrations. To determine the adsorption constants, different concentrations of MB were used.

2.4. Analyses

Before analysis, the aqueous samples were filtered through 0.45 μm Millipore discs to remove TiO₂ agglomerates in suspension and to protect the various chromatographic columns. A “Safas Monaco 2000” UV/VIS spectrometer recording the spectra over the 190–750 nm range was used for the determination of MB concentration to follow its kinetics of disappearance. A Beer–Lambert diagram was established to correlate the absorbance at 670 nm to MB concentration. The chemical oxygen demand (COD) was determined by using a Bioblock COD analyzer based on the method of acidic oxidation by dichromate. Anions and cations were analysed by HPLC using a Waters 501 isocratic pump, a Waters 431 conductivity detector, and an IC-PAK HR anion column (l = 50 mm, i.d. = 4.6 mm, particles = 10 μm) or a Vydac Cation IC40 (l = 50 mm, i.d. = 4.6 mm). Eluents were, respectively, borate/gluconate at 0.9 ml min⁻¹ and HNO₃ 2.5 mM at 1.5 ml min⁻¹. Total organic carbon (TOC) was determined by using a Shimazu TOC analyzer (model 5050A).

Intermediate compounds were identified by GC/MS and LC/MS (photodiode arrays and API-ES negative). A CP-Sil 5CB (L = 25 m, ∅ = 0.32 mm, e = 1.2 μm) and a Resteck Stabilwax (L = 30 m, ∅ = 0.25 mm, e = 0.5 μm) were used in GC/MS analysis. The column temperature program was: 313 K (2 min); 313–473 K (5 K min⁻¹, hold time: 10 min). For LC/MS, a CAR-H (L = 300 mm, ∅ = 7.8 mm) and an Hypersil (L = 150 mm, V = 3.6 mm) were employed.

3. Results and discussion

3.1. Photocatalytic degradation of methylene blue in water by TiO₂/UV

3.1.1. Adsorption of methylene blue on TiO₂

The kinetics of MB adsorption in the dark performed in reactor 1 for different initial concentrations is represented in Fig. 1. It can be seen that they are of the Langmuirian type with an equilibrium adsorption reached within 1 h, whatever the initial concentrations. From the number of adsorbed molecules at a given final concentration, a linear transform can

\[ q = \frac{K_a C}{1 + K_a C} \]

*Fig. 1. Kinetics of adsorption of MB in the dark.*
be determined by plotting \(1/n_{\text{ads}}\) as a function of \(C_{\text{eq}}\).

According to the Langmuir model, the coverage \(\theta\) varies as

\[
\theta = \frac{n_{\text{ads}}}{n_0} = \frac{KC}{1 + KC}
\]  

(10)

Thence

\[
\frac{1}{n_{\text{ads}}} = \frac{1}{n_0} + \left( \frac{1}{n_0K} \right) \frac{1}{C}
\]  

(11)

where \(n_0\) is the total number of adsorption sites and \(K\) is the adsorption constant of MB. The linear transform is given in Fig. 2. It can be calculated that \(K\) is equal to \(6.25 \times 10^3\) l mol\(^{-1}\) and \(n_0\) equal to 0.135 site nm\(^{-2}\). The value of \(K\) is in agreement with that of other pollutants easily soluble in water. The value of \(n_0\) is quite equal to that of indigo carmine, which has an analogous structure with two aromatic rings [39].

Fig. 3 reports the increase in adsorption when the pH increases from 3 to 9. This is in agreement with the influence of pH on the ionization state of titania. At low pH (pH = 3), lower than the pzc of titania, the surface becomes positively charged, whereas at pH > pzc it becomes negative according to

\[
\text{TiOH} + H^+ \rightleftharpoons \text{TiOH}_2^+
\]  

(12)

Since MB has a cationic configuration, its adsorption is favored in alkaline solution.

