Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.848667

53 (2015) 951–963
January

Taylor & Francis
Taylor & Francis Group

Effect of pH and inorganic salts on the photocatalytic decolorization of methyl orange in the presence of TiO_2 P25 and PC500

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Received 24 November 2012; Accepted 17 September 2013

ABSTRACT

The photocatalytic decolorization of aqueous solution of methyl orange has been investigated using TiO_2 Degussa P25 and Millennium PC500 in the presence of UV medium pressure mercury lamp (UV-A light at λ_{max} = 365 nm). The effect of pH, electron acceptor such as H_2O_2, and inorganic anions (Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-, and HPO_4^{2-}) in the presence of both catalysts is discussed. The evolution of apparent rate constant k_{app} as a function of pH indicates that it plays an important role on the kinetics of degradation of MeO in the presence of different protons sources in the range of the acidic medium. The dye adsorption on both catalysts shows a strong dependence on the pH, and the adsorption plays a role in the photocatalytic reaction in acidic and alkaline medium. The decolorization was strongly enhanced in the presence of hydrogen peroxide (H_2O_2). Addition of salts such as NaCl, KCl, $CaCl_2$, $BaCl_2$, Na_2SO_4, Na_2HPO_4, Na_2CO_3, and $NaHCO_3$ significantly reduces decolorization efficiencies.

Keywords: Azo dye; Methyl orange; Inorganic salt; Adsorption; Photocatalysis; TiO_2

1. Introduction

Textile mills are major consumers of water and consequently one of the largest groups of industries causing intense water pollution. The industrial effluents arising from textile industry are strongly colored, and it was stated that a total of 15% of the world production of dyes is lost during the dyeing process and is released in textile effluents [1]. Among these dyes, azo dyes constitute the largest and the most important class of commercial dyes. The nature of pollution that accompanies this industry is primarily due to the non-biodegradable nature of the dyes along with the strong presence of toxic trace metals, acid, alkali, and carcinogenic aromatic amines traceable in the effluents. New methods of treatment have emerged in the last 30 years including advanced oxidation process, very interesting for the degradation of recalcitrant organic molecules. One way to obtain chemically, degradation of these organic pollutants, is to generate in the medium very reactive entities such as hydroxyls radicals $^\bullet OH$ by applying the heterogeneous photocatalysis using TiO_2 as photocatalyst. Heterogeneous photocatalysis is an emerging technology with key advantages including operation at ambient conditions and the possible use of solar

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irradiation. Experimental observations indicate almost complete oxidation of most of the organic compounds to CO_2, H_2O, and inorganic anions via photocatalytic processes. The photocatalytic degradation of organic molecules in wastewater utilizing titanium dioxide TiO_2 is initiated by light of wavelength ≤ 390 nm. This process begins when the TiO_2 particles absorb light. Then, electrons are excited from the valence band (VB) to the conduction band (CB), generating positive holes (h^+) and free electrons (e^-). These pairs are able to initiate oxidation and reduction reactions at the TiO_2 surface. The positive holes can oxidize the organic molecules adsorbed at the surface, through the formation of hydroxyl radicals ($^\bullet OH$). The electron (e^-) in the conduction band can react with O_2 to produce superoxide radical anion of oxygen $O_2^{\bullet -}$. According to this, the degradation of dyes by heterogeneous photocatalysis using TiO_2 as photocatalyst can be expressed as follows [2]:

$$\mathrm{TiO_2} + h\nu\ \ (UV)\ \ \rightarrow \mathrm{TiO_2}(\mathrm{e}^-_{\mathrm{CB}} + h^+_{\mathrm{VB}}) \quad (1)$$

$$\mathrm{TiO_2}(h^+_{\mathrm{VB}}) + \mathrm{H_2O} \rightarrow \mathrm{TiO_2} + \mathrm{H}^+ + ^\bullet \mathrm{OH} \quad (2)$$

$$\mathrm{TiO_2}(\mathrm{h}^+_{\mathrm{VB}}) + \mathrm{OH}^- \rightarrow \mathrm{TiO_2} + ^\bullet \mathrm{OH} \quad (3)$$

$$\mathrm{O_2} + \mathrm{TiO_2}(e^-_{\mathrm{CB}}) \rightarrow \mathrm{TiO_2} + \mathrm{O}_2^{\bullet -} \quad (4)$$

$$\mathrm{Dye} + ^\bullet \mathrm{OH} \rightarrow \text{degradation products} \quad (5)$$

$$\mathrm{Dye} + h^+_{\mathrm{VB}} \rightarrow \text{oxidation products} \quad (6)$$

$$\mathrm{Dye} + e^-_{\mathrm{CB}} \rightarrow \text{reduction products} \quad (7)$$

Azo dyes are commonly used in the textile industry, mainly to produce bright, warm colors in the yellow to red range. They are also used in many paints. Most are apparently non-toxic, but recent studies have suggested a link between some azo dyes and cancer [3]. Methyl orange (MeO) is a model compound of a series of common water soluble azo dyes widely used in chemistry, textiles, and paper industries. In previous work, investigations were made to study the factors influencing the photodegradation of MeO in aqueous suspension containing TiO_2 such as catalyst loading, pH, temperature, addition of H_2O_2, initial concentration of the dye, and the adsorption isotherm has been investigated [4–6]. Other works present the review of the effects of operating parameters on the degradation of MeO using pillared clays as catalysts [7,8].

In the present work, we proposed to study the other effects of experimental parameters, such as the electron acceptor (H_2O_2), inorganic salts, solution pH to control the reaction rate of photodecomposition of MeO employed as a model dye molecule. The aim of this study is to compare the photocatalytic degradation of methyl orange in the presence of TiO_2 Degussa P25 and Millennium PC500 and correlating previous adsorption in the dark with photocatalysis process. In textile industries, various salts are added in the bath in order to improve color fastness; the effect of the inorganic anions such as Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-, and HPO_4^{2-}on the dye decolorization rates was also investigated in order to clarify their inhibitory effect on the photocatalytic process by acting as scavengers of $^\bullet OH$ radicals or to a competitive adsorption with the dye molecules.

2. Experimental

2.1. Materials

Methyl orange (MeO) (C.I.13025; molecular formula: $C_{14}H_{14}N_3SO_3Na$, molecular weight = 327.34 g/moL) was supplied by Merck reactifs and used as a model compound. Its molecular structure are shown in Fig. 1. The commercially available photocatalysts Degussa P25 TiO_2 (80% anatase and 20% rutile; specific surface area 50 m^2/g; a density of 3.85 g/cm^3 and a mean particle size of 30 nm) and Millennium PC500 TiO_2 (100% anatase; specific surface area 340 m^2/g and a mean particle size of 5–10 nm).

