

UV or visible light induced photodegradation of AO7 on TiO₂ particles: the influence of inorganic anions

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Abstract

In this paper, the effects of various inorganic anions (NO₃⁻, Cl⁻, SO₄²⁻, HCO₃⁻, H₂PO₄⁻) on the photodegradation of an azo dye, acid orange 7 (AO7) were investigated under UV or visible light irradiation in the presence of TiO₂ particles. The effects of inorganic anions on the photodegradation of AO7 under visible light irradiation were significantly different from UV irradiation pathway. In TiO₂/UV system, inorganic anions inhibited the photodegradation of the dye by their trapping hydroxyl radicals. In TiO₂/Vis system, the observed inhibition effects of inorganic anions can be interpreted by competitive adsorption. In addition, the results indicated that the photodegradation of AO7 took place mainly in the bulk solution under UV light irradiation, while under visible light irradiation, the reaction occurred on the catalyst surface.

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1. Introduction

Dye-containing wastewater generated from textile industries is a major source of environmental pollution. Azo dyes, which are the largest group of coloring agents [1], are widely used in the industry. Since azo dyes are intentionally designed to resist degradation, traditional methods such as flocculation, carbon adsorption, reverse osmosis and activated sludge process have low mineralization efficiency for this class of xenobiotics [2]. In recent years, heterogeneous photocatalysis has attracted much attention for the treatment of dye-containing wastewater [3]. Many dye pollutants can be degraded effectively and ultimately mineralized using TiO₂ photocatalysts under UV light irradiation [4–6]. In these reactions, organic pollutants are oxidized by photo-generated positive holes (h⁺) or by reactive oxygen species (OH•, HOO•, O₂•⁻) formed on the TiO₂ surface under UV light irradiation [3,7]. However, TiO₂ particles cannot absorb visible light and artificial UV light sources are expensive. Therefore, the use of visible light of solar energy, which is free and inexhaustible, has recently drawn considerable attention.

Some studies on the visible light induced photodegradation of dye pollutants in the presence of TiO₂ particles have been reported [8–12], and several mechanisms have been proposed to explain dye pollutants decomposition. Under visible light irradiation, the excited dye molecule will inject an electron to the conduction band of TiO₂ particles, whereas the dye is converted to cationic dye radical. The injected electron can reduce surface chemisorbed oxygen molecule to form the oxidizing species similar to those under UV light irradiation. These reactive radicals bring about photodegradation.

Dye-containing wastewater usually contains not only organic contaminants, but also considerable concentrations of common inorganic anions, such as chloride, carbonate, sulfate, nitrate, and phosphate. They can inhibit the photodegradation of dye pollutants. Although some studies have examined the effects of various inorganic anions on the photodegradation of dye pollutants under UV light irradiation [5,13,14], less attention has been expended on the effect of the type of light source (UV or visible light) on the photodegradation of dye pollutants in the presence of different inorganic anions. A study on the effects of inorganic anions is expected to provide some details on the photodegradation mechanism of dye pollutants under different light source. In this paper, NaNO₃, NaCl, Na₂SO₄, NaHCO₃ and NaH₂PO₄ were selected as

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additives and acid orange 7 (AO7) was used as test dye pollutant.

2. Experimental section

2.1. Materials

Acid orange 7 shown in Fig. 1 was obtained from Sigma Chemical Co. and was used without further purification. TiO₂ (P-25, ca. 80% anatase, 20% rutile; BET area, ca. 50 m²/g; mean particle size, ca. 30 nm) was supplied by Degussa Co. NaNO₃, NaCl, Na₂SO₄, NaHCO₃ and NaH₂PO₄ were of analytical reagent grade quality and were employed without further purification. All experiments were carried out using deionized and double distilled water. The pH of the solution was adjusted with HNO₃ or NaOH.

2.2. Photoreactor and light source

Photodegradation of AO7 under UV light irradiation was conducted in a quartz reactor of 450 ml capacity at batch mode. In the center of cylindrical reactor, two 6 W ($E_{\max} = 365$ nm) UV lamps were used as a UV light source. It was cooled by re-circulation water to 20 ± 2 °C during the experiments.

Photodegradation of AO7 under visible light irradiation was performed in a Pyrex reactor of 1000 ml capacity. A 175 W metal halide lamp (Philips), as a visible light source, was positioned inside a cylindrical Pyrex vessel surrounded by a jacket. NaNO₂ (2 M) solutions were circulated through the jacket to filter out the UV emission of the lamp below 400 nm and cool the reactor to 20 ± 2 °C.

