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Short communication

Degradation of pararosaniline dye photoassisted by visible light

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Abstract

The photoassisted degradation of pararosaniline dye has been investigated in aqueous solutions under illumination by visible light. Illumination of the dye solution in the presence of oxygen or argon does not degrade the dye molecule. Degradation occurs in the presence of H_2O_2. Pararosaniline dye can be easily decomposed in the TiO_2 suspensions using oxygen and hydrogen peroxide as electron acceptors. The degradation kinetics followed first-order type equation in all cases. Based on the data obtained the reaction mechanism was proposed.

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Keywords: Photoassisted degradation; Pararosaniline dye; TiO_2 catalyst; Degradation mechanism

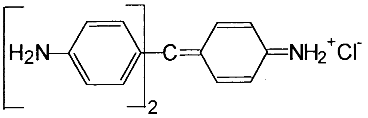
1. Introduction

Titanium(IV) oxide suspended in water has proven to be as one of the most active photocatalyst. Extensive work has shown that a wide range of organic pollutants in aqueous solutions containing UV light illuminated TiO_2 particles are completely oxidized [1–5]. But, it is known that only 3–5% of the solar energy reaching the surface of the earth is available to excite TiO_2 directly and the artificial UV light sources are expensive and unstable. Therefore, many recent studies have been directed at exploring methods that can utilize visible light or sunlight for degradation of organic pollutants. These investigations have shown that colored compounds can be degraded in the presence of TiO_2 under the visible light illumination because of their absorption spectra in the visible region [6–11]. The degradation of colored substance occurs through electron injection from its excited state into the conduction band of TiO_2 particles [12–15]. TiO_2 has a significant role as an electron carrier leading to the separation of the injected electrons and cationic dye radicals. Such assisted photoprocesses provide an attractive way to treat or pretreat dye polluted water.

The aim of this study was to investigate the photocatalytic degradation of pararosaniline dye in the presence of TiO_2 with a light source simulating solar spectrum. This compound was chosen as a representative member of triphenylmethane derivatives to obtain some valuable informations on the efficiency of the assisted photodegradation. Nothing, as far as we know, has been reported about its photocatalytic destruction. Since it has a high molar absorption coefficient, the decrease of pararosaniline dye concentration during the degradation could be monitored up to very small amounts. The effect of oxygen and hydrogen peroxide on the degradation was studied, since they are often suggested as the primary acceptors of the conduction band electrons. The kinetics and some mechanism details of the degradation under different experimental conditions are discussed on the basis of the experimental results.

2. Experimental details

Pararosaniline dye is a derivative of the triphenylmethane structure. In the present work pararosaniline hydrochloride $(4\text{-}NH_2C_6H_4)_2C(C_6H_4NH_2Cl)$ was used (see structure below). The dye and other chemicals were of analytic grade and were used without further purification.



The solutions containing 1×10^{-5} mol dm^{-3} of pararosaniline dye were prepared in doubly distilled water. In all cases the pH of the solution was 5.9, except in experiments where the effect of pH on the absorption spectra was studied.

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Simulated solar light (a 150 W halogen lamp, Osram 9.7 V and a concave mirror of selective reflection) was used as the light source. The process was carried out in an oxygen stream at room temperature, in a cell (sample volume 20 cm^3) made of pyrex glass. In the experiments studying the effect of H_2O_2 on the degradation of pararosaniline dye, the oxygen was swept out of the reaction vessel with a stream of argon. During illumination there was not any change of the pH value of the solution, except in the presence of TiO_2 when a small decrease of about 0.2 units was observed.

Photocatalytic experiments were carried out using 2.5 $mg\,cm^{-3}$ aqueous suspensions of TiO_2 (Degussa P-25, predominantly anatase, specific area of 50 $m^2\,g^{-1}$, non-porous). Suspension was sonicated for 15 min before illumination to make the TiO_2 particle size uniform. During the exposure, the reaction mixture was stirred. TiO_2 particles were removed after illumination by centrifugation of the suspension.

Variations in the concentration of the dye were monitored by an UV–visible spectrophotometer (Specord UV–VIS). Absorbances were measured in situ at the wavelength of maximum absorption (at 545 nm). In the photo-Fenton experiments the molar excess of H_2O_2:dye was 50.