3.2. Real photocatalytic nature of the reaction

To obtain relevant information about the photocatalytic degradation, it was necessary to carry out experiments from which direct photolysis was excluded. Experiments were made in the absence of TiO\(_2\) (neat photochemical regime) at two different ranges of wavelengths (\(\lambda \geq 290\) and 340 nm). The results are given in Fig. 4. It can be seen that both photolyses could be neglected with respect to their corresponding photocatalyses. As observed for other aqueous pollutants, the photocatalytic nature of the organic contaminant disappearance can presently be confirmed. In addition, suspended titania can play the role of inner filter and the real photochemical part in presence of a suspension should be much smaller than that shown in homogeneous phase.

3.3. Kinetics of methylene blue disappearance

The kinetics of disappearance of MB is represented in Fig. 4, with an adsorption period in the dark of
90 min and with two $\lambda$ ranges. It follows an apparent first order in agreement with a generally observed Langmuir–Hinshelwood mechanism, with the rate $r$ being proportional to the coverage $\theta$ which becomes proportional to $C$ at low concentrations.

\[ r = k\theta = \frac{kKC}{1 + KC} \approx kKC = k_{app}C \tag{14} \]

The total disappearance was achieved within 60 and 120 min for $\lambda \geq 290$ and $\lambda \geq 340$ nm, respectively. The apparent first order linear transforms are given in
3.4. Catalytic quantum yield

The catalytic quantum yield is defined as the ratio of the reaction rate $r$ to the photonic flux $\varphi$, i.e. as the ratio of the number of molecules transformed per second to the number of incident efficient photons (i.e. absorbable by titania) per second

$$\rho_0 = \frac{r_0}{\varphi}$$  \hspace{1cm} (15)

The initial rate of disappearance of MB was found to be equal to 1.1 and to 3.5 $\mu$mol l$^{-1}$ min$^{-1}$ for $\lambda \geq 340$ and 290 nm, respectively. The corresponding efficient photonic fluxes $\varphi$ were found equal to $2.39 \times 10^{-7}$ and to $6.94 \times 10^{-7}$ mol photons s$^{-1}$. The resulting initial photocatalytic quantum yields were found equal to $\rho_0 = r_0/\varphi = 0.12$ and 0.14%, respectively.

These similar values underline the intrinsic character of the quantum yield. They are quite in good agreement with a previous value given by Matthews [18] and are of the same order of magnitude as those found in our laboratory for other pollutants’ elimination. It has to be mentioned that, since the kinetics $r = f(C)$ follows a Langmuir–Hinshelwood mechanism, with a linear increase of $r$ at low concentrations [6], this catalytic quantum yield could be consequently higher for higher concentrations. It is high enough to ensure a reasonable degradation rate for diluted colored water solutions.

3.5. Mineralization

The degradation leads to the conversion of organic carbon into harmless gaseous CO$_2$ and that of nitrogen and sulfur heteroatoms into inorganic ions, such as nitrate and ammonium, and sulfate ions, respectively. The formation of inorganic ions is reported in Fig. 6 for an irradiation period of 1000 min.

The shape of the curves of sulfate and ammonium ion evolution indicates that both products are initial ones with a non-nil initial formation rate. Heteroatom S seems to undergo a direct oxidation from the oxidation degree $-2$ to the highest final stable $+6$ one in SO$_4^{2-}$. However, the quantity of sulfate ions released is lower than that expected from stoichiometry. This
could be first explained by a loss of sulfur-containing volatile compounds such as H$_2$S and/or SO$_2$. However, this is not probable since both gases are very soluble in water and known as readily oxidizable into sulfate by photocatalysis [6]. The more probable explanation for the quantity of SO$_4^{2-}$ obtained smaller than that expected from stoichiometry is given by the partially irreversible adsorption of some SO$_4^{2-}$ ions at the surface of titania as already observed [6,9]. However, this partial adsorption of SO$_4^{2-}$ ions does not inhibit the photocatalytic degradation of pollutants [6,9]. The higher amount of ammonium and nitrate ions is due to the stoichiometric ratio $N/S = 3$ in the initial BM molecule.