2.3. Procedures and analyses

In TiO₂/UV system, an aqueous TiO₂ dispersion was prepared by adding 0.9 g of TiO₂ powder to 450 ml solution containing AO7 and inorganic anions at designed concentrations. Prior to irradiation, the dispersions were magnetically stirred in the dark for ca. 1 h to achieve the adsorption equilibrium of AO7 on the catalyst. The concentration of substrate in bulk solution at this point was used as the initial value of the further kinetic treatment of the photodegradation process. All irradiation were carried out under constant stirring. At given irradiation time intervals, the dispersion was sampled (10 ml), centrifuged, and then filtered through a Millipore filter (pore size 0.22 μm) in order to remove

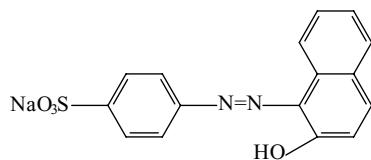


Fig. 1. The structure of the AO7 molecule.

the TiO₂ particles. The filtrates were analyzed for UV-Vis absorbance and TOC. UV-Vis absorption spectra were measured with a Shimadzu UV1206 spectrophotometer. The determination wavelength is 484 nm for AO7, which is the maximum absorption wavelength. The determined absorption was converted to concentration through the standard curve of the dye ($r = 0.9999$). Total organic carbon (TOC) of the filtrates was determined by an Apollo 9000 TOC analyzer (catalytic oxidation on Pt at 680 °C).

In TiO₂/Vis system, the experiment procedures were similar to that in TiO₂/UV system, except that the suspension was prepared by addition of 2 g TiO₂ to 1000 ml solution containing AO7 and inorganic anions at designed concentrations.

2.4. Adsorption experiments

All equilibrium adsorption experiments were carried out in a 100 ml suspension with 0.2 g of TiO₂ particles. The pH of the suspension was adjusted with either diluted HNO₃ or NaOH. The suspension was equilibrated 24 h in a shaker at 20 ± 2 °C. Then the suspension was centrifuged, and subsequently filtered through a Millipore filter (pore size 0.22 μm) to remove TiO₂ particles. The equilibrium concentration of AO7 was determined by measuring the absorbance of the filtrates at 484 nm.

3. Results and discussion

3.1. Decolorization

Fig. 2 shows UV-Vis spectral changes of AO7 in aqueous TiO₂ dispersion as a function of irradiation time under UV or visible light irradiation. The absorption spectrum of AO7 in water was characterized by four bands in the UV-Vis region. Two bands in visible region, with a major absorption peak at 484 nm and a shoulder band at 430 nm, are due to the hydrazone form and azo form of AO7, respectively. Two bands in the ultraviolet region located at 230 and 310 nm attribute to the benzene and naphthalene rings of AO7, respectively [6]. In the presence of TiO₂ particles, the extent of the adsorption of AO7 (40 ppm) on the catalyst surface was ca. 25%. Under visible light irradiation, the characteristic adsorption band at 484 nm decreased rapidly and almost disappeared after ca. 6 h, resulting in complete decolorization of the suspension; concomitantly, the intensities of the absorption bands at 230 and 310 nm decreased rather slowly and then remained practically constant at the end of experiment, indicating that part of benzene and naphthalene ring of the dye was still not decomposed. While under UV light irradiation, the intensity of the band at 484 nm decreased rapidly with time and almost disappeared after about 4 h. When complete decolorization of the suspension occurred, the intensities of the bands at 230 and 310 nm continued to decrease, indicating