Since the photoassisted degradation occurs predominantly on the TiO_2 surface, studies of the adsorption of pararosaniline dye from aqueous solution onto TiO_2 are important. Experiments on adsorption were carried out in a reaction vessel. Suspensions, prepared by the addition of TiO_2 at a concentration of 2.5 $mg\,cm^{-3}$, were pre-equilibrated for 2 h by vigorous stirring. This period of time was determined as optimal for the adsorption/desorption equilibrium to be achieved at room temperature. After removing TiO_2 particles, the extent of adsorption was evaluated from decrease of concentration of pararosaniline dye in the solution.

3. Results and discussion

3.1. Absorption spectra of the dye

Fig. 1 shows the absorption spectra of the pararosaniline dye in water solution of different pH values. The main absorption maximum in the visible region occurs at 545 nm. The absorption band in the UV region is apparently due to electron transitional states of molecule [16]. It should be noted that the position of the absorption maximum and the corresponding molar absorption coefficient depend somewhat on the solvent [17]. Those two parameters vary also with the pH of the solution. We have observed that decreasing of the pH value of the solution causes a noticeable reduction of absorption bands with the maximum at 545 and 285 nm, to disappear completely below pH 1.5.

Absorption bands with peaks at 206 and 235 nm do not depend noticeably on the pH of the solution. Absorption bands at 545 and 285 nm can be ascribed to a highly colored form of the molecule, while bands with peaks at 206 and 235 nm can be ascribed to a certain uncolored isomer of the molecule. Absorbances of the dye molecule decrease also by increasing pH of the solution above 6.3 and completely disappear at pH 10.5.

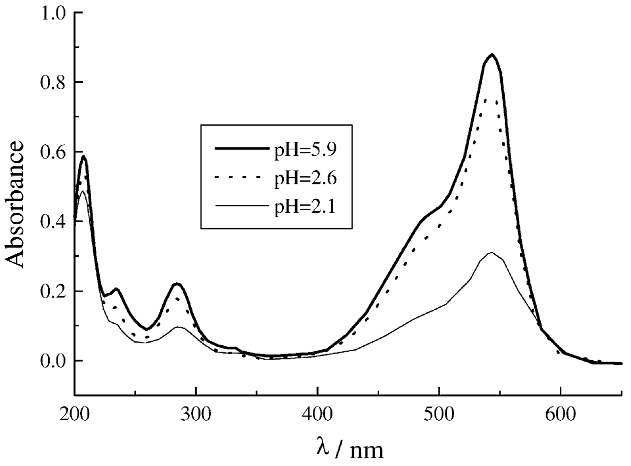

Fig. 1. The influence of pH on the absorption spectra of pararosaniline dye in aqueous solution.

Because of the variations of the absorbances with pH, all experiments were performed using natural pH value (pH = 5.9) as initial pH of the solution. The value of molar absorption coefficient was determined as $9.88 \times 10^3\,m^2\,mol^{-1}$ in our experimental conditions, and it was independent on the pH of the solution between 3.6 and 5.9. Since the optical spectrum remains invariant in this pH range, the structure of the dye molecule does not change.

3.2. Illumination of dye solution

Illumination of the pararosaniline dye solution in the presence of oxygen or argon leads to the decrease of the dye absorption. Decreasing of absorption at 545 nm during illumination is presented in Fig. 2a. Disappearance of the dye under illumination follows second-order kinetics with the rate constant of $6.3 \times 10^3\,dm^3\,mol^{-1}\,min^{-1}$ ($t_{1/2}$ = 19.84 min, $r = 0.992$). The dye appears slowly in the dark in an illuminated sample up to 80% of initial concentration after 3 h (Fig. 2b). This indicates that the chromophore group of pararosaniline dye is not broken during illumination, but only a recurrent change of conjugated π-system happens under visible light illumination.

Illumination of the dye solution in the presence of hydrogen peroxide causes decomposition of the dye molecules. A blank experiment conducted in the presence of H_2O_2 in the dark resulted in negligible degradation. During photolysis with visible light in the presence of $1 \times 10^{-3}\,mol\,dm^{-3}$ H_2O_2 in the argon stream the absorption at 545 nm decreased with increasing the illumination time and disappeared after 30 min (Fig. 3).