The natural pH of the aqueous dye solution is 6.3. The pH of the solutions was adjusted using H_2SO_4, $HClO_4$, HCl, and HNO_3 from Merck and NaOH from Carlo Erba. H_2O_2, NaCl, KCl, and $BaCl_2$ were supplied by Labosi, and $CaCl_2$, Na_2SO_4, $NaHCO_3$, Na_2CO_3, and Na_2HPO_4 were purchased from Prolabo. Water was purified by Milli-Q system (Millipore) and was used to prepare experimental solutions. None of the salts

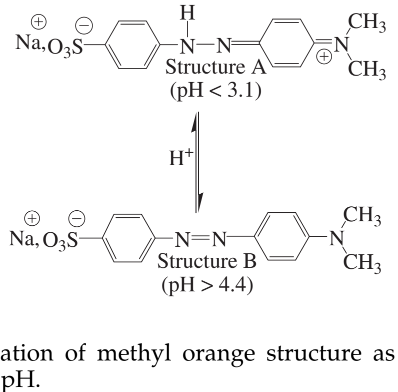

Fig. 1. Variation of methyl orange structure as a function of solution pH.

used had any effect on the dye spectra in the absence of UV light.

Adsorption and photocatalytic experiments were carried out in a Pyrex cylindrical reactor with a double envelope with about 3 cm in diameter, open to air. The reactor assembly was placed on a magnetic stirring plate to maintain TiO_2 in suspension. The photoreactor was exposed to the radiation sources composed of four low pressure mercury UV lamps type Philips HPW 125, (UV-A, $\lambda_{max} = 365$ nm). The mean value of flux intensity reaching the middle of the reacting suspension wax measured with a radiometer type VLX 3 W.

2.2. Procedure and analysis

The adsorption experiments were carried out, using 50 ml of MeO solution. The adsorption equilibrium took 30 min for the photocatalysts used. The irradiation experiments were carried out with 50 ml of solution with a desired dye concentration (10 mg/L) at natural pH and TiO_2 loading (1 g/L) and 20˚C. During both dark adsorption and UV-irradiation periods, samples of 3 ml were collected at regular times and filtered on a Millipore filter, 0.45 μm prior to analysis. The concentration was monitoring by measuring the absorbance at λ_{max} = 465 nm, using a UNICAM HELIOS α UV–visible spectrophotometer. The indicated absorbance is proportional to the Beer–Lambert law in the studied initial concentration of dye.

2.2.1. Adsorption study

The amount of dye adsorbed onto the TiO_2 (mg/g) was calculated using the following relationship:

$$Q_{ads} = \frac{(C_o - C_t)V}{m} \tag{8}$$

where Q_{ads} is the adsorbed quantity at time t (mg/g), C_o is the initial concentration of the substrate (mg/L), C_t is the concentration of the substrate (mg/L) at the moment t of the process of adsorption, V is the volume of the solution (L), and m is the mass of adsorbent (g).

The percentage of removal of the dye by adsorption was calculated using the following equation:

$$R\ (\%) = \frac{(C_o - C_e)}{C_0} \times 100 \tag{9}$$

R (%) is the removal of the dye, C_o is the initial concentration of the substrate (mg/L), C_e is the concentration of the substrate (mg/L) at adsorption equilibrium (contact time: 30 min).

2.2.2. Kinetics of photocatalytic decolorization

The decolorization of dye solutions was also subjected to kinetic analysis. Firstly, the data were subjected to first-order kinetics, which in its usual form is given by:

$$\ln\left(\frac{C_o}{C_t}\right) = k_{app}t \tag{10}$$

where C_o is the initial concentration of the dye (mg/L), C_t is the instant concentration in the sample at time t (mg/L), k_{app} is the pseudo-first-order reaction rate constant (min^{-1}), and t is the reaction time (min). A plot of ln (C_0/C_t) vs. t will yield a slope of k_{app}.

The percentage of removal of the dye by photocatalytic decolorization was calculated using the following equation:

$$R\,(\%) = \frac{(C_e - C_t)}{C_e} \times 100 \tag{11}$$

where R (%) is the removal of the dye, C_e is the concentration of the dye (mg/L) at adsorption equilibrium, C_t is the concentration of the dye (mg/L) at the moment t of the process of photocatalytic decolorization.

3. Results and discussion

3.1. UV–visible spectrophotometry

The UV–vis absorption spectra from 200 to 800 nm of a MeO solution 10 mg/L at natural pH (pH = 6.3) show two absorption maxima, as shown in Fig. 2, with the first band centered at 272 nm in ultraviolet region and the second band at 465 nm in the visible region with a molar absorption coefficient of 9,460 L/mol cm and 27,094 L/mol cm, respectively. The main absorbance at 465 nm is due to the $\pi \rightarrow \pi^*$ transition of the azo group (–N = N–), representing the color of dye solution. The other absorbance at 272 nm is due to the $\pi \rightarrow \pi^*$ transition in the aromatic ring, representing the aromatic content of the MeO.

In acidic medium (pH = 3), we note that the absorption spectrum UV–visible of MeO on the molecular shape has a bathochromic shift of the main

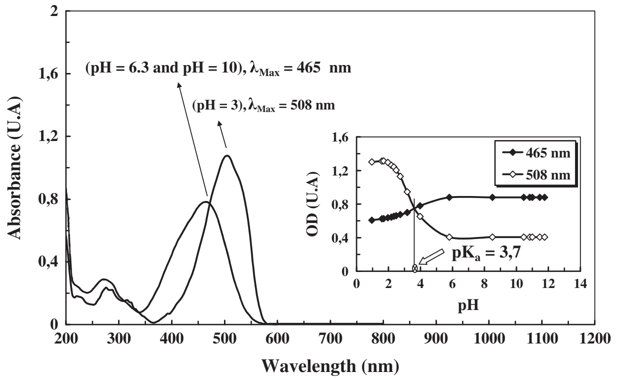

Fig. 2. UV–visible spectra of MeO at different pH. In the inset: evolution of the absorbance of molecular and anionic form of MeO as a function of pH.

band being at 508 nm and a significant increase in the optical density (ε = 38,881 L/mol cm). However, in alkaline medium (pH = 10), the anionic form predominates and no changement in absorption spectrum was observed.

To determine the pK_a of MeO, we recorded the spectrum of a solution at several pH. Inset in Fig. 2 shows the variation of the optical density (OD) of MeO acid/base couple with varying the initial pH of aqueous solution from 1 to 12. The value of pK_a is found by the intersection of the plots at two wavelengths. According to the results, the pK_a is 3.7 and is in perfect agreement with that given by the literature (the theoretical value of pK_a = 3.44 [9]). For pH > pK_a, MeO is in anionic form while molecular form predominates at very acidic pH (pH < pK_a −1) and which can fix a proton as shown in Fig. 1.