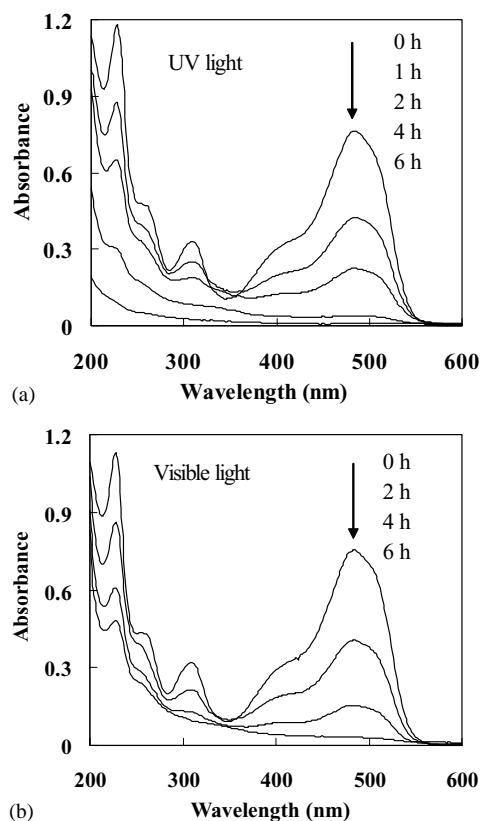


Fig. 2. UV-Vis spectral changes of AO7 in aqueous TiO₂ dispersion as a function of irradiation time under (a) UV or (b) visible light irradiation: pH 5.6; C₀ = 40 ppm; [TiO₂] = 2.0 g/l.

that most of benzene and naphthalene ring of the dye was destroyed.

Blank experiments established that AO7 did not degrade in aqueous TiO₂ suspensions in the dark or when irradiated with UV or visible light in the absence of TiO₂ particles. Therefore, both light source (UV or visible light) and TiO₂ semiconductor are indispensable to the photodegradation of AO7.

3.2. Mineralization

Changes of TOC and AO7 concentration under UV or visible light irradiation are presented in Fig. 3. The temporal concentration changes of AO7 followed the pseudo-first-order kinetics. Apparent rate constants for the photodegradation of AO7 under UV and visible light irradiation were 0.990 ($r = 0.975$) and 0.513 h⁻¹ ($r = 0.952$), respectively. Therefore, the photodegradation rate of AO7 under UV light irradiation was 1.93 times higher than that under visible light irradiation. Similar results were also reported in literature [15]. It was observed that TOC of the solution disappeared rapidly under UV light irradiation and continued to decrease after the suspension was completely discolored. It was also observed that the mineralization rate of AO7 under visible light irradiation was very slow, com-

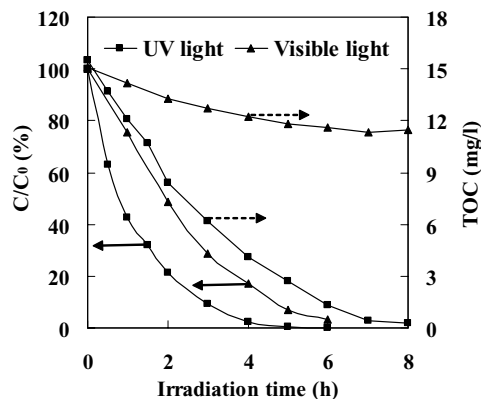


Fig. 3. Changes of TOC and AO7 concentration as a function of irradiation time under UV or visible light irradiation: pH 5.6; C₀ = 40 ppm; [TiO₂] = 2.0 g/l.

pared with that under UV light irradiation. It was worth noting that the final TOC (11.6 mg/l) of the solution was unchanged after the suspension was completely discolored under visible light irradiation, indicating the formation of some long-lived by-products, which were no longer mineralized under further irradiation by visible light.

3.3. Influence of inorganic anions

The presence of inorganic anions such as chloride, sulfate, carbonate, nitrate, and phosphate is common in textile effluents. These ions may affect the adsorption of the degrading species, act as hydroxyl radicals scavengers and absorb UV light as well [16], resulting in the inhibition effect on the photodegradation of dye pollutants.

Since TiO₂ semiconductor suspended in water behave similar to diprotic acids, the adsorptive properties of TiO₂ particles depend significantly on the solution pH. The point of zero charge (pzc) for P-25 is about 6.25 pH units [7]. For pH value higher than 6.25, the surface of P-25 particles becomes negatively charged and it is the opposite for pH smaller than 6.25. Since AO7 is an anionic dye in aqueous solution, at low pH solution (pH 5.6), attractive forces between the organic anion and the catalyst surface will favor adsorption. Inorganic anions, such as Cl⁻, HCO₃⁻, SO₄²⁻, and H₂PO₄⁻ can be adsorbed on the positively charged surface of the catalyst by electrostatic attraction under the same conditions, leading to the competitive adsorption. In order to investigate the effect of these inorganic anions on the photodegradation of AO7, a series of experiments were conducted in the presence of P-25 particles with UV or visible light irradiation at pH 5.6.