Fig. 6 shows that the initial formation of nitrogen-containing ions is that of ammonium ions exclusively, since the evolution curve of nitrate ions has a sigma shape with an initial rate close to zero. NH$_4^+$ ions are subsequently slowly oxidized into nitrate ions, corresponding to the stable maximum oxidation state of nitrogen (+5). This is in agreement with the molecular structure of MB with all the three nitrogen atoms in the $-3$ oxidation state.

Therefore, the initial step of MB degradation can be ascribed to the cleavage of the bonds of the C–S$^+=$C functional group in MB, leading to sulfate ions, probably via the formation of a sulfoxide, a sulfone and a sulfonic group as observed in Fenamiphos degradation [40]. The adsorption mode of BM by a coulombic interaction between the C–S$^+=$C functional group and basic TiOH or TiO$_2^-$ sites of the surface of titania confirms this hypothesis. The initial steps of the degradation do not concern the amino groups, allowing nitrogen to conserve its initial $(-3)$ oxidation state.

The mineralization of organic carbon was followed by TOC disappearance (Fig. 7) at $\lambda \geq 340$ nm for both photochemistry and photocatalysis. Whereas photochemistry gives a very limited initial decrease of TOC, photocatalysis produces a TOC disappearance, which follows an apparent first order kinetics with a conversion in CO$_2$ of ca. 80% in 6 h.

Simultaneously, the oxidative mineralization process was followed by chemical oxygen demand (COD) disappearance (Fig. 8). The kinetic curve has a sigma shape indicating that it is related to the formation of final products. The inflection point corresponds to a reaction time of ca. 30 min, which is equal to the major part of MB disappearance. It could correspond to the aromatic rings opening with the transient formation of carboxylic acids followed by the evolution of CO$_2$ according to the “photo-Kolbe”
Fig. 7. Kinetics of disappearance of total organic carbon (TOC) (a) by photochemistry (without TiO$_2$) and (b) by photocatalysis (TiO$_2$+UV).

Fig. 8. Kinetics of disappearance of chemical oxygen demand (COD).
3.6. Influence of the pH

The pH is a complex parameter since it is related to the ionization state of the surface:

\[
\begin{align*}
\text{TiOH} + \text{H}^+ & \leftrightarrow \text{TiOH}_2^+ \quad (12) \\
\text{TiOH} + \text{OH}^+ & \leftrightarrow \text{TiO}^- \quad (13)
\end{align*}
\]

as well as to that of reactants and products such as acids and amines. Presently, three pH values have been selected: one reasonably acidic (3), one reasonably basic (9) and natural pH (6.7). The kinetics of MB disappearance for the three pH values are given in Fig. 9. It can be seen at time \( t = 0 \), that the quantities of MB adsorbed increased with pH and that the disappearance of MB was favored at basic pH. As seen above, the reaction rate \( r \) is given by

\[
r = k\theta = \frac{kKC}{1 + KC} \approx kKC = k_{\text{app}}C \quad (14)
\]

where \( k \) is the true rate constant and is a complex function of several physical parameters (light flux, wavelength, oxygen pressure, temperature, mass and texture of the catalyst). If the protons have any kinetic influence on the rate limiting step, therefore \( r \) should be a function of \([\text{H}^+]\), with the following formal form:

\[
r = f(C; [\text{H}^+]) = k\theta_{\text{H}^+} = \left( \frac{kKC}{1 + KC} \right) \theta_{\text{H}^+} \approx kKC\theta_{\text{H}^+} = k_{\text{app}}C\theta_{\text{H}^+}
\]

\[
k_{\text{app}}C[\text{H}^+]^n \quad (16)
\]

where \( k'_{\text{app}} \) is the pH-independent apparent rate constant and \( n \) is the kinetic partial order with respect to proton concentration. At constant \( C \), the log–log plot of Eq. (16)

\[
\log r = \log k' + n \log[\text{H}^+] = \log k' - n\text{pH} \quad (17)
\]

has given a linear transform \( \log r = f(\text{pH}) \), whose slope \((-n)\) was found equal to +0.08. This means that the kinetic partial order \( n \) equal to \(-0.08\) is significantly negative but its absolute value can be neglected. Similar results for \( n \) were obtained by plotting the log of the mean reaction rate of DCO disappearance as a function of pH. This clearly demonstrates that no protons will intervene in the rate-determining step of the whole process.
4. Identification of intermediate products