3.2. Effect of pH

The wastewater from textile industries usually has a wide range of pH values. Generally, pH plays an important role both in the characteristics of textile wastes and generation of hydroxyl radicals. The role of solution pH in the photocatalytic degradation of MeO was investigated under the determined experimental condition with initial MeO concentration of 10 mg/L, light intensity of 2.5 mW/cm^2, and TiO_2 dosage of 1 g/L for both catalysts. The pH was adjusted using sodium hydroxide (NaOH) in the case of alkaline solutions and using sulfuric acid (H_2SO_4) in the case of acidic solutions. Figs. 3 and 4 show the variation of the apparent rate constant of the photocatalytic degradation with varying the initial pH of aqueous solution from 1 to 12 for P25 and PC500, respectively. The decolorization rate constant in acidic condition is higher than that in alkaline medium. The maximal k_{app} is obtained in the pH range of 2–3. The point of zero charge (*pzc*) of P25 is known to occur at pH ≈ 6.8 [10] and at pH = 6.2 for PC500 [11], at which the surface of the particles is electrically neutral. Below the *pzc*, the surface of TiO_2 is positively charged (Eq. (12)), and above the *pzc*, it is negatively charged (Eq. (13)) according to the following equilibria [12,13]:

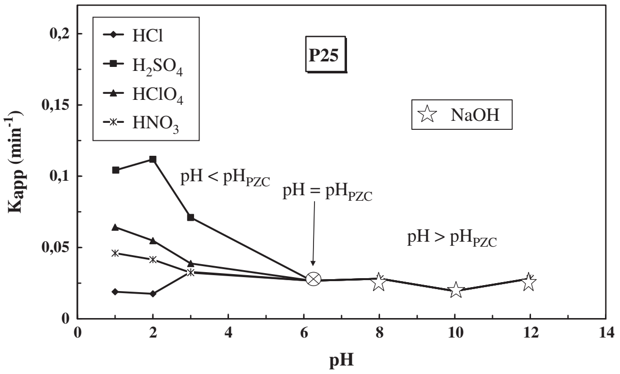

Fig. 3. Effect of pH on the photocatalytic decolorization of MeO in the presence of TiO_2 P25. ([MeO] = 10 mg/L, [P25] = 1 g/L, I = 2.5 mW/cm^2 and T = 20˚C).

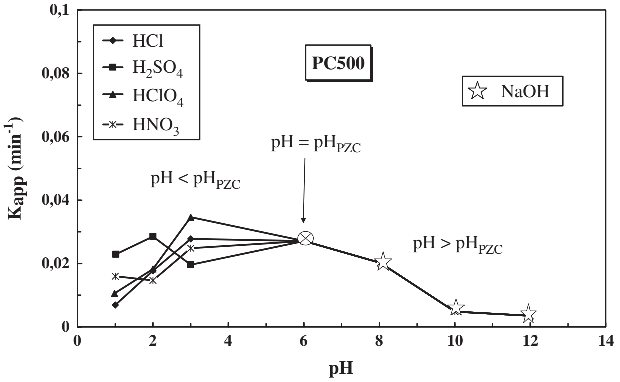

Fig. 4. Effect of pH on the photocatalytic decolorization of MeO in the presence of TiO_2 PC500. ([MeO] = 10 mg/L, [PC500] = 1 g/L, I = 2.5 mW/cm^2 and T = 20˚C).

$$pH < PZC : Ti - OH + H^+ \rightarrow TiOH_2^+ \qquad (12)$$

$$pH > PZC : Ti - OH + OH^- \rightarrow TiO^- + H_2O \qquad (13)$$

The MeO dye in solution is negatively charged. The sodium sulfonate group is hydrolyzed to form dye anion:

$$\Phi - SO_3Na \rightarrow \Phi - SO_3^- + Na^+ \tag{14}$$

where Φ represents a part of the dye structure. The pK_a of MeO is known to occur at pK_a=3.7, at which the structure of the MeO is electrically neutral. As shown in Fig. 1, the structure of MeO is in accordance with values of pH, the structure A is characteristic at pH < 3.1, and the structure B is characteristic at pH > 4.4. At values of pH that are included in 3.1 and 4.4 both structures of MeO can be found [14]. At high pH value, the MeO is negatively charged (structure B), whereas the catalyst is also negatively charged above *pzc*, thus the photocatalytic activity decreases. This result can be explained by electrostatic repulsion between the catalyst surface (TiO^-) and sulfonate groups of dye (SO_3^-). In contrast, the surface of the TiO_2 photocatalyst becomes positively charged when the solution pH is lower than its *pzc*. These opposite charges between the dissolved MeO (structure A) and the TiO_2 particles favorably lead to enhancing the photocatalytic decolorization rate constant due to the increase in their induced interaction. The similar effect trends of pH were observed in the photodegradation of MeO in other reaction systems [4,5]. In addition, the increased decolorization rate constant at this acidic pH can be possibly explained on the basis that at this low pH, $HO_2^{\bullet}$ radical is also able to form, and this can compensate with the decrease in the generated $^{\bullet}OH$ radical concentration [15].

The influence of proton sources of pH on the decolorization of MeO by TiO_2 P25 and PC500 was studied in acidic medium at different pH. The pH was adjusted using sulfuric acid (H_2SO_4), hydrochloric acid (HCl), perchloric acid ($HClO_4$), and nitric acid (HNO_3). The evolution of apparent rate constant k_{app} plotted in Figs. 3 and 4 as a function of pH indicates that it plays an important role on the kinetics of MeO degradation. These results are directly correlated with the ionization state of the catalyst surface, the charge of the molecule studied, and the nature of the acid used to adjust the pH. It can be seen that the photocatalytic activity of P25 (80% anatase and 20% rutile) is greater than that of PC500 (100% anatase), despite the large surface area of the latter. Rutile phase can be excited by visible light, but has a fast charge recombination rate. However, anatase has a slow recombination rate but can only be excited by UV lights. Thus, it is reasonable to produce a mixed phase photocatalyst to increase the total efficiency [16–18]. Earlier studies have shown that Degussa P25 showed better activity for the photocatalytic degradation of a large number of organic compounds, and there is no correlation between photocatalytic activity and specific surface area of TiO_2 [19–22]. In acidic medium (pH < 6.3), the decrease in pH increases the apparent rate constant of disappearance of MeO for the catalyst P25 and contrasting for PC500. At acidic pH (pK_a < pH < pH$_{pzc}$), the catalyst surface is positively charged, increasing the rate constant of degradation can be explained by the attraction between the $TiOH_2^+$ charges of catalyst and sulfonate groups (SO_3^-) of MeO anionic form (structure A). Moreover, at too low pH (pH< pK_a) with the excess concentration of H^+, the proton can interact with the azo link (–N=N–), which can be particularly subject to be the electrophilic attack by the hydroxyl radicals, leading to decreasing the electron densities at the azo group. Consequently, the reactivity of the hydroxyl radicals by the electrophilic mechanism decreases [23]. It is found that the variation in the rate constant of degradation of the dye is strongly correlated with the nature of the acid used. This difference in kinetics is directly related to the counter ion of each acid. The efficiency of photocatalytic degradation of MeO is higher using H_2SO_4 and $HClO_4$ than other acids for P25 and PC500, respectively. As shown in Fig. 3, the results obtained for P25 show an acid pH optimum of degradation at pH = 2 only with H_2SO_4 and the increased degradation rate constant varies with varying the anions in the order: SO_4^{2-} > ClO_4^- > NO_3^-. However, the optimum pH for degradation of MeO for PC500 is around pH=3 (Fig. 4), and the increased k_{app} varies with varying the anions in the order: ClO_4^- > NO_3^- >SO_4^{2-}. Figs. 5 and 6 show the amount evolution of dye adsorbed as a function of pH for both catalysts. It could be mentioned that initial pH influence strongly the adsorption state, which is essential to have a highest decolorization of the dye. These results indicate that the adsorption plays a role in the photocatalytic reaction. However, for both