3.3.1. Influence of NO₃⁻ on the photodegradation of AO7

Fig. 4 shows the changes of the adsorption and the photodegradation of AO7 with increasing the NaNO₃ concentration under UV or visible light irradiation. Since the common cation of all the added salts, Na⁺, is inert, only

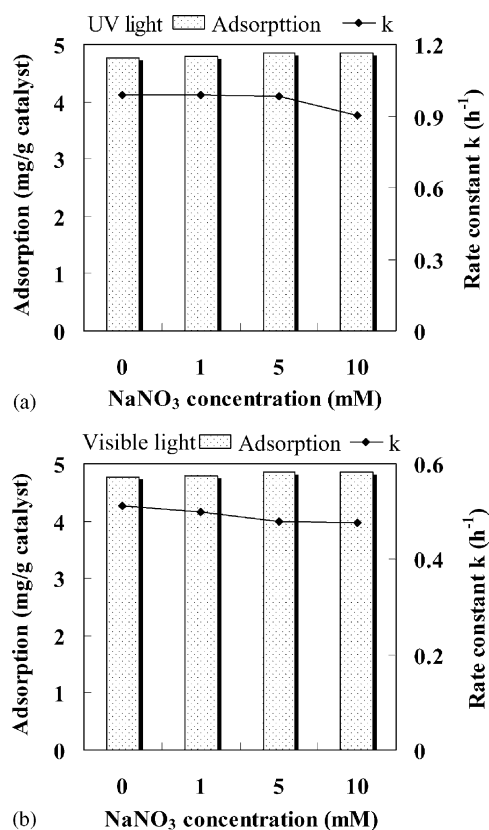


Fig. 4. The effects of different concentrations of NaNO₃ on the adsorption and the photodegradation of AO7 under (a) UV or (b) visible light irradiation: pH 5.6; C₀ = 40 ppm; [TiO₂] = 2.0 g/l.

anions are involved in the inhibition effect. As shown in Fig. 4, the addition of NO₃⁻ to the solution did not make any significant effect on the adsorption and the photodegradation rate of AO7 under UV or visible light irradiation. Abdullah et al. [17] had also reported that the presence of NaNO₃ had negligible effect on the photodegradation of ethanol and 2-propanol under UV light irradiation.

3.3.2. Influence of Cl⁻ on the photodegradation of AO7

The effect of Cl⁻ on the photodegradation of AO7 under UV or visible light irradiation was investigated by adding NaCl to the solution (Fig. 5). Obviously, with increasing the Cl⁻ concentration, both adsorption of AO7 on the catalyst and the photodegradation rate decreased gradually under UV or visible light irradiation. In TiO₂/UV system, the observed inhibition effect is often explained by competitive adsorption [18]. The other probability is that chloride ions act as scavengers of OH• radicals through the following reaction:



Since Cl• is less reactive than OH• radicals, the excess Cl⁻ may have the inhibition effect on the photodegradation of AO7. In TiO₂/Vis system, OH• radicals in solution although detectable, are only a small part of the active oxygen radicals produced under visible light irradiation and not the main ac-

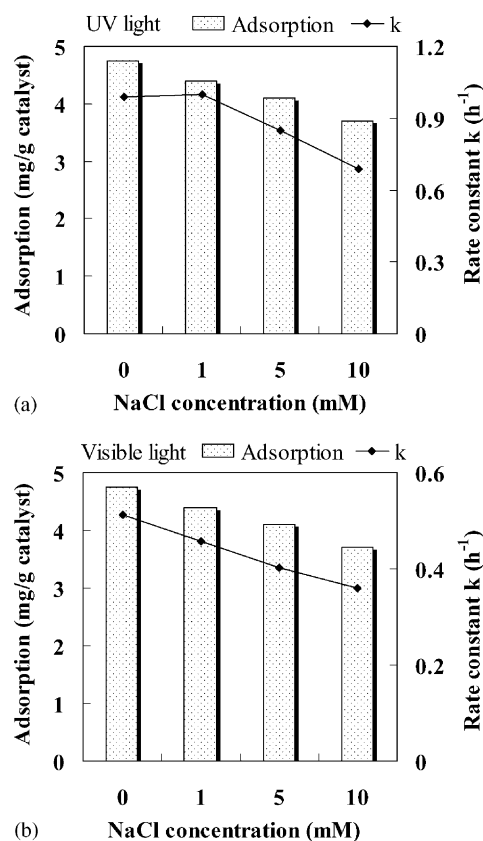


Fig. 5. The effects of different concentrations of NaCl on the adsorption and the photodegradation of AO7 under (a) UV or (b) visible light irradiation: pH 5.6; C₀ = 40 ppm; [TiO₂] = 2.0 g/l.

tive species for the photodegradation of the dye [19]. Therefore, the inhibition effect of Cl⁻ ions in TiO₂/Vis system can be interpreted by competitive adsorption.