The dye did not appear after illumination in the illuminated sample indicating that the addition of hydrogen

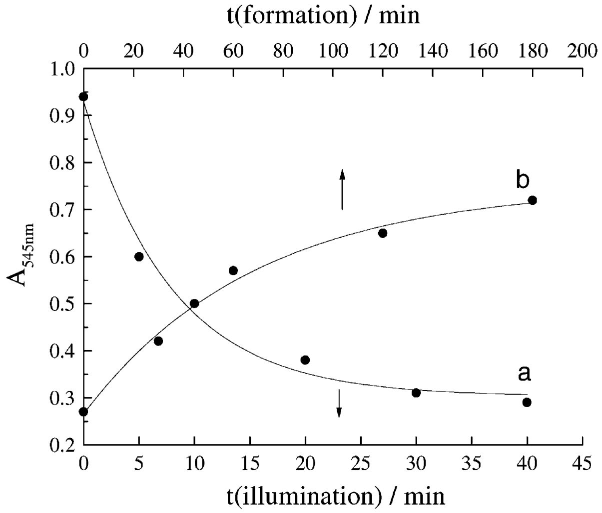

Fig. 2. Changes of pararosaniline dye concentration in aqueous solution pH 5.9: (a) disappearance of the dye during visible light illumination; (b) formation of the dye in the dark after illumination of the solution.

peroxide caused degradation of pararosaniline dye molecules under visible light illumination. Degradation of the dye under present conditions follows first-order kinetics with the rate constant $k = 0.072\,\mathrm{min}^{-1}$ ($t_{1/2} = 9.63\,\mathrm{min}$, $r = 0.987$). We assume that the excitation of pararosaniline dye molecules is followed by a reaction with hydrogen peroxide which results in hydroxyl radical production and leads to decomposition of the dye. Cation radical produced by charge transfer reaction can be degraded in reaction with hydroxyl radicals also

$$\mathrm{Dye} + h\nu \rightarrow \mathrm{Dye}^* \qquad (1)$$

$$\mathrm{Dye}^* + \mathrm{H_2O_2} \rightarrow \mathrm{Dye}^+ + {}^\bullet\mathrm{OH} + \mathrm{OH}^- \qquad (2)$$

$$\mathrm{Dye\ or\ Dye}^+ + {}^\bullet\mathrm{OH} \rightarrow \mathrm{Products} \qquad (3)$$

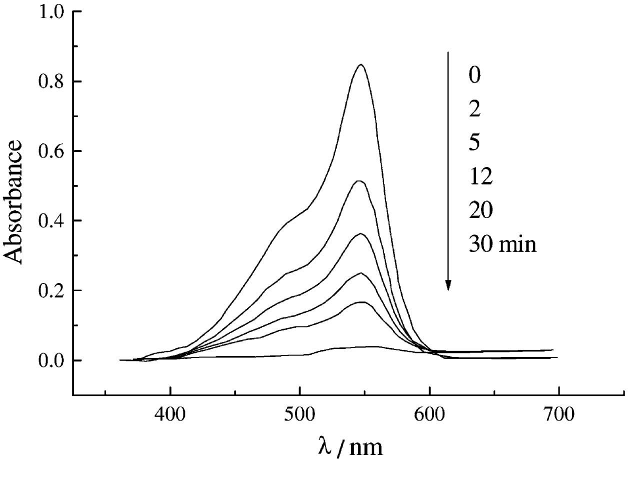

Fig. 3. Spectral changes of pararosaniline dye solution during illumination in the presence of $1 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ $\mathrm{H_2O_2}$. Argon saturated solution (wavelengths >400 nm).

Photo-Fenton reaction is known as one of the most effective methods of generation of hydroxyl radicals. Photo-Fenton experiments were performed in the presence of $5 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$ $\mathrm{H_2O_2}$ and $5 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$ $\mathrm{Fe^{2+}}$ under visible light illumination. Under these experimental conditions pararosaniline dye was decomposed very fast (within 2 min). This observation confirms that degradation of pararosaniline dye is caused by reaction with hydroxyl radicals.