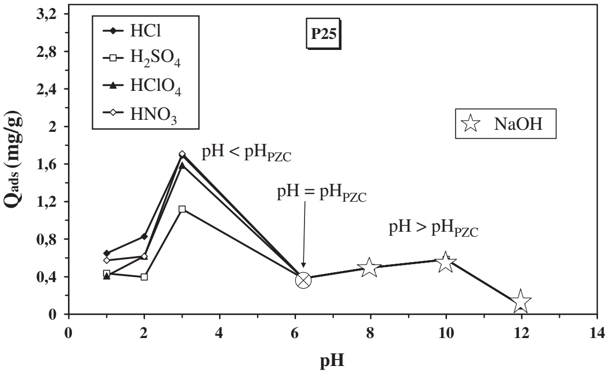

Fig. 5. Effect of pH on the adsorption of MeO on TiO_2 P25. ([MeO] = 10 mg/L, [P25] = 1 g/L, T = 20°C and contact time: 30 min).

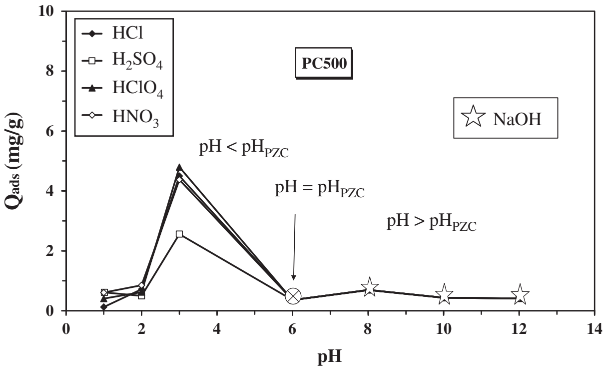

Fig. 6. Effect of pH on the adsorption of MeO on TiO_2 PC500. [MeO] = 10 mg/L, [PC500] = 1 g/L, $T = 20$°C and contact time: 30 min).

catalysts, a different behavior of hydrochloric acid was observed while the k_{app} of degradation decreases with decrease in pH. This can be explained by the inhibitory effect of chloride ions on the reaction, because they readily adsorb on the surface of TiO_2 and compete with the dye molecules for adsorption sites, leading to the decrease in MeO amount adsorbed. In addition, the scavenging of photoproduced $^{\bullet}OH$ by Cl^- was pronounced at very acidic pH, and consequently, the decolorization was slowed with decreases in solution pH from 3 to 1. The overall process can be depicted by Eq. (15) [24].

$$Cl^- + {}^{\cdot}OH \rightarrow Cl^{\cdot} + OH^- \quad k = 3.0 \times 10^9\ M^{-1}S^{-1} (\text{at pH } 2-3) \tag{15}$$

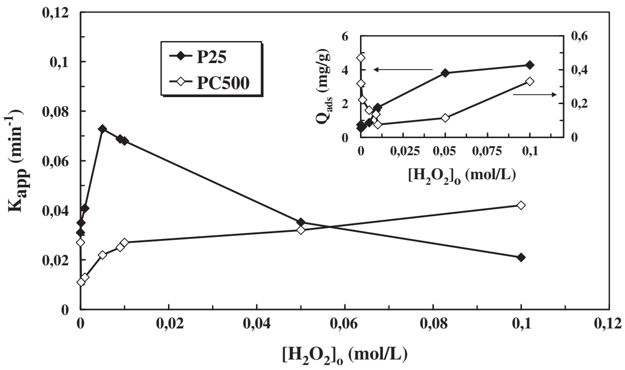

Fig. 7. Effect of hydrogen peroxide concentration on the photocatalytic decolorization of MeO. In the inset: effect of presence of H_2O_2 on adsorption of MeO on TiO_2 (P25 and PC500). ([MeO] = 10 mg/L, [P25] = [PC500] = 1 g/L, I = 2.5 mW/cm^2, pH ≈ 6.3, $T = 20$°C and contact time: 30 min).

This result is confirmed by the good correlation between adsorption and photocatalytic removal of the dye at acidic pH, indicating that photocatalysis occurs mainly at the surface. However, in the presence of other anions (SO_4^{2-}, .ClO_4^-., and NO_3^-), this correlation is not always found. This may be explained by the size of these anions which cannot easily adsorb on TiO_2 at this range of pH. At alkaline pH (pH > 6.3), where $^{\bullet}OH$ were expected to be the predominant species, repulsive forces between negatively charged MeO molecules (SO_3^- groups) and negatively charged TiO^- particles minimized the adsorption of the dye, therefore, observed decolorization of MeO slowed down.

3.3. Effect of H_2O_2 addition

The effect of H_2O_2 concentration within the range of 10^{-4} to 10^{-1} mol/L on the decolorization of the dye was investigated, and the results are depicted in Fig. 7. The H_2O_2 concentration noticeably influenced the color removal of MeO on P25 and PC500, and a different behavior of photocatalytic reaction constant was observed with evolution of H_2O_2 concentration in the presence of these photocatalysts. The amounts of MeO adsorbed on the both photocatalysts are changed by using different H_2O_2 concentrations, as shown in the inset of Fig. 7. As a result, higher adsorption and consequently higher degradation are observed at higher H_2O_2 concentration for both photocatalysts. For PC500, it was observed that the decolorization rate constant (0.027 min^{-1}) in the absence of H_2O_2 decreased to 0.011 min^{-1} due to the presence of 1×10^{-4} mol/L H_2O_2 and increased to 0.042 min^{-1} at 1×10^{-1} mol/L H_2O_2. It has been found that lower concentration of H_2O_2 has higher inhibiting capacity than higher concentration. These results are correlated with dark adsorption of MeO, indicating that the adsorption plays a role in the photocatalytic reaction in the presence of H_2O_2 (inset of Fig. 7). However, in the presence of P25, it can be seen that the rate constant increases with an increase in the concentration of H_2O_2 from 10^{-4} to 10^{-2} mol/L and a further increase in H_2O_2 concentration, k_{app} values decreases. Hence, 5×10^{-3} mol/L H_2O_2 concentration appears to be optimal for the degradation. A similar observation (an increase in H_2O_2 level enhanced the degradation rate up to optimal load beyond which inhibition occurs) had been reported in organic substrates degradation [25–28]. The enhancement of decolorization by addition of low H_2O_2 dosage is due to an increase in the hydroxyl radical concentration as shown by the following equations:

$$\mathrm{TiO_2} \xrightarrow{h\nu \leqslant 400\,\mathrm{nm}} \mathrm{TiO_2(e^-_{CB}) + TiO_2(h^+_{VB})} \tag{16}$$

$$\mathrm{H_2O_2 + TiO_2}(e^-_{\mathrm{CB}}) \rightarrow \mathrm{TiO_2 + OH^- + {}^{\bullet}OH} \tag{17}$$

$$\mathrm{H_2O_2 + O_2^{\bullet -}} \rightarrow \mathrm{{}^{\bullet}OH + OH^- + O_2} \tag{18}$$

But on further increasing the H_2O_2 concentration though the formation of hydroxyl radical is increased, the scavenging reaction of the hydroxyl radicals predominates and resulted in the reduced dye degradation rates [29–31].

$$\mathrm{H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O} \tag{19}$$

$$\mathrm{HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2} \tag{20}$$

3.4. Effect of inorganic salts

Wastewater commonly contains significant amounts of inorganic anions, which have serious effect on water properties. The effects of various salts at different concentrations in the range of 10^{-4} to 10^{-1} mol/L on the decolorization of MeO by UV/TiO_2 process using Degussa P-25 TiO_2 and Millennium PC500 (1 g/L) were examined for an initial dye concentration of 10 mg/L at natural pH and 20°C under a constant light intensity (I = 2.5 mW/cm^2). The effect of chloride, carbonate, bicarbonate, sulfate, and hydrogen phosphate was investigated.

3.5.1. Effect of chloride with different cations

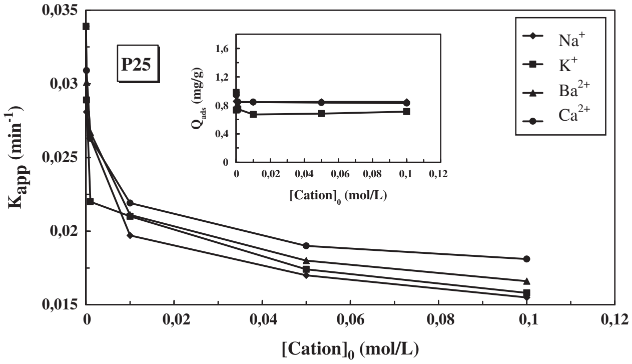

Fig. 8. Effect of presence of cations on photocatalytic decolorization of MeO in the presence of TiO_2 P25. In the inset: Effect of presence of cations on adsorption of MeO on TiO_2 P25. ([MeO] = 10 mg/L, [P25] = 1 g/L, I = 2.5 mW/cm^2, pH ≈ 6.3, T = 20°C and contact time: 30 min).

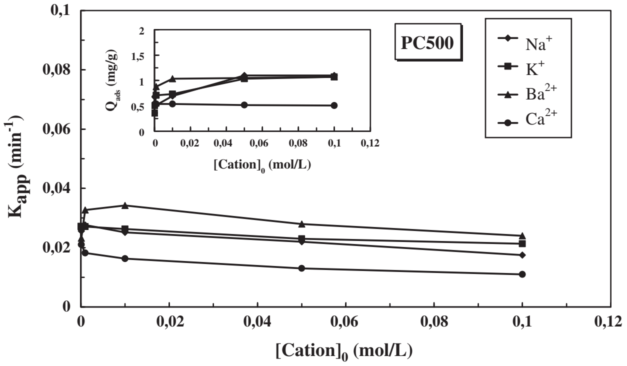

Fig. 9. Effect of presence of cations on photocatalytic decolorization of MeO in the presence of TiO_2 PC500. In the inset: Effect of presence of cations on adsorption of MeO on TiO_2 PC500. ([MeO] = 10 mg/L, [PC500] = 1 g/L, I = 2.5 mW/cm^2, pH ≈ 6.3, T = 20°C and contact time: 30 min).

The influence of NaCl, KCl, $CaCl_2$, and $BaCl_2$ on the photocatalytic oxidation of MeO has been studied for both catalysts. The pseudo-first-order plots of MeO on the photocatalysts P25 and PC500 at different concentrations of salts are shown in Figs. 8 and 9, respectively. These results showed the inhibitory effect of inorganic salts addition on the photocatalytic efficiency, due to the formation of an inorganic salts layer at the surface of TiO_2, which limit the approach of MeO molecules. A correlation between the amount of MeO adsorbed and the rate constant of its photocatalytic degradation was observed as shown in the inset of Figs. 8 and 9, indicating that photocatalysis occurs mainly at the surface. The amount of dye adsorbed on these catalysts reaches a plateau which varied in the following order: $K^+ > Na^+ \approx Ca^{2+} \approx Ba^{2+}$ and $Na^+ \approx K^+ \approx Ba^{2+} > Ca^{2+}$ for P25 and PC500, respectively. For PC500, the effect of addition of salts is an increase in the adsorption of MeO, but in the presence of P25 the amount of MeO adsorbed decreases with an increase in the salts concentration. However, in the presence of barium ions (Ba^{2+}) with PC500, the degradation rate constant of MeO solutions was considerably enhanced and reach a plateau at 10^{-3} mol/L. This result indicates that the adsorption of dye is a prerequisite for the degradation process, and there is a correlation between adsorption and photocatalytic degradation with addition of Ba^{2+} as shown in the inset of Fig. 9. In the remaining cases for both catalysts, it is clear that the decolorization rate constant of dye decreased dramatically with increase the salts concentrations. A similar observation was reported in the organic pollutant degradation at different salts [32–35]. This inhibition can be explained by the presence of chloride ion which is due to the hole scavenging properties of chloride ion according to the following reactions [36]:

$$Cl^- + h^+_{VB} \rightarrow Cl^{\cdot} \quad (21)$$

$$Cl^{\cdot} + Cl^- \rightarrow Cl_2^{\cdot -} \quad (22)$$

$$Cl^- + {}^{\cdot}OH \rightarrow HOCl^{\cdot -} \quad (23)$$

$$HOCl^{\cdot -} + H^+ \rightarrow Cl^{\cdot} + H_2O \quad (24)$$

The $Cl^{\bullet}$ radicals are in principle also capable of oxidizing pollutants, but at lower rates than the $^{\bullet}OH$ radicals, due to their lower oxidation power [37].