3.3.3. Influence of SO₄²⁻ on the photodegradation of AO7

The effect of increasing Na₂SO₄ concentration on the photodegradation of AO7 under UV and visible light irradiation are shown in Fig. 6. At pH 5.6, the main inorganic anion in solution was SO₄²⁻. Under UV light irradiation, SO₄²⁻ can inhibit the photodegradation of the dye in two ways: (1) competitive adsorption with the dye on the TiO₂ surface; (2) trapping positive holes (h⁺) and hydroxyl radical (OH•) through the following reactions:



In TiO₂/UV system, it was observed that the adsorption of AO7 on TiO₂ was inhibited significantly with increasing the SO₄²⁻ concentration, while the photodegradation rate of AO7 was decreased slightly in the presence of SO₄²⁻ ions. Obviously, the binding of the SO₄²⁻ with the catalyst was very strong, compared with NO₃⁻ and Cl⁻ ions. In this study, the significant reduction of the adsorption of AO7 did not lead to the appreciable retardation of the

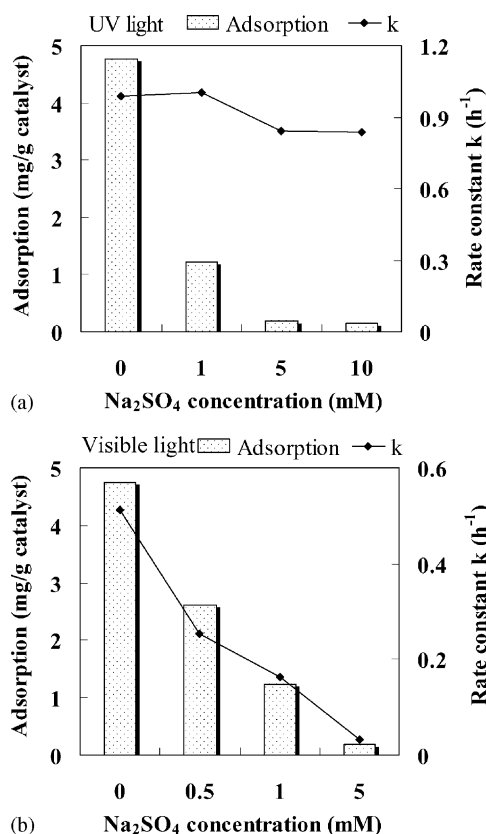


Fig. 6. The effects of different concentrations of Na₂SO₄ on the adsorption and the photodegradation of AO7 under (a) UV or (b) visible light irradiation: pH 5.6; C₀ = 40 ppm; [TiO₂] = 2.0 g/l.

photodegradation rate of the dye, which suggested that the photodegradation of AO7 under UV light irradiation occurred mainly in the aqueous solution. Moreover, SO₄²⁻ may react with OH[•], leading to the generation of less reactive radical SO₄^{•-}. But in the present study, SO₄²⁻ ions had non-appreciable inhibition effect on the photodegradation of AO7. The results added support to the view that SO₄²⁻ was inefficient hydroxyl radical scavenger [20]. In TiO₂/Vis system, both the adsorption of AO7 and the photodegradation rate was decreased significantly, indicating that the degradation of AO7 took place mainly at the catalyst surface.

3.3.4. Influence of HCO₃⁻ on the photodegradation of AO7

The effects of different concentrations of NaHCO₃ on the adsorption and the photodegradation of AO7 under UV or visible light irradiation are presented in Fig. 7. It was observed that HCO₃⁻ showed higher adsorption compared with nitrate, chloride, and sulfate ions. In TiO₂/UV system, the adsorption of AO7 on TiO₂ was affected significantly by HCO₃⁻. The adsorption of AO7 on TiO₂ decreased rapidly with increasing the HCO₃⁻ concentration. When the HCO₃⁻ concentration increased to 10 mM, the adsorption of AO7 on the catalyst was insignificant. The presence of HCO₃⁻ had a negligible inhibition on the photodegradation of AO7, which suggested that competitive

