

Why inorganic salts decrease the TiO₂ photocatalytic efficiency

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ABSTRACT. Methylene Blue (MB) has been chosen as a model molecule to evaluate the impact of inorganic salts, present in textile waste waters, on the adsorption properties and on the photocatalytic efficiency of TiO₂. No OH[•] radical scavenging by anions such as NO₃⁻, Cl⁻, SO₄²⁻, PO₄³⁻, and CO₃²⁻ was observed at neutral and basic pH, while this phenomenon can be suggested at acidic pH for some anions except carbonate anions which are totally neutralized and/or eliminated as CO₂ in these conditions. The decrease in the rate MB photocatalytic degradation in the presence of inorganic salts was shown to be due to the formation of an inorganic salt layer at the surface of TiO₂, which inhibits the approach of MB molecules. The correlation between the amount of MB adsorbed and the rate of its photocatalytic degradation, whatever the nature of the salt, its concentration and the pH of the solution, indicates (i) that photocatalysis occurs at the surface and not in the solution and (ii) that OH⁻ ions added at basic pH do not participate to the increase in the photocatalytic efficiency by inducing an increase in OH[•] formation. They increase the surface density in adsorption sites TiO⁻. The effect of various salts is similar on various titania samples of industrial origin (Millennium TiO₂ PC 500, PC 50, and Degussa P 25). It is however more important on Millennium PC 10 probably because of its smaller surface area.

1. INTRODUCTION

15% of the total world production of dyes is lost during the dyeing processing and is released in textile effluents [1, 2]. The release of those colored waste waters in the ecosystem is a dramatic source of esthetic 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 [3], biological methods (biodegradation) [4, 5] and chemical methods (chlorination, ozonation [6]) are the most frequently used.

However, each of these processes present drawbacks. While physical methods concentrate and/or transfer the pollution, chemical processes can produce secondary pollution [7] or persistent final compounds. The biological degradation is generally slow and, in some cases, is quite inefficient [8].

Since an important part of textile industries are situated in hot countries, (North Africa, South-East Asia, Latin America), the development of alternative treatments using solar energy, which is free, renewable and quasi inexhaustible, will become important.

Among the new oxidation methods or "Advanced Oxidation Processes" (AOP), heterogeneous photocatalysis, which can use solar energy, appears as an emerging destructive technology leading to the total mineralization of most of organic pollutants [9–17].

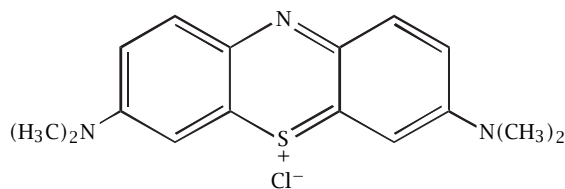
The treatment of colored aqueous effluents via photocatalytic processes has been extensively studied [16, 18–26]. However, dye baths contain important amounts of inorganic salts and few studies have been reported on their effect on dye photocatalytic degradation [24, 29]. According to literature [30–34], the presence of inorganic salts decreases more or less the photocatalytic efficiency depending of their nature, their concentration and the pH of the solution. However, it is not totally clear whether these inhibiting effects are due to OH[•] scavenging induced by some anions in particular carbonates or to a competitive adsorption, although the first hypothesis was more often suggested.

The aim of this work is to contribute to the clarification of the above mentioned points by comparing and correlating the adsorption of inorganic additives with the inhibition of the photocatalytic degradation of methylene blue, employed as model dye molecule. Its developed formula is given in Scheme 1. The present publication concerns the influence of inorganic salts on (i) MB adsorption and (ii) its photocatalytic degradation. Various sodium salts (nitrate, chloride, sulphate, phosphate, and carbonate) and in some cases

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Table 1. Characteristics of different industrial TiO₂ catalysts and amount of MB adsorbed on these TiO₂ samples at natural pH.

| | Degussa P-25 | Millennium PC-10 | Millennium PC-50 | Millennium PC-500 |
|----------------------------------|----------------------------|---------------------|---------------------|----------------------|
| Structure | 80% anatase, 20% rutile | 100% anatase | 100% anatase | 100% anatase |
| Surface area (m ² /g) | 50 | 10 | 50 | 340 |
| Particulate size (nm) | 30 | 85 | 20-30 | 5-10 |
| MB adsorbed (mg/g) | 7.2 | 5.8 | 6.9 | 5.5 |



Scheme 1. Developed formula of Methylene Blue (MB).

potassium ones were selected as additives at different concentrations and at different pH's to determine the impact of their presence in the photocatalytic treatment of textile dyes. The behavior of different TiO₂ samples in the presence of these additives have also been examined.

2. EXPERIMENTAL

2.1. Materials. Four different industrial photocatalysts have been used: Titania Degussa P-25 and three TiO₂ catalysts prepared by Millennium Inorganic Chemicals (PC-10; PC-50, PC-500) have been used. Their characteristics are given in Table 1.