These experiments were carried out with different cations, even if they should have few influences on the degradation rate constant. However, the nature of the cations (Na^+, K^+, Ca^{2+}, and Ba^{2+}) could be important since the comparison of the amount of dye adsorbed and the decolorization rate constant. The inhibition by inorganic salts of the degradation of MeO is in the following order: Na^+>K^+ >Ba^{2+}> Ca^{2+} and Ca^{2+}>Na^+>K^+ for P25 and PC500, respectively.

3.5.2. *Effect of CO_3^{2-} and HCO_3^- on the decolorization of MeO*

The effect of addition of Na_2CO_3 into the solution of MeO (which maintains the pH around 10.8 (CO_3^{2-} is the predominant species as pK_a HCO_3^-/CO_3^{2-} = 10.2)) and $NaHCO_3$ (HCO_3^- is the predominant species at pH 8.3) on the photocatalytic oxidation of MeO has been studied, and the results are shown in Figs. 10 and 11 for P25 and PC500, respectively. The amount of MeO adsorbed on TiO_2 surface with different CO_3^{2-} and HCO_3^- concentrations is shown in the inset in Figs. 10 and 11 for P25 and PC500, respectively. The amount of MeO adsorbed in the presence of CO_3^{2-} ions decreases with an increase in the CO_3^{2-} concentration for both catalysts, and the photocatalyst PC500 has higher inhibitory capacity than P25. However, results show that in the presence of HCO_3^-, the increase in the HCO_3^- concentration leads to an increase in the MeO amount adsorbed on the photocatalyst PC500 and decrease on the photocatalyst P25. For P25, increase in the CO_3^{2-} addition decreases the decolorization rate constant of dye. It has been reported that CO_3^{2-} has higher inhibiting effect than HCO_3^- [38,39]. Carbonate is known to react with $^{\bullet}OH$ 45 times faster than bicarbonate [40], and more marked inhibition of degradation is therefore expected. The decrease in decolorization of the dye can be explained as the reaction of positive holes (h^+) and hydroxyl radical ($^{\bullet}OH$) by carbonates (CO_3^{2-}) and bicarbonates (HCO_3^-) as per the following reactions [41,42]:

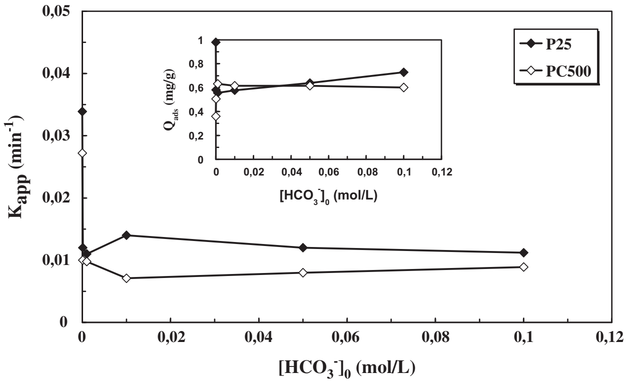

Fig. 10. Effect of HCO_3^- on photocatalytic decolorization of MeO in the presence of TiO_2 (P25 and PC500). In the inset: effect of presence of HCO_3^- on adsorption of MeO on TiO_2 (P25 and PC500). ([MeO] = 10 mg/L, [P25] = [PC500] = 1 g/L, I = 2.5 mW/cm², pH ≈ 8.3, T = 20°C and contact time: 30 min).

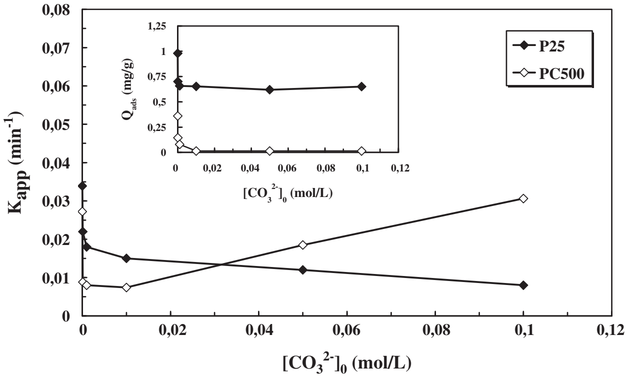

Fig. 11. Effect of CO_3^{2-} on photocatalytic decolorization of MeO in the presence of TiO_2 (P25 and PC500). In the inset: effect of presence of CO_3^{2-} on adsorption of MeO on TiO_2 (P25 and PC500). ([MeO] = 10 mg/L, [P25] = [PC500] = 1 g/L, I = 2.5 mW/cm², pH ≈ 10.8, T = 20°C and contact time: 30 min).

$$CO_3^{2-} + {}^{\cdot}OH \rightarrow OH^- + CO_3^{\cdot -} \quad k = 3.9 \times 10^8\ M^{-1}\ S^{-1} \quad (25)$$

$$HCO_3^- + {}^{\cdot}OH \rightarrow H_2O + CO_3^{\cdot -} \quad k = 8.5 \times 10^6\ M^{-1}\ S^{-1} \quad (26)$$

The carbonate radical is a very selective and strong one-electron oxidant. The oxidation reaction corresponds to second-order rate constants covering a broad range of values. Like the hydroxyl radical, the carbonate radical may react by electron or hydrogen transfer [43]. In addition, it was recently shown that the presence of carbonate or bicarbonate anions could increase the concentrations of active radicals and their capabilities for wide and efficient oxidation of organic pollutants existing in wastewater [44]. Behar et al. [45] reported the possibility of generating carbonate radical anions ($CO_3^{\bullet -}$) with the help of hydroxyl radicals ($^{\bullet}OH$). Thus, the free hydroxyl radical which is a primary source (oxidant) for the photocatalytic degradation decreases gradually with increase in carbonate ions. But in the presence of PC500, the enhancement of the degradation rates constants was observed for the higher concentrations of CO_3^{2-}. The enhancement of degradation by addition of higher concentrations of CO_3^{2-}can be explained by the formation of $CO_3^{\bullet -}$ radical which is less reactive than $^{\bullet}OH$ radical, minimizing the combination of $CO_3^{\bullet -}$ that decays by reacting with itself according to Eqs. (27) or (28).

$$CO_3^{\cdot -} + CO_3^{\cdot -} \Leftrightarrow C_2O_6^{2-} \rightarrow CO_4^{2-} + CO_2 \quad k = 2 \times 10^7\ \mathrm{M^{-1}\ S^{-1}} \tag{27}$$

$$CO_3^{\cdot -} + CO_3^{\cdot -} \xrightarrow{H_2O} 2CO_2 + HO_2^- + OH^- \quad k = 2 \times 10^7\ \mathrm{M^{-1}\ S^{-1}} \tag{28}$$

$$2^{\cdot}OH \rightarrow H_2O_2 \quad k = 5.5 \times 10^9\ \mathrm{M^{-1}\ S^{-1}} \tag{29}$$

The combination of $^{\bullet}OH$ (Eq. (29)) is known to be 275 times higher than that the reaction of $CO_3^{\bullet -}$ with itself [46,47]. The substitution of $^{\bullet}OH$ with $CO_3^{\bullet -}$ could enhance degradation if the latter, although less reactive than $^{\bullet}OH$, undergoes radical–radical recombination at a lesser extent than the hydroxyl radical.