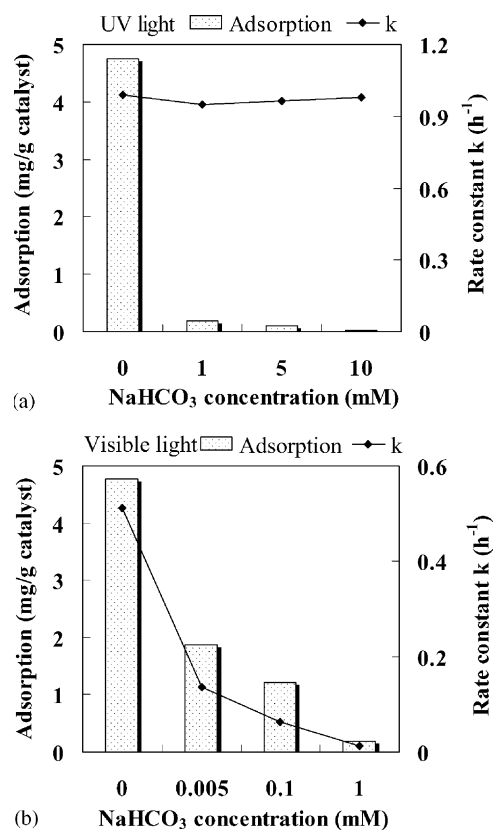
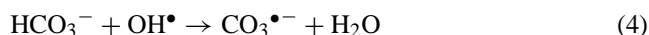


Fig. 7. The effects of different concentrations of NaHCO₃ on the adsorption and the photodegradation of AO7 under (a) UV or (b) visible light irradiation: pH 5.6; C₀ = 40 ppm; [TiO₂] = 2.0 g/l.

adsorption of HCO₃⁻ ions did not lead to the retardation effect of the photodegradation under UV light irradiation. In TiO₂/UV system, HCO₃⁻ can trap hydroxyl radicals to produce CO₃^{•-} (reaction (4)), which is less reactive [21]:



Although this reaction may occur in TiO₂/UV system, it appears to be of minor importance on the photodegradation of the dye. In TiO₂/Vis system, it was observed that the photodegradation rate of AO7 decreased rapidly with increasing the HCO₃⁻ concentration, which was in consistent with the change of the adsorption of AO7 on TiO₂. The results also indicated that the photodegradation of AO7 occurred mainly on the catalyst surface.

3.3.5. Influence of H₂PO₄⁻ on the photodegradation of AO7

The effect of H₂PO₄⁻ on photodegradation of AO7 was studied by adding NaH₂PO₄ to the solution of AO7. At pH 5.6, the phosphate ions were virtually in the H₂PO₄⁻ form. As shown in Fig. 8, the presence of H₂PO₄⁻ inhibited significantly the adsorption of AO7 on the catalyst. With increasing the H₂PO₄⁻ concentration, the adsorption of AO7 on TiO₂ decreased quickly. Flaig-Baumann

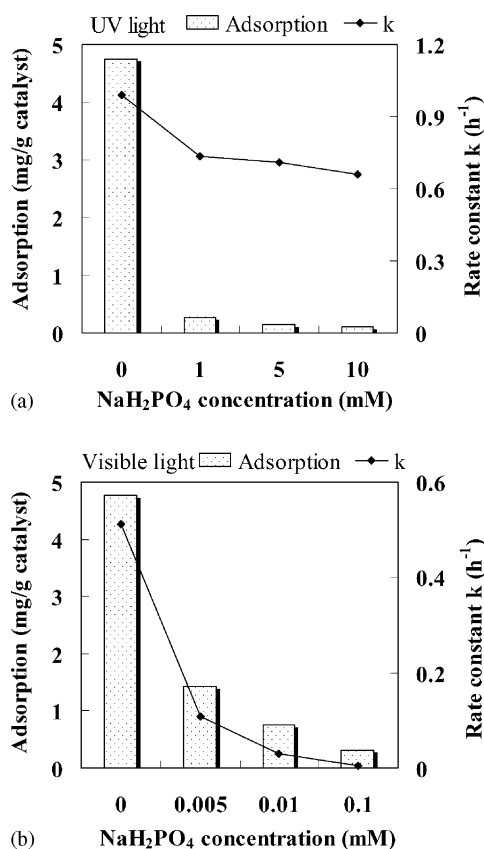


Fig. 8. The effects of different concentrations of NaH_2PO_4 on the adsorption and the photodegradation of AO7 under (a) UV or (b) visible light irradiation: pH 5.6; $C_0 = 40$ ppm; $[\text{P-25}] = 2.0$ g/l.