The intermediates generated during the degradation process were analysed by GC/MS and LC/MS and identified by comparison with commercial standards and by interpretation of their fragment ions in the mass spectra. It has been attempted to identify the main aromatic metabolites resulting from MB decomposition.
They are presented in Scheme 1, where they are logically reported according to their decreasing molecular weight.

The titania-based photocatalytic oxidation in water is not selective by contrast with the selective mild oxidation in pure organic gaseous or liquid phase of aliphatic or substituted aromatic hydrocarbons performed with the same titania catalyst as discussed in [6]. Two oxidative agents can be considered: the photo-produced holes $h^+$ (mainly involved in the decarboxylation reaction ('photo-Kolbe) (Eq. 9)) and/or the $\text{OH}^\circ$ radicals, which are known as strongly active and degrading but non-selective agents and can be generated by the following reactions:

1. Oxidation of water by holes
   
   $$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- + h^+ \rightarrow \text{H}^+ + \text{OH}^\circ$$

2. Transient formation of hydroperoxide radicals
   
   $$\text{O}_2(\text{g}) + e^- \rightarrow \text{O}_2^\circ^-$$
   $$\text{O}_2^\circ^- + \text{H}^+ \rightarrow \text{HO}_2^\circ$$
   $$2\text{HO}_2^\circ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$$
   $$\text{H}_2\text{O}_2 + e^- \rightarrow \text{OH}^- + \text{OH}^\circ$$

In the present case, photo-holes are certainly not concerned by the initial step since the reactant is cationic and not electron donor. By contrast, the $\text{OH}^\circ$ radicals can attack the C–S$^+=$C functional group in MB, which is in direct coulombic interaction with titania’s surface as evidenced by the influence of the pH. Therefore, the initial step of MB degradation can be ascribed to the cleavage of the bonds of the C–S$^+=$C functional group in MB

$$\text{R}–\text{S}^+ = \text{R}’ + \text{OH}^\circ \rightarrow \text{R}–\text{S}(=\text{O})–\text{R}’ + \text{H}^+$$

Actually, the sulfoxide was identified by GC/MS at $m/e = 303$ (Scheme 1). The electrophilic attack of $\text{OH}^\circ$ concerned the free doublet of heteroatom S, making its oxidation degree pass from $-2$ to $0$. However, the passage from C–S$^+=$C to C–S(=O)–C requires the conservation of the double bond conjugation, which induces the opening of the central aromatic ring containing both heteroatoms, S and N. The origin of H atoms necessary to C–H and N–H bond formation can be proposed from the proton reduction by photogenerated electrons as already observed in alcohol dehydrogenation [41] and pesticide degradation [42].

$$\text{H}^+ + e^- \rightarrow \text{H}^\circ$$

An alternative rearrangement of the phenothiazine structure is presented in Scheme 2.

The sulfoxide group can undergo a second attack by an $\text{OH}^\circ$ radical producing the sulfone (non-detected) and causing the definitive dissociation of the two benzenic rings

$$\text{NH}_2–\text{C}_6\text{H}_3(\text{R})–\text{S}(=\text{O})–\text{C}_6\text{H}_4–\text{R} + \text{OH}^\circ$$

$$\rightarrow \text{NH}_2–\text{C}_6\text{H}_3(\text{R})–\text{SO}_2 + \text{C}_6\text{H}_5–\text{R}$$

and/or

$$\text{NH}_2–\text{C}_6\text{H}_3(\text{R})–\text{S}(=\text{O})–\text{C}_6\text{H}_4–\text{R} + \text{OH}^\circ$$

$$\rightarrow \text{NH}_2–\text{C}_6\text{H}_4–\text{R} + \text{SO}_2–\text{C}_6\text{H}_4–\text{R}$$