3.5.3. *Effect of SO_4^{2-} on the decolorization of MeO*

The effect of sulfate SO_4^{2-} (from Na_2SO_4) on the photocatalytic degradation process has been studied for both catalysts. Fig. 12 shows the variation of the apparent rate constant of the photocatalytic degradation by varying the initial concentration of SO_4^{2-}. In addition, the variation of the amount of MeO adsorbed on the photocatalyst as function of concentrations of salts of both catalysts is shown in the inset of Fig. 12. This figure indicates that the amount of MeO adsorbed in the presence of sulfate ions decreases with increase in the sulfate concentration for PC500. However, in the presence of P25, the amount of MeO adsorbed is favored with the presence of sulfate ions. The degradation apparent rate constant decreased with an increase in initial concentration of sulfate ions. In comparison, the inhibition of the degradation of MeO is faster in the presence of PC500 than P25. Inhibition effect of sulfate anion can be explained as the reaction of positive holes and hydroxyl radicals with this anion, resulting a prolonged color removal as shown in the following equations [41,48]:

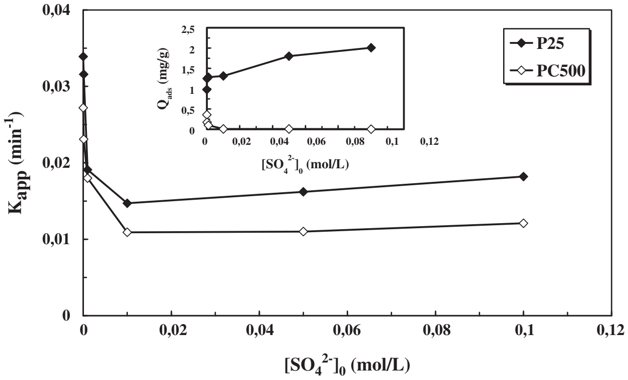

Fig. 12. Effect of presence of SO_4^{2-} on photocatalytic decolorization of MeO in the presence of TiO_2 P25. In the inset: effect of presence of SO_4^{2-} on adsorption of MeO on TiO_2 (P25 and PC500). ([MeO] = 10 mg/L, [P25] = [PC500] = 1 g/L, I = 2.5 mW/cm², pH ≈ 6.8, T = 20°C and contact time: 30 min).

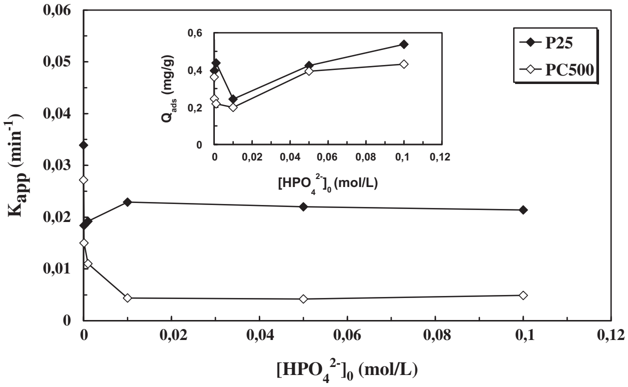

Fig. 13. Effect of presence of HPO_4^{2-} on photocatalytic degradation decolorization of MeO in the presence of TiO_2 P25. In the inset: effect of presence of HPO_4^{2-} on adsorption of MeO on TiO_2 (P25 and PC500). ([MeO] = 10 mg/L, [P25] = [PC500] = 1 g/L, I = 2.5 mW/cm², pH ≈ 9.3, T = 20°C and contact time: 30 min).

$$\mathrm{SO}_4^{2-} + h_{VB}^{+} \rightarrow \mathrm{SO}_4^{\cdot -} \tag{30}$$

$$\mathrm{SO}_4^{2-} + {}^{\cdot}\mathrm{OH} \rightarrow \mathrm{OH}^{-} + \mathrm{SO}_4^{-} \quad k = 1 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{S}^{-1} \tag{31}$$

3.5.4. *Effect of* HPO_4^{2-} *on the decolorization of MeO*

The effect of disodium hydrogen phosphate $\mathrm{Na_2HPO_4}$ on the photocatalytic degradation process of an aqueous solution of MeO (initial pH = 9.3 so the HPO_4^{2-} is the predominant species (pK_a (HPO_4^{2-}/ PO_4^{3-}) = 12.1)) has been studied for both catalysts. The results showed that the rate constants decrease with increase in HPO_4^{2-} concentration as shown in Fig. 13 for both catalysts. The variation of the amount of MeO adsorbed on the photocatalyst as function of HPO_4^{2-} concentration is shown in the inset in Fig. 13. For both catalysts, the inhibition effect of HPO_4^{2-} on the adsorption and the oxidation of MeO have been decreased at high concentration of HPO_4^{2-}. This inhibition effect is related to the reaction of hydrogen phosphate (HPO_4^{2-}) and hydroxyl radical ($^{\bullet}\mathrm{OH}$) as per the following reaction:

$$\mathrm{HPO}_4^{2-} + {}^{\cdot}\mathrm{OH} \rightarrow \mathrm{OH}^{-} + \mathrm{HPO}_4^{\cdot -} \quad k < 1 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{S}^{-1} \tag{32}$$

The excess of HPO_4^{2-} reduces the photodegradation of the dye. They can also scavenge $^{\bullet}\mathrm{OH}$ to form the corresponding anion radicals $\mathrm{HPO}_4^{\bullet -}$, which leads to the decrease in the oxidation process [49].