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.

2.2. Photoreactor and light source. A Pyrex photoreactor (1 L), open to air, was equipped with a plunging tube containing a medium-pressure mercury lamp (Philips HPK-125 W). This tube had a Pyrex cylindrical jacket in which water was circulated to avoid the heating of the solution. Pyrex glass played also the role of an optical window ($\lambda > 290$ nm). The UV-radiation entering the reactor ($\lambda > 290$ nm) delivered an efficient photonic flux (i.e., absorbable by titania) equal to 6×10^{-6} Einstein/s (1 Einstein = 1 mol of photons).

2.3. Procedure. The adsorption and the photocatalytic degradation of methylene blue (MB), were performed using a volume of 750 mL of MB introduced in the photoreactor with 375 mg of powder TiO₂, corresponding to a concentration of titania in slurry equal to 0.5 g TiO₂/L. The concentration of MB was chosen

equal to 84.2 μ mol/L, i.e., identical to that used in our previous studies on dye removal.

Adsorption and degradation were carried out at 293 K and at three different pH's, adjusted by using either NaOH or HClO₄.

For the photocatalytic degradation of MB, the suspension was first stirred in the dark for 120 min before irradiation. This was sufficient to reach an equilibrated adsorption in the dark as deduced from the steady-state concentrations measured.

The influence of inorganic electrolytes was determined by using sodium salts: NaNO₃, NaCl, Na₂SO₄, Na₂CO₃, Na₃PO₄, unless otherwise stated.

2.4. Analyses. Before analysis, the aqueous samples were filtered through 0.45 μ m Millipores discs to remove TiO₂ agglomerates. A "Safas Monaco 2000" UV/Vis spectrophotometer 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 concentrations. The Chemical Oxygen Demand (COD) was determined by using a Bioblock COD analyzer, based on the method of acidic oxidation by dichromate.

3. RESULTS AND DISCUSSION

3.1. Adsorption of methylene Blue (MB) in presence of inorganic ions. The adsorption of methylene blue (MB) in presence of ions was studied by monitoring MB concentration in the aqueous phase following three distinct procedures as already used by Chen et al. [34]: (i) simultaneous additions at time zero of MB and of inorganic salts to TiO₂ suspensions, (ii) pre-adsorption of MB on TiO₂ and subsequent addition of inorganic salts and (iii) pre-adsorption of inorganic salts on TiO₂ and subsequent addition of MB.

The pre-adsorption of ions or of MB was carried out by stirring the solution during 2 hours in the dark. This time was found sufficient to equilibrate both adsorptions of ions and of MB on titania. In all experiments, the slurry concentration of TiO₂ was 0.5 g/L. The pH was equal to 5.1 except for phosphate and carbonate solutions, for which it was near to 6-7 when their concentration C was equal to 0.02 mol/L and equal ca. 8

Table 2. Quantities of MB adsorbed at equilibrium on TiO₂ Degussa P-25 (Q_e: mg/g) for three different procedures described in the text.

| Inorganic salts [2 × 10 ⁻² mol/L] | Q _e : mg/g (TiO ₂) | | |
|---|---|---------------------|----------------------------|
| | Simultaneous adsorption of MB and ions | Preadsorption of MB | Preadsorption of salt ions |
| Blank | 7.2 | 7.2 | 7.2 |
| NaNO ₃ | 6.7 | 6.5 | 6.6 |
| NaCl | 5.8 | 6.2 | 5.6 |
| NaSO ₄ | 5.2 | 6 | 5 |
| Na ₂ PO ₄ | 4.7 | 5 | 4.1 |
| Na ₂ CO ₃ | 4.0 | 4.6 | 4 |

for C = 0.2 mol/L. At pH = 8 phosphate was present as 75% HPO₄²⁻ and 25% H₂PO₄⁻, whereas carbonate was mainly present as HCO₃⁻.

The specific quantity of MB adsorbed (Q) has been plotted as a function of time for the three procedures. The simultaneous addition of MB and ions (procedure 1) and the addition of MB after pre-adsorption of inorganic ions (procedure 3) lead to very similar curves (Figures 1a-b). Figure 1c shows the desorption kinetics of MB by addition of ions. In all cases, the equilibrium was reached after about 90 min.

3.1.1 Influence of the nature of the sodium inorganic salts on MB adsorption

The specific amounts of MB adsorbed at equilibrium (in mg/g) are given in Table 2. Whatever be the procedure used, the specific quantities of MB adsorbed were similar, but they slightly differ according to the nature of the anion. The pattern of adsorption by the various anions is the following:

Nitrate < chloride < sulfate < phosphate < carbonate

A competitive adsorption between the dye and the anions, where ions should modify the superficial properties of TiO₂ can be envisaged to explain this behaviour.