3.3. TiO_2-assisted photodegradation

The degradation of aqueous suspension of pararosaniline dye was performed in the presence of $\mathrm{TiO_2}$ as a photocatalyst and $\mathrm{O_2}$ as an electron acceptor. The absorption bands of the absorption spectra corresponding to the dye decreased during illumination (Fig. 4), and disappeared after 20 min indicating the total degradation of dye molecules. During illumination no new absorption bands appeared both in the visible and ultraviolet regions, especially absorption bands of aromatic compounds and other similar intermediates. This is a marked contrast to the direct photocatalyzed degradation of many organics in the presence of $\mathrm{TiO_2}$ under UV illumination, in which they are easily detected by absorption spectra [18]. Small decrease of the pH of the solution of about 0.2 units can be ascribed to the formation of some acidic products of the dye degradation.

The degradation of pararosaniline dye in oxygenated $\mathrm{TiO_2}$ suspension (Fig. 4, inset) follows first-order kinetics with the rate constant $k = 0.143\,\mathrm{min}^{-1}$ ($t_{1/2} = 4.85\,\mathrm{min}$, $r = 0.994$). Based on the mechanism of the sensitized photocatalysis under visible light illumination [12–15] the following reactions (Eqs. (4)–(6)) may be proposed for the degradation of pararosaniline dye in the presence of $\mathrm{TiO_2}$ in oxygenated aqueous solutions:

$$\mathrm{Dye}^* + \mathrm{TiO_2} \rightarrow \mathrm{Dye}^+ + \mathrm{TiO_2(e^-)} \qquad (4)$$

$$\mathrm{TiO_2(e^-)} + \mathrm{O_2} \rightarrow \mathrm{O_2}^- \qquad (5)$$

$$\mathrm{Dye}^+ + \mathrm{O_2}^- \rightarrow \mathrm{DO_2} \rightarrow \mathrm{Product} \qquad (6)$$

Since the photoassisted degradation mechanism proposes direct electron injection from the excited dye to the conduction band of $\mathrm{TiO_2}$, pararosaniline dye molecules must be adsorbed on the semiconductor surface. We observed that about 0.9 μmol/g $\mathrm{TiO_2}$ were adsorbed from $1 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$ solution of pararosaniline dye, which is $22.5 \pm 3.5\%$ of the initial concentration. The obtained value represents the average value of several measurements. This observation is in accordance with the proposed mechanism of sensitized photocatalysis.

Hydrogen peroxide was used throughout this study as an alternative electron acceptor. Hydrogen peroxide was considered to have two functions in the process of photoassisted degradation [19]. It accepts electrons from the conduction band and thus promotes the formation of OH

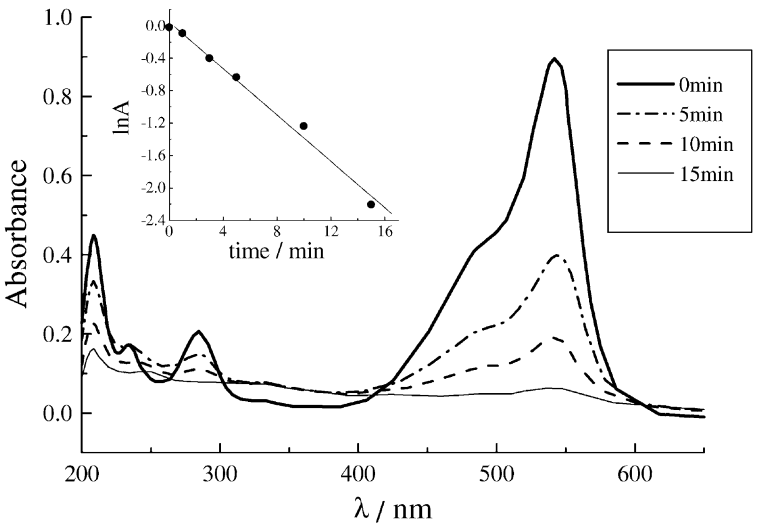

Fig. 4. Absorption spectra of pararosaniline dye in aqueous TiO_2 dispersion with illumination time. Inset: first-order kinetics plot.