The oxidation degree of sulfur has now increased from 0 to $+5$. Subsequently, the sulfone can be attacked itself by a third $\text{OH}^\circ$ radical for giving a sulfonic acid detected in metabolites at $m/e = 230, 218$ and 158.

$$\text{SO}_2–\text{C}_6\text{H}_4–\text{R} + \text{OH}^\circ \rightarrow \text{R}–\text{C}_6\text{H}_4–\text{SO}_3\text{H}$$

Presently, sulfur has reached its final, stable and maximum oxidation degree ($+6$) and the final release

![Scheme 2. Electronic reorganization during the passage of MB adsorbed to the sulfoxide form.](image-url)
of SO$_4^{2-}$ ions can be attributed to a fourth attack by OH$^\circ$.

$$\text{R}\text{-C}_6\text{H}_4\text{-SO}_3\text{H} + \text{OH}^\circ \rightarrow \text{R}\text{-C}_6\text{H}_4\text{O}^\circ + \text{SO}_4^{2-} + 2\text{H}^+$$  \hspace{1cm} (23)

Radical R\text{-C}_6\text{H}_4\text{O}^\circ can subsequently react either with OH$^\circ$ giving a phenolic compound (see Scheme 1) or with a H$^\circ$ radical generated by reaction (19).

Concerning the mineralization of the three nitrogen-containing groups in MB molecule, two cases have to be examined. First, the central imino-group undergoes a N=C double bond cleavage induced by the cleavage of the double bond of the –S$^+$ group in para position in the central aromatic ring. The saturation of the two amino bonds is obtained by H$^\circ$ radicals mentioned above, yielding a substituted aniline as seen for products at m/e = 303, 230 and 218 in Scheme 1. As previously observed, the amino group can be substituted by an OH$^\circ$ radical forming the corresponding phenol and releasing a NH$_2^\circ$ radical which generates ammonia and ammonium ions, estimated to be primary products as mentioned above.

$$\text{R}\text{-C}_6\text{H}_4\text{-NH}_2 + \text{OH}^\circ \rightarrow \text{R}\text{-C}_6\text{H}_4\text{-OH} + \text{NH}_2^\circ$$ \hspace{1cm} (24)

$$\text{NH}_2^\circ + \text{H}^\circ \rightarrow \text{NH}_3$$ \hspace{1cm} (25)

$$\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$$ \hspace{1cm} (26)

The other two symmetrical dimethyl-phenyl-amino groups undergo a progressive degrading oxidation of one methyl group by an attack by OH$^\circ$ radical producing an alcohol (not detected), then an aldehyde (Scheme 1), which is spontaneously oxidized into acid, which decarboxylates into CO$_2$ by photo-Kolbe reaction.

$$\text{R}\text{-C}_6\text{H}_4\text{-N(}\text{CH}_3\text{)}_2 + \text{OH}^\circ \rightarrow \text{R}\text{-C}_6\text{H}_4\text{-N(}\text{CH}_3\text{)}\text{-CH}_2^\circ + \text{H}_2\text{O}$$ \hspace{1cm} (27)

$$\text{R}\text{-C}_6\text{H}_4\text{-N(}\text{CH}_3\text{)}\text{-CH}_2^\circ + \text{OH}^\circ \rightarrow \text{R}\text{-C}_6\text{H}_4\text{-N(}\text{CH}_3\text{)}\text{-CH}_2\text{OH}$$ \hspace{1cm} (28)

$$\text{R}\text{-C}_6\text{H}_4\text{-N(}\text{CH}_3\text{)}\text{-CH}_2\text{OH} + \text{OH}^\circ \rightarrow \text{R}\text{-C}_6\text{H}_4\text{-N(}\text{CH}_3\text{)}\text{-CH}^\circ\text{-OH} + \text{H}_2\text{O}$$ \hspace{1cm} (29)

$$\text{R}\text{-C}_6\text{H}_4\text{-N(}\text{CH}_3\text{)}\text{-CH}^\circ\text{-OH} + \text{OH}^\circ \rightarrow \text{R}\text{-C}_6\text{H}_4\text{-N(}\text{CH}_3\text{)}\text{-CHO} + \text{H}_2\text{O}$$ \hspace{1cm} (30)