This hypothesis agrees (i) with the affinity of TiO₂ surface for phosphate, sulfate, and chloride anions, found by a radioactive tracer method with labelled anions [35] and also (ii) with the greater adsorption of phosphate ions compared with that of nitrate and chloride ions, observed by Boehm [36]. However, a cationic dye such as MB cannot adsorb on the same site as those of an anion. No steric hindrance of the anions can be invoked since the carbonate ions have a smaller size than sulfate and phosphate. Therefore, a competition of adsorption could exist only if it was the counterion of salt, Na⁺, which was in competition with MB. In this case, the smaller inhibition of monosodic salts (nitrate and chloride) compared to disodic salts (sulfate and carbonate) could be explained by the amount of sodium present in the solution. Sodium phosphate

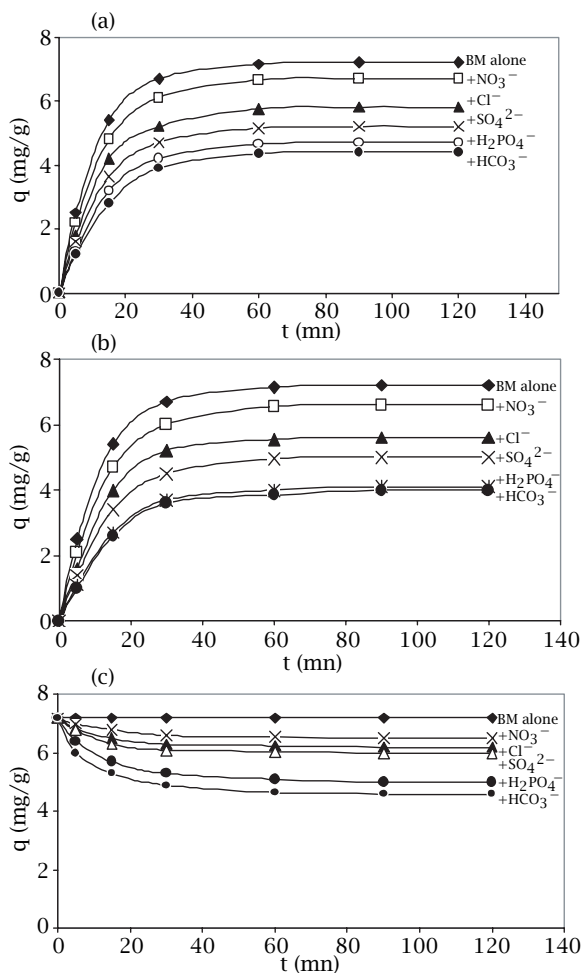


Figure 1. Adsorption kinetics of MB in presence of sodium inorganic salts (nitrate, chloride, sulfate, phosphate et carbonate) [BM]_i = 84.2 μmol/L, [ion]_i = 0.02 mol/L, [TiO₂ P25] = 0.5 g/L (a) co-adsorption of MB and ions (b) ions pre-adsorbed (c) MB pre-adsorbed.

contains three sodium atoms and should be more inhibitor for MB adsorption than carbonate but it is not the case. Another hypothesis to explain the inhibition

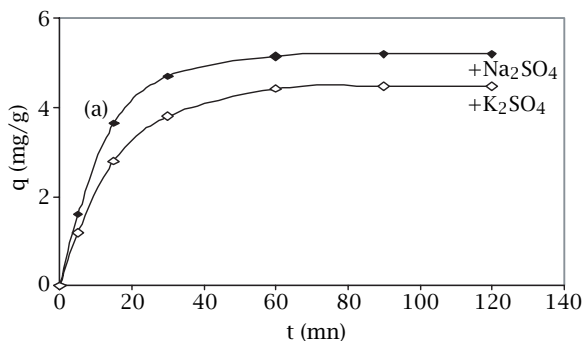


Figure 2. Comparative adsorption kinetics of MB in presence of either sodium sulfate or potassium sulfate. $[BM]_i = 84.2 \mu\text{mol/L}$ $[Na_2SO_4] = [K_2SO_4] = 0.02 \text{ mol/L}$, $[P25] = 0.5 \text{ g/L}$.

pattern of various sodium salts is the formation of an inorganic layer at the TiO_2 surface more or less important depending on the salt solubility [37]. A high salt solubility decreases adsorption of salts and consequently favors that of MB. The effect of the solubility on adsorption has already been observed by one of us for organic compounds [38]. This was confirmed by studying the adsorption of MB in presence of sodium and potassium sulfates (Figure 2). MB is less adsorbed in presence of potassium than in presence of sodium because of the smaller solubility of potassium sulfate.

The influence of ions on the inhibition of adsorption of dichloroethane (DCE) has been studied by Chen et al. [34] who found the following order

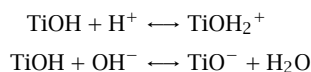
phosphate > sulfate > carbonate > nitrate > chloride

They considered a competition between DCE and anionic species. This was possible considering the neutrality of the organic molecule studied.