radicals (Eq. (7))

$$TiO_2(e^-) + H_2O_2 \rightarrow {}^\bullet OH + OH^- + TiO_2 \quad (7)$$

susceptible to attack the dye (Eq. (3)). Experiments were carried out in deoxygenated solutions. The similar changes in absorption spectra were observed under present experimental conditions in comparison with the results obtained in experiments using oxygen (Fig. 5). Degradation also follows first-order kinetics with the rate constant $k = 0.127\,\text{min}^{-1}$ ($t_{1/2} = 5.46\,\text{min}$, $r = 0.994$). The initial concentration of H_2O_2 in the range of 5×10^{-4}–$3 \times 10^{-3}\,\text{mol}\,\text{dm}^{-3}$ does not affect significantly the degradation rate.

In the presence of H_2O_2 in TiO_2 dispersion pararosaniline dye molecules could undergo two degradation reactions: a reaction taking place at the surface of the TiO_2 particles (Eqs. (3) and (7)) and a reaction occurring in the bulk of the solution (Eqs. (2) and (3)). Thus, the observed degradation rate should be the sum of these two reaction rates. The effect of the reduction of the degradation rate of pararosaniline dye we detected in the presence of H_2O_2 is quite different from that obtained in direct photocatalysis using UV–TiO_2 systems. In these systems a significant enhancement on the degradation rate has been detected when H_2O_2 was added into the suspension [20–22]. Under the same conditions as in this study (concentrations of H_2O_2, O_2 and TiO_2) we obtained that the photocatalytic activity increases by a factor of about 2.5 comparing to the results with oxygen [23]. The observed discrepancy can be explained on the basis of the difference in the primary mechanisms of direct and sensitized photocatalysis [14].

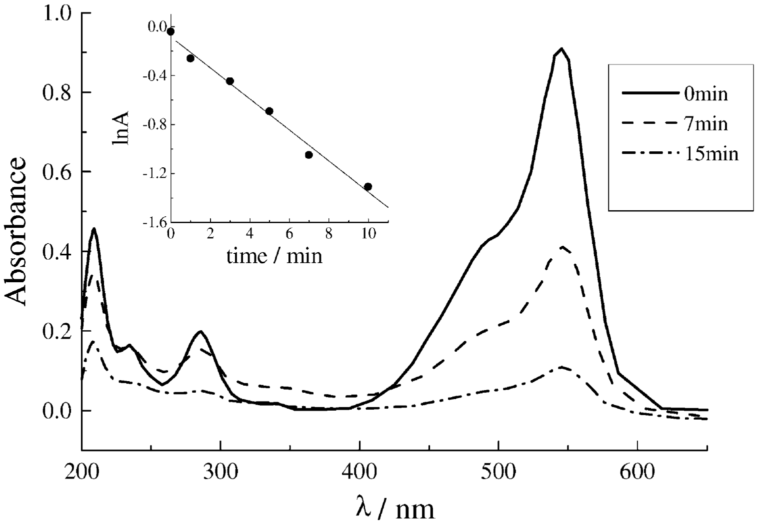

Fig. 5. Variation in the absorption spectra of pararosaniline dye in aqueous TiO_2 dispersion in the presence of $1 \times 10^{-3}\,\text{mol}\,\text{dm}^{-3}$ H_2O_2 during illumination. Argon saturated solution. Inset: first-order kinetics plot.

4. Conclusions

Experimental results indicate that visible light illumination of the pararosaniline dye solution does not degrade dye molecules. New bands appeared neither in ultraviolet nor visible region. Illumination in the presence of hydrogen peroxide causes decomposition of the dye. Very fast destruction by photo-Fenton reaction points out that degradation of the dye is caused by reaction with hydroxyl radicals. Sensitized photocatalytic process using TiO_2 as a semiconductor leads to degradation of dye molecules also. Reduction of the rate of degradation was obtained in the presence of hydrogen peroxide as an electron acceptor instead of oxygen. The obtained results confirm that the sensitized photocatalysis extends the range of excitation energies into the visible region, making use of solar energy for the destruction of colored pollutants.

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