Methylene blue could be successfully decolorized and degraded by titania-based photocatalysis at room temperature. A detailed reaction mechanism could be presented from the initial step of adsorption involving the cationic functional group of MB molecule, which is probably adsorbed perpendicularly to the surface down to the final products (CO$_2$, SO$_4^{2-}$, NH$_4^+$ and NO$_3^-$). The degradation intermediates originated from the initial opening of the central aromatic ring and their subsequent metabolites were formed in agreement with general rules already put in evidence in the degradation of other complex molecules in water. It can be concluded that photocatalysis can decontaminate colored used waters. Photocatalysis appears as the only sub-discipline of heterogeneous catalysis, which is able to convert organic pollutants to CO$_2$ in water without heating nor using high pressure of oxygen nor requiring chemical reactants or additives. In addition, since our experiments can be successfully extrapolated to solar pilot devices, this advanced oxidation technology can be envisaged to

$$\text{R}\text{-C}_6\text{H}_4\text{-N(CH}_3\text{)}\text{-CHO} + \text{OH}^\circ \rightarrow \text{R}\text{-C}_6\text{H}_4\text{-N(CH}_3\text{)}\text{-C}=\text{O} + \text{H}_2\text{O}$$ \hspace{1cm} (31)

$$\text{R}\text{-C}_6\text{H}_4\text{-N(CH}_3\text{)}\text{-C}=\text{O} + \text{OH}^\circ \rightarrow \text{R}\text{-C}_6\text{H}_4\text{-N(CH}_3\text{)}\text{-COOH}$$ \hspace{1cm} (32)

$$\text{R}\text{-C}_6\text{H}_4\text{-N(CH}_3\text{)}\text{-COOH} + \text{h}^+ \rightarrow \text{R}\text{-C}_6\text{H}_4\text{-N}^\circ\text{-CH}_3 + \text{H}^+$$ \hspace{1cm} (33)

Subsequently, the phenyl-methyl-amine radical is degraded, probably by successive attacks by OH$^\circ$ radicals. The aromatic ring will undergo hydroxylations producing phenolic metabolites whose degradation has already been studied, hydroxyhydroquinone being the last aromatic compound detected before the ring opening. The amino group can form ammonium ions as developed above, which are slowly oxidized into nitrate or can be directly oxidized into hydroxylamine leading also to nitrate [43].

Many other hydroxylated intermediates have certainly been formed but they were difficult to detect because of their poor extractibility owing to their hydrophilic character.

5. Conclusions

Methylene blue could be successfully decolorized and degraded by titania-based photocatalysis at room temperature. A detailed reaction mechanism could be presented from the initial step of adsorption involving the cationic functional group of MB molecule, which is probably adsorbed perpendicularly to the surface down to the final products (CO$_2$, SO$_4^{2-}$, NH$_4^+$ and NO$_3^-$). The degradation intermediates originated from the initial opening of the central aromatic ring and their subsequent metabolites were formed in agreement with general rules already put in evidence in the degradation of other complex molecules in water. It can be concluded that photocatalysis can decontaminate colored used waters. Photocatalysis appears as the only sub-discipline of heterogeneous catalysis, which is able to convert organic pollutants to CO$_2$ in water without heating nor using high pressure of oxygen nor requiring chemical reactants or additives. In addition, since our experiments can be successfully extrapolated to solar pilot devices, this advanced oxidation technology can be envisaged to
clean colored effluents in semi-arid countries such as Tunisia to re-use or recycle water, which is becoming a precious raw material all around the world.

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