3.1.2 Influence of pH on MB adsorption in presence of inorganic ions

Figure 3 reports the quantities of adsorbed MB at the equilibrium, with and without different salts at three different pH's.

When the pH increases from 3 to 9, MB adsorption increases [18]. This is in agreement with the influence of the pH on the ionization state of titania by considering that MB adsorption involves the (S^+) cationic part of the molecule. Indeed, 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



Whatever the pH, the order of inhibition by inorganic ions on MB adsorption was the same indepen-

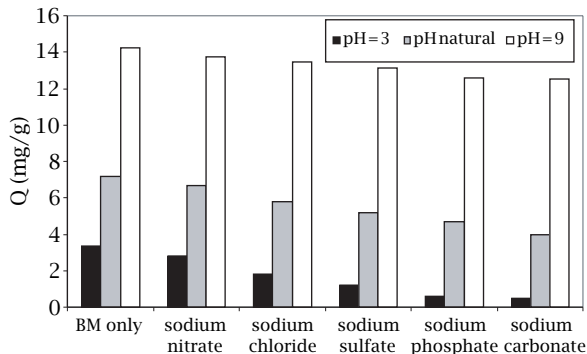


Figure 3. Quantities of MB adsorbed at equilibrium (in mg MB/g cat) in presence of different salts at three different pH's. $[BM]_i = 84.2 \mu\text{mol/L}$ $[salt] = 0.02 \text{ mol/L}$, $[TiO_2 P25] = 0.5 \text{ g/L}$.

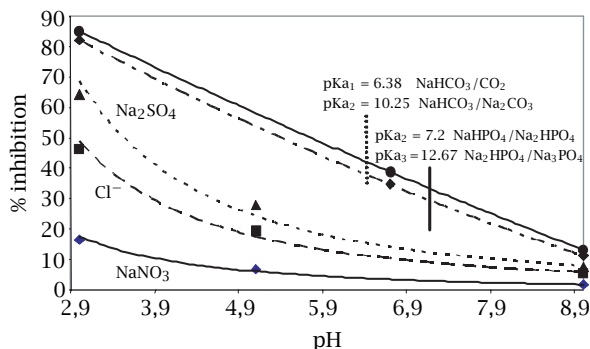


Figure 4. percentage of inhibition of MB adsorption, by different inorganic salts, as a function of pH. $[BM]_i = 84.2 \mu\text{mol/L}$ $[salt] = 0.02 \text{ mol/L}$, $[P25] = 0,5 \text{ g/L}$.

dently of the anionic state: at neutral pH (6.5), HCO_3^- and $H_2PO_4^-$ are mainly present, whereas at $pH = 9$, HPO_4^{2-} and a mixture of HCO_3^-/CO_3^{2-} are present (Figure 4). Therefore, the anionic state does not seem to be at the origin of the modification of MB adsorption.

The inhibition factor of adsorption can be defined as:

$$\% \text{ inhibition} = ((Q_0 - Q_s) / Q_0) \times 100$$

where Q_0 and Q_s are the amounts of MB adsorbed in the absence and in the presence of salt, respectively.

Since there are no carbonate anions at $pH = 3$, the inhibition observed is probably due to ClO_4^- added as perchloric acid to decrease the pH.

Figure 4 shows that, whatever the salt used, the inhibition of adsorption is higher at acidic pH, because cationic MB^+ is repelled by positive $Ti-OH_2^+$ species present in that case and attracted by TiO^- present at basic pH's.

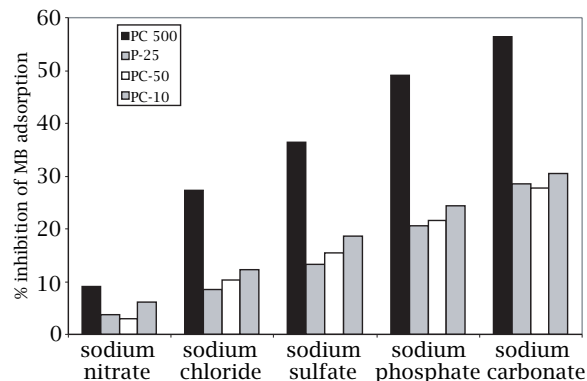


Figure 5. percentage of inhibition of MB adsorption on different industrial TiO₂ catalysts by different inorganic salts. [BM]_i = 84.2 μmol/L at natural pH (pH = 5 except in the case of the addition of carbonate and phosphate where the pH is around 6.9); [salt] = 0.02 mol/L.