et al. [22] had proposed an adsorption mechanism consisting of an exchange reaction between the surface hydroxyl groups of TiO_2 and H_2PO_4^- . In TiO_2/UV system, the photodegradation rate of AO7 decreased slowly with increasing the H_2PO_4^- concentration. Under UV light irradiation, H_2PO_4^- ions reacted with positive holes (h^+) and hydroxyl radicals (OH^\bullet) to form less reactive radicals $\text{H}_2\text{PO}_4^\bullet$ [23], resulting in the decrease of the photodegradation of AO7. In TiO_2/Vis system, the behavior of H_2PO_4^- ions was similar to HCO_3^- ions in that the photodegradation of AO7 was inhibited markedly as soon as NaH_2PO_4 was introduced.

3.3.6. Influence of adsorption on the photodegradation of AO7

Fig. 9 shows the effect of adsorption on the photodegradation of AO7 in the presence of different inorganic anions under UV or visible light irradiation. In TiO_2/UV system, no correlation was found between the photodegradation rate and the adsorption of AO7 on TiO_2 . The result indicated clearly that the inhibition effects of inorganic anions were not through competitive adsorption and the photodegradation of AO7 under UV light irradiation took place mainly in the bulk solution. While in TiO_2/Vis system, a perfectly linear correlation was observed between the photodegradation

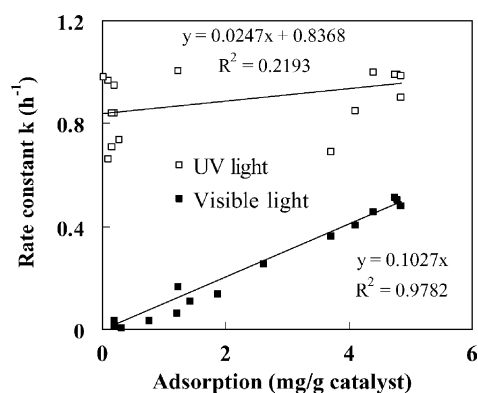


Fig. 9. The effect of the adsorption on the photodegradation of AO7 in the presence of different inorganic anions under UV or visible light irradiation: pH 5.6; $C_0 = 40$ ppm; $[\text{TiO}_2] = 2.0$ g/l.

rate and the adsorption of AO7 on TiO_2 . This correlation suggested that the observed retardation effects of inorganic anions were due to the competitive adsorption with the dye on the catalyst surface and the photodegradation of AO7 under visible light irradiation occurred mainly on the catalyst surface.

4. Conclusion

The effects of various inorganic anions on the photodegradation of AO7 were investigated under UV or visible light irradiation. The results in present work indicated that the effects of the inorganic anions on the photodegradation of AO7 depended strongly on the type of light source. The competition of inorganic anions with AO7 for adsorption was in the order of: $\text{NO}_3^- < \text{Cl}^- < \text{SO}_4^{2-} < \text{HCO}_3^-$, H_2PO_4^- . Under UV light irradiation, HCO_3^- ions had negligible effect on the photodegradation of AO7, while NO_3^- , Cl^- , SO_4^{2-} , and H_2PO_4^- ions had little inhibition on the photodegradation of AO7. No significant relationship between the adsorption of AO7 and the photodegradation rate of the dye under UV light irradiation was observed in the experiment, indicating that inorganic anions inhibited the photodegradation of the dye by their trapping hydroxyl radicals (OH^\bullet) and the photodegradation of the dye mainly took place in the bulk solution. Under visible light irradiation, the inhibition effect of inorganic anions on the photodegradation of AO7 was in the order: $\text{NO}_3^- < \text{Cl}^- < \text{SO}_4^{2-} < \text{HCO}_3^-$, H_2PO_4^- . A perfectly linear relationship between the adsorption of AO7 and the photodegradation rate of the dye under visible light irradiation indicated that inorganic anions affected the photodegradation of the dye by competitive adsorption and the photodegradation of AO7 occurred mainly on the catalyst surface under visible light irradiation. It should be noted that it was difficult to compare the present results with other reported studies as the inhibition effect appeared to vary according to the dye and pH of the solution [18].

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