3.5.5. *Comparison of the inhibition effect of salts on adsorption and photocatalysis*

The variation of the percentage of MeO removal for both the adsorption and photocatalytic decolorization, for P25 and PC500 with a concentration of salts at 10^{-2} mol/L, are shown in Figs. 14 and 15, respectively. This study has been investigated at 10 mg/L dye concentration, 1 g/L catalyst loading for both catalysts, at natural pH and a light flux of 2.5 mW/cm^2. The pattern of adsorption on the both photocatalysts by the various salts is in the following order for P25: MeO only > $\mathrm{CaCl_2}$ ≈ $\mathrm{BaCl_2}$ ≈ NaCl ≈ $\mathrm{Na_2SO_4}$ > KCl > $\mathrm{Na_2CO_3}$ > $\mathrm{NaHCO_3}$ > $\mathrm{Na_2HPO_4}$, and for PC500: $\mathrm{BaCl_2}$ > KCl > NaCl > $\mathrm{NaHCO_3}$ > $\mathrm{CaCl_2}$ > MeO only > $\mathrm{Na_2HPO_4}$ > $\mathrm{Na_2SO_4}$ > $\mathrm{Na_2CO_3}$. It has been found that $\mathrm{Na_2HPO_4}$ and $\mathrm{Na_2CO_3}$ have higher inhibiting capacity than other salts in the amount of MeO adsorbed for P25 and PC500, respectively. Moreover, the decrease in the R (%) by photocatalytic decolorization was observed in the following order: P25: MeO only > $\mathrm{Na_2HPO_4}$> $\mathrm{CaCl_2}$ > KCl ≈ $\mathrm{BaCl_2}$ > NaCl > $\mathrm{Na_2CO_3}$ ≈ $\mathrm{Na_2SO_4}$ ≈ $\mathrm{NaHCO_3}$, and PC500: $\mathrm{BaCl_2}$ > MeO only > KCl ≈ NaCl > $\mathrm{CaCl_2}$ > $\mathrm{Na_2SO_4}$ > $\mathrm{Na_2CO_3}$ ≈ $\mathrm{NaHCO_3}$ > $\mathrm{Na_2HPO_4}$. It has been found that $\mathrm{NaHCO_3}$ and $\mathrm{Na_2HPO_4}$ have higher inhibiting capacity than other salts in photocatalytic degradation of MeO for P25 and PC500, respectively.

Addition of salts in the presence of $\mathrm{TiO_2}$ significantly reduces adsorption and decolorization efficiencies for both catalysts. The behavior of the two catalysts is generally similar; however, the

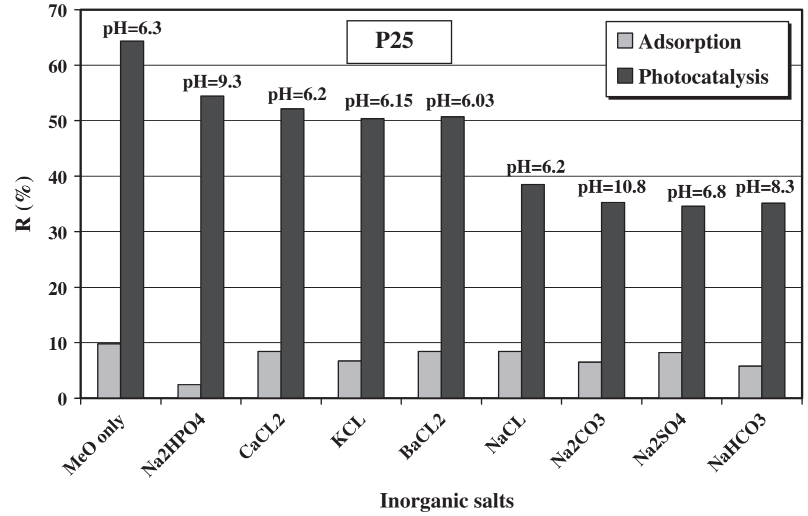

Fig. 14. Effect of absence and presence of salts on photocatalytic decolorization of MeO in the presence of $\mathrm{TiO_2}$ P25. ([Salts] = 10^{-2} mol/L, [MeO] = 10 mg/L, [P25] = 1 g/L, I = 2.5 mW/cm^2, T = 20˚C and contact time: 30 min).

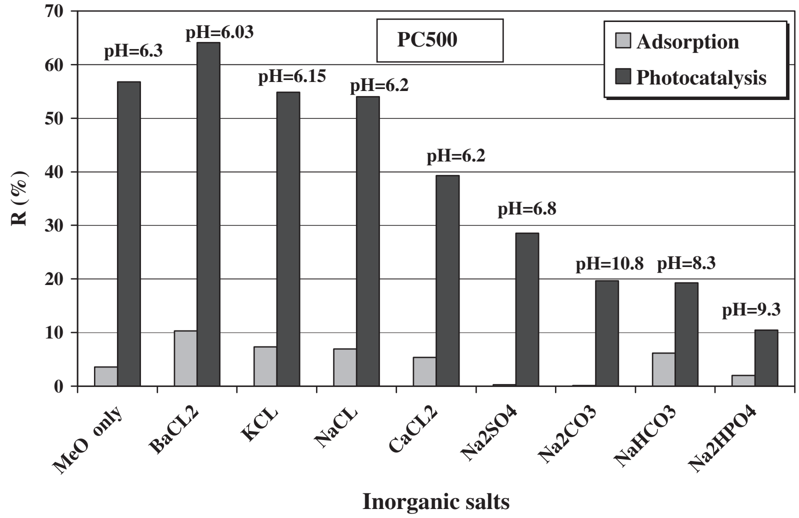

Fig. 15. Effect of absence and presence of salts on photocatalytic decolorization of MeO in the presence of TiO_2 PC500. ([Salts] = 10^{-2} mol/L, [MeO] = 10 mg/L, [PC500] = 1 g/L, $I = 2.5$ mW/cm^2, $T = 20$°C and contact time: 30 min).

changes in the pH of the solution by the presence of alkali salts like carbonate, bicarbonate, and hydrogen phosphate lead to differentiation of their behavior, since the two catalysts react differently with the variation of pH.

4. Conclusion

The photodegradation of mono azo anionic dye from aqueous solution in the presence of TiO_2 (P25 and PC500) under UV light irradiation was investigated. The adsorption of dye is a prerequisite for the degradation process, and there is a correlation between dark adsorption and photocatalytic degradation at acidic and alkaline mediums. These results are directly correlated with the ionization state of the catalyst surface, the charge of the molecule studied, and the nature of the acid used to adjust the pH. The decolorization rate constant in acidic condition is higher than that in neutral and alkaline condition. The enhancement of the degradation rates constants observed for the lower concentrations of H_2O_2 in the presence of P25 and contrasting in the presence of PC500. Addition of salts such as NaCl, KCl, $CaCl_2$, Na_2SO_4, Na_2HPO_4, Na_2CO_3, and $NaHCO_3$ in the presence of TiO_2 significantly reduces adsorption and decolorization efficiencies for both catalysts. However, $BaCl_2$ seems to enhance adsorption and degradation rate of MeO in the presence of TiO_2 PC500. The behavior of the two catalysts is generally similar; however, the changes in the pH of the solution by the presence of alkali salts like carbonate, bicarbonate, and hydrogen phosphate lead to differentiation of their behavior, since the two catalysts react differently with the variation of pH.

Acknowledgment

This work was financially supported by the Ministry of Higher Education and Scientific Research of Algeria.

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