3.1.3 Influence of the nature of TiO₂ on MB adsorption in presence of inorganic ions

Figure 5 compares the inhibition percentage of MB adsorption in presence of inorganic salts for different industrial TiO₂ samples. The characteristics of the industrial TiO₂ samples and the amount of MB adsorbed on these TiO₂ samples without addition of inorganic salt are given Table 1. The accuracy of the measurements is only ca. 10%. So, it is difficult to discuss about the difference observed. It can be only noticed that the amount of MB adsorbed does not seem to be related to the BET specific surface area of the catalyst. Whatever the TiO₂ sample, the order of inhibition of MB adsorption by ions is the same. However the percentage of inhibition depends on the TiO₂ samples. Taking into account the slight difference observed between the behaviour of P-25, PC-50, and PC-10, it can be considered that the salt have a very similar effect on these samples. However, the inhibition effect of inorganic salts on MB adsorption is twice higher on PC-500. The values of the adsorption rate constants k_a of MB on P-25 and PC-500 in presence of different inorganic salts show a twice slower adsorption of MB on PC-500 (Table 3).

3.2. Photocatalytic degradation of MB in presence of ions

3.2.1 Influence of ions at natural pH on the photocatalytic degradation rate

Taking into account the UV-Vis spectrum of MB which presents two strong absorption peaks at $\lambda \approx 290$ nm and 670 nm, we have checked that there is less than 5% of MB degraded after 1 hour by pure photolysis (i.e., without TiO₂), using a special "virgin" photoreactor, which has importantly never been previously contacted with titania. It was observed before that some

Table 3. Apparent first order kinetic constants of adsorption, k_a (min⁻¹), of MB on TiO₂ Degussa P-25 and on TiO₂ PC-500 in presence of inorganic salts. In all cases MB and salts were simultaneously introduced.

| Inorganic salts | k_a (min ⁻¹) | |
|---------------------------------|----------------------------|--------|
| | P 25 | PC-500 |
| MB only | 0.082 | 0.054 |
| NaNO ₃ | 0.0815 | 0.047 |
| NaCl | 0.079 | 0.043 |
| Na ₂ SO ₄ | 0.075 | 0.041 |
| Na ₂ PO ₄ | 0.076 | 0.037 |
| Na ₂ CO ₃ | 0.075 | 0.035 |

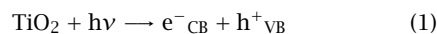
invisible titania particles could remain attached on the glass walls of a photoreactor and could subsequently provide an artificially high kinetics of a supposed pure photochemical degradation.

The kinetics of disappearance of MB, in presence of TiO₂, with and without addition of different sodium salts are represented in Figure 6a. It appears a slight inhibition of photocatalytic activity of MB in the presence of ions.

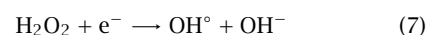
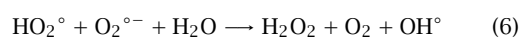
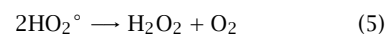
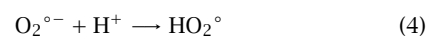
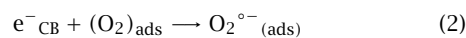
Several hypotheses were suggested in literature to explain the inhibition of photocatalysis by the presence of ions: (i) the reduction of light absorption by the photocatalyst induced by ions such as (Fe³⁺) [39] which play the role of inner filter; (ii) the increase in recombination of h⁺ and e⁻ [40]; (iii) the trapping of OH[•] radicals or other oxidizing species [31, 41-43] and (iv) the competition of adsorption with the reactant at the catalyst surface [42, 43].

The photocatalytic degradation of a reactant R generally obeys to the following mechanism.

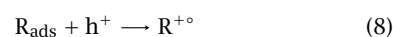
- Absorption of efficient photons ($h\nu \geq E_g = 3.2$ eV, i.e., $\lambda < 400$ nm) by titania, and formation of e⁻/h⁺ pairs



- Reactions of e⁻_{CB} and h⁺_{VB} with O₂ and H₂O to form other active species such as OH[•]



- Reaction of R with either h⁺_{VB} or OH[•]:



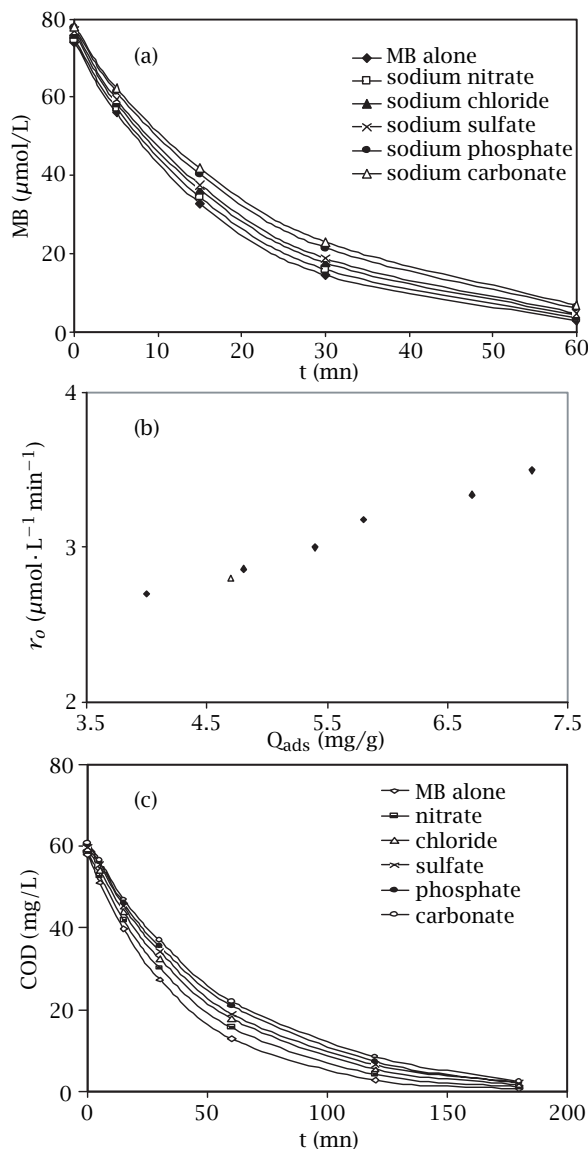


Figure 6. (a) Influence of inorganic salts on the initial MB degradation rate (r_o) in presence of TiO₂ P25 at natural pH; (b) MB degradation rate (r_o) as a function of the quantity of MB adsorbed on TiO₂ (Q_{ads}). The amount of MB adsorbed is modified by the addition of different sodium inorganic salts. The triangles represent the degradation rate observed by using potassium sulfate. $[BM]_i = 84.2 \mu\text{mol/L}$, $[\text{salt}] = 0.02 \text{ mol/L}$, concentration of titania Degussa P25 = 0.5 g/L , pHn, $V = 750 \text{ mL}$.

or



According to literature, the oxidation by OH[°] species can occur either at the particle surface [44–47] or in the solution [48–51].

The salts used in this study do not absorb photons efficient for titania. It has been mentioned in the literature that NO₃⁻ could possibly absorb photons. However, with $\epsilon_{\text{max}} = 7 \text{ L mol}^{-1} \text{ cm}^{-1}$ at $\lambda = 300 \text{ nm}$, any inner filter effect due to NO₃⁻ has to be neglected.

The trapping of hydroxyl radicals by anions cannot explain the inhibition pattern found for the different salts:

Nitrate < chloride < sulphate < phosphate < carbonate

Indeed, the scavenging rate constants of OH[°] by HCO₃⁻ or H₂PO₄⁻ species are about 100 times smaller than that by Cl⁻ or SO₄²⁻ (Table 4). Moreover, the reaction rate constant of OH[°] with HCO₃⁻ is less important than those with a large number of organic compounds [52]. If the inhibition by different salts were due to the scavenging of OH[°] by the anion, the activity pattern should be, at natural pH, in the following order:

Sulphate > chloride > nitrate > carbonate > phosphate

Since the inhibition patterns by the different sodium salts are identical either for MB adsorption or for photocatalytic activity and since the reaction rates are proportional to the amount of MB adsorbed (Figure 6b), it can be suggested that the observed inhibition is due to the formation of an inorganic layer at the surface of TiO₂, which decreases MB adsorption. This is in agreement with the lower photocatalytic activity of TiO₂ in presence of potassium sulphate whose smaller solubility favours its adsorption. This is illustrated by Figure 6b where the value of r_o as a function of the quantity of MB adsorbed is represented by an open triangle.

In addition, it can be noted that the inhibition pattern observed for MB disappearance is conserved for COD (Chemical Oxygen Demand) disappearance (Figure 6c).

3.2.2 Influence of pH on the inhibition of MB degradation by inorganic ions

Figure 7 represents the photocatalytic degradation rate of MB at different pH's in the presence of various salts. Whatever the pH, the photoactivity inhibition pattern by the different salts remains the same, except at acidic pH, at which carbonate ions do not exist anymore. However the percentage of inhibition due to ions increases when the acidity increases because of a decrease in the number of active sites, which are of anionic nature because of the cationic nature of MB. The decrease in titania's efficiency in presence of ions is still related to that of the amount of MB adsorbed on TiO₂.

The amounts of MB adsorbed are changed by using different ion concentrations. In the insert of Figures 8a, b it can be seen that photocatalytic activity decreases

Table 4. Rate constants of OH° with different anions.

| Anions | Rate constants (L mol ⁻¹ s ⁻¹) | References |
|---|--|--|
| NO ₃ ⁻ | 1.4 × 10 ⁸ | Y. Katsumura, J. Phys. Chem. 95 (1991), 4435. |
| Cl ⁻ | 4.3 × 10 ⁹ | G. V. Buxton, C. L. Greenstock, W. P. Helman, and A. B. Ross, J. Phys. Chem. Data 17 (2) (1988), 513. |
| HCO ₃ ⁻ | 8.5 × 10 ⁶ | |
| CO ₃ ²⁻ | 3.9 × 10 ⁸ | |
| SO ₄ ²⁻ | 1 × 10 ¹⁰ | J. Holcman, T. Logager, K. Sehested, and V. Klaning, in Laboratory Studies on Atmospheric Chemistry, York, September 23-25, 1991, p. 41. |
| HSO ₄ ⁻ | 3.5 × 10 ⁵ | B. Lesigne, C. Ferradini, and J. Pucheault, J. Phys. Chem. 76 (1972), 24. |
| H ₂ PO ₄ ⁻ | < 10 ⁶ | J. K. Thomas, Trans. Faraday Soc. 61 (1965), 1324. |

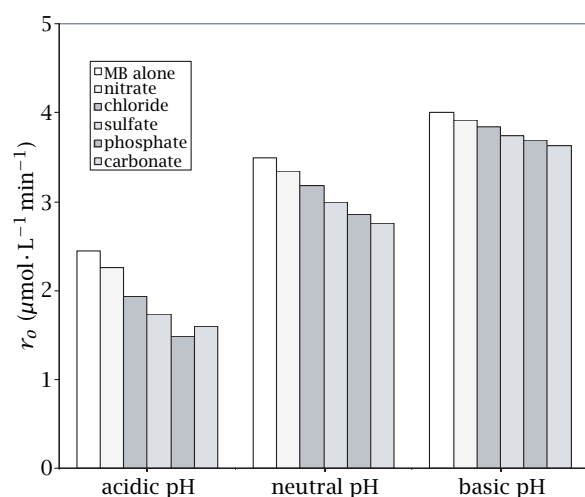


Figure 7. Influence of inorganic salts at different pH's on the rate of MB photocatalytic degradation. The pH was adjusted with HClO₄ or NaOH. [BM]_i = 84.2 μmol/L, [salt] = 0.02 mol/L, [P25] = 0.5 g/L, pH₀, V = 750 mL.

as a function of the concentration of salt added. This inhibition is directly proportional to the quantity of MB adsorbed whatever the pH (Figures 8a, b). At natural pH, the nature of the anion does not influence the photocatalytic activity, whereas, at acidic pH, MB degradation seems to depend on it.

Figure 9 represents all the initial reaction rates of MB disappearance observed at different pH's, with different ions at different concentrations.

At natural and basic pH, the main factor modifying MB photocatalytic degradation rate is the amount of MB adsorbed. This quantity is a function of the increase of anionic sites TiO⁻ and of the formation of an inorganic salt layer at the TiO₂ surface. At basic pH, the increase in rates is to be more attributed to a favourable adsorption of MB⁺ than to a possible increase in OH° formation since their precursors, the OH⁻ anion's are repelled by the negatively charged TiO⁻ surface species. This re-

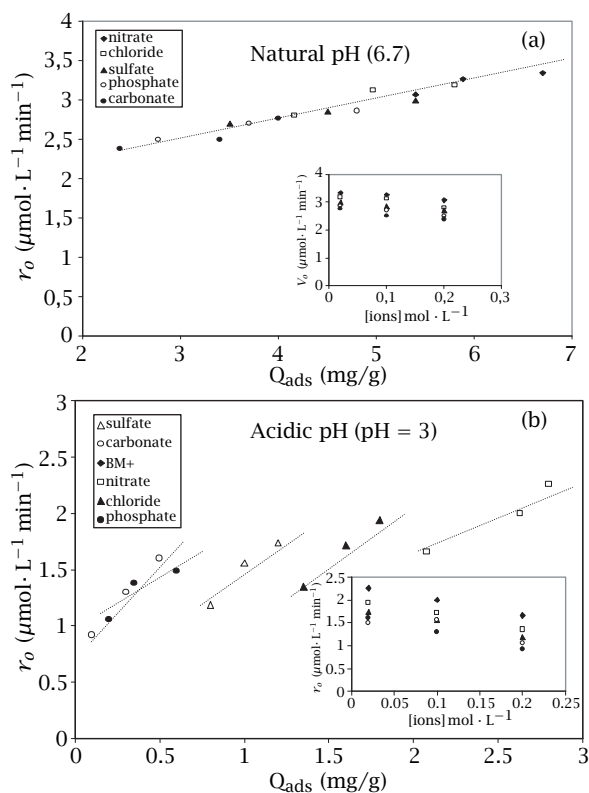


Figure 8. Variations of the initial rate of MB disappearance r_o as a function of the quantity Q of MB adsorbed at neutral pH with different ions concentration. In insert: r_o as a function of ions concentration; (b) r_o as a function of MB adsorbed, at acidic pH, with different concentration of ions. In insert: r_o as a function of ions concentration.

sult agrees *a contrario* with the influence of pH on the degradation of Orange G, which has a lower rate of disappearance at basic pH because of its anionic character [53].

At acidic pH, the same deviation from the straight line which is only valid above pH3 (Figure 9) is observed for all additives, pointing out the presence of another

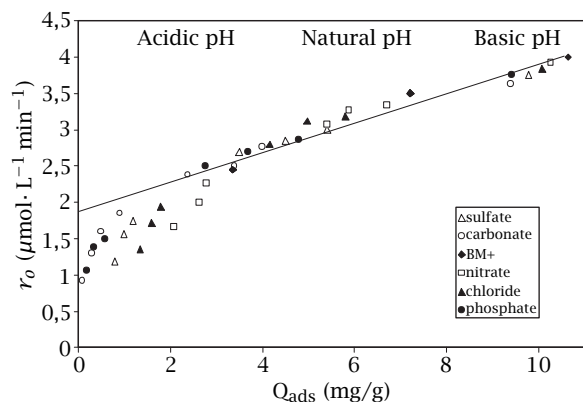


Figure 9. Variations of the initial rate of MB disappearance r_0 as a function of the quantity Q of MB adsorbed at different pH's, for different salts at different concentration.

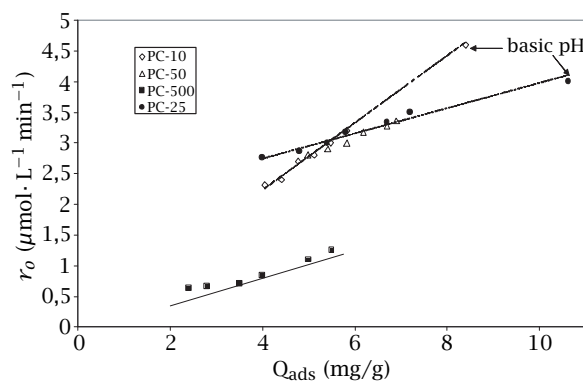


Figure 10. Variations of the initial rate of MB disappearance r_0 as a function of the quantity Q of MB adsorbed for different photocatalysts of industrial origin.

phenomenon which differs from the inhibition of MB adsorption by the formation of an inorganic salt layer at the TiO_2 surface. It can be suggested that inorganic anions scavenge some OH^\bullet radicals because of the strong attraction of anions by the positive TiOH_2^+ sites.

3.2.3 Influence of the nature of the photocatalyst

Figure 10 shows similar behaviours of Millennium PC-50 and Degussa P-25 photocatalysts in the presence of salts. The factor regulating their efficiencies seems to be their adsorption properties. PC-10 photocatalyst is much more inhibited by the addition of inorganic salts. However, it is worth noting that, at basic pH, PC-10 is more efficient than Degussa P-25 although a less important quantity of MB is adsorbed. This result is in agreement with those obtained previously [54].

In the case of PC-500, at same amount of MB adsorbed, PC-500 photocatalyst is less efficient than the other photocatalysts studied, probably because of its

porosity. However, taking into account the slope of the curve, the effect of the inorganic salt inhibition on PC 500 is similar to that observed for P-25 or PC 50.

4. CONCLUSIONS

At neutral and basic pH, the decrease in titania's photoefficiency induced by addition of inorganic salts is mainly due to the formation of an inorganic layer at the TiO_2 surface which inhibits MB adsorption and rather than the scavenging of active species by anions as generally admitted. In the special case of carbonate ions, at natural pH (pH = 6.8 after addition of carbonate), HCO_3^- ions are only present (no CO_3^{2-} ions). Taking into account the reaction rate constant of OH^\bullet with the different ions given in the literature, the value for HCO_3^- is small compared to the values given for the other salts, although carbonate salt added is always the most inhibitor salt.

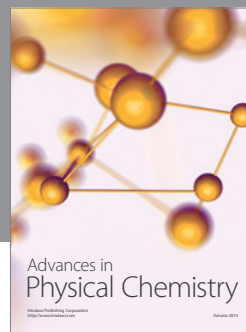
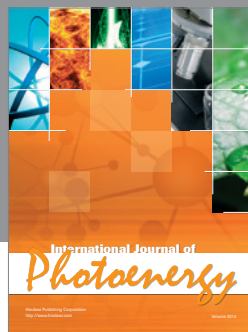
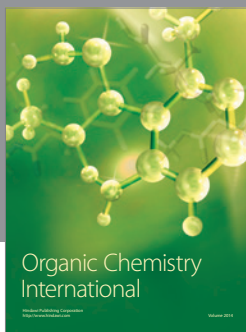
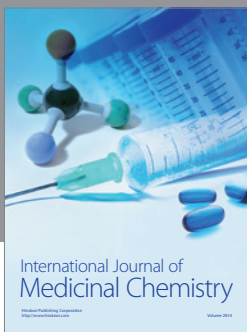
The increase in photocatalytic efficiency of titania at basic pH is mainly attributed to an increase of in the surface density of TiO^- adsorption sites rather than to an increase of formation of more OH^\bullet radicals formed by reaction of OH^- with h^+ .

Depending on the origin of industrial TiO_2 samples, the adsorption properties and the inhibition by inorganic salts are modified. Further studies should be performed to better understand their different photoactivities observed.

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