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Photocatalytic activation of TiO_2 under visible light using Acid Red 44

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Abstract

The activation of TiO_2 photocatalyst for photocatalysis under the visible light using Acid Red 44 ($C_{10}H_7N = NC_{10}H_3(SO_3Na)_2OH$) is described. Adjustment of the pH enhanced the photocatalytic activation of TiO_2 in the presence of visible light. This confirms that the adsorption of a dye on TiO_2 surface is an important factor in dye-photosensitization. The differences in the photocatalytic activation mechanism under visible irradiated conditions with that of UV irradiated condition are proposed. The dye-sensitized photocatalysis under visible light was applied to the decomposition of phenol, is a toxic chemical used in industry and frequently discharged into water.

Keywords: Photocatalysis; Dye; Sensitization; Visible light; TiO_2

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1. Introduction

The semiconductor TiO_2 frequently used as a photocatalyst and numerous applications have been described. This material is of interest because it can split water into hydrogen and oxygen under irradiation by light and is currently of interest for generating clean energy, such as hydrogen generation [1] and solar cells [2]. The mechanism of water-splitting is a red-ox reaction involving the generation of electrons and positive charges, and can be applied to clean technology such as the decomposition of organic compounds [3]. Photocatalysis has many merits in terms of the removal of toxic organic compounds, waste water treatment, and clean-up of polluted air. Organic compounds are not fully converted to minerals by conventional technology. However, organic compounds can be completely decomposed to H_2O and CO_2 by photocatalysis and no secondary pollutants are generated. Conventional technology for the removal of pollutants requires a suitable concentration of pollutant, but photocatalysis can be used over a broad range of concentration. In addition, TiO_2 photocatalyst is non-toxic, inexpensive, more stable than other photocatalyst in ambient conditions and can be recycled [4,5]. For these reasons, TiO_2 would be ideal for use in clean technology.

The TiO_2 photocatalyst mainly absorbs UV light of which the wavelength is lower than 400 nm, and catalyzes the decomposition of organic compounds by a inducing red-ox reaction [6]. However, the amount of UV in solar light is less than 5%. To enhance the activity of photoefficiency, activation in the visible light region is required and a number of studies have been

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published for the purpose. One example is the use of a Ru complex as a sensitizer [7–9]. This sensitizer absorbs visible light leading to the excitation of an electron. The excited electron of the sensitizer is then transferred to TiO_2 after which, the TiO_2 has an induced photoactivation under visible light [9]. However, the sensitizer is also an organic compound and is decomposed by photocatalysis. In the case of the Ru complex, the synthesized dye is too expensive to be discharge and, as a result, it is difficult to apply to clean technology.

In this research, we used a conventional dye as a sensitizer with adjustment of the pH environment. A TiO_2 photocatalyst was activated under the visible light using Acid Red 44 ($C_{10}H_7N = NC_{10}H_3(SO_3Na)_2OH$). The application of this system was examined by a study of decomposition of phenol, a toxic industrial chemical that is frequently discharged into water.

2. Experimental

2.1. Materials

Conventional Degussa P-25; TiO_2 powder with an average diameter of 30 nm was used as received. Acid Red 44 was purchased from Aldrich (content ~80%) and was used as a photosensitizer without further purification. Dye solutions were prepared by dissolving the dye in deionized water (18 MΩ cm, Barnstead). The pH of the solution was adjusted with NaOH (SIGMA) and HCl (JUNSEI), after the addition of the catalyst. Phenol (MERCK) was used as a model toxic organic material.

2.2. EFISPS method in solution

For certification of activation under visible light, the electric field induced surface photovoltage

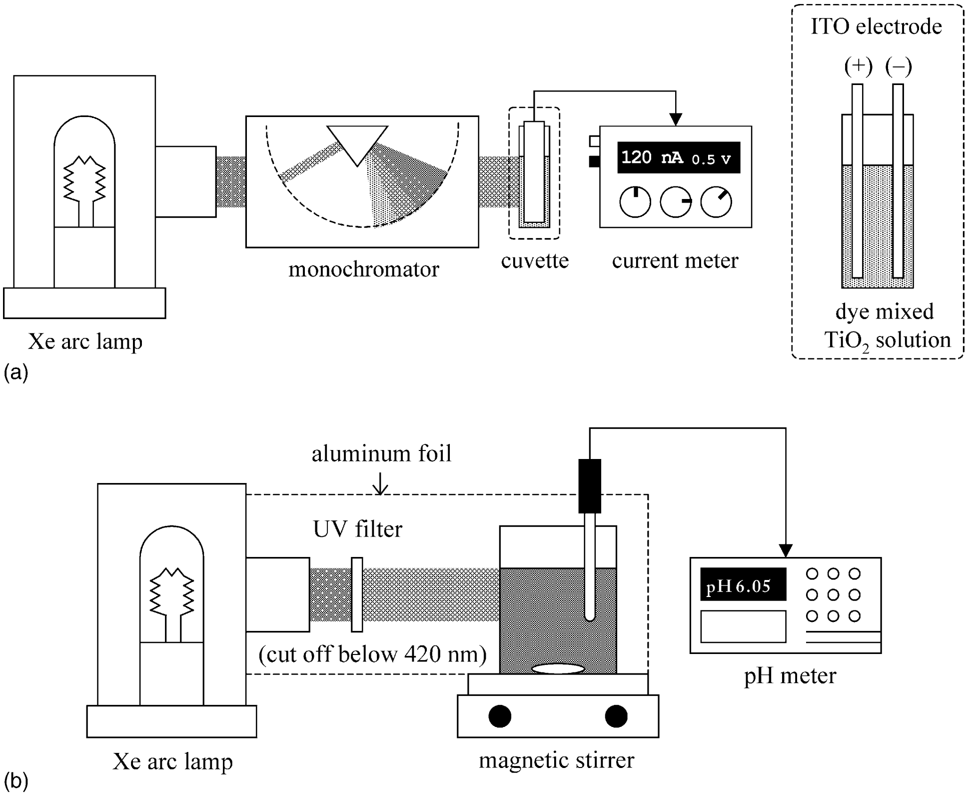


Fig. 1. (a) Scheme for the electric field induced surface photovoltage spectroscopy (EFISPS) experiment. A TiO_2 only solution and a dye mixed TiO_2 solution were used in this experiment. $[TiO_2] = 100$ ppm, $[dye] = 20$ ppm, the amount of solution is about 3 ml. (b) The photoreactor configuration used in the degradation of dye by TiO_2 under the visible light (UV filter used) and UV (UV filter removed).

spectroscopy (EFISPS) technique was used in a solution of TiO_2 and dye mixed TiO_2. The experimental set up is shown in Fig. 1(a). A Xe arc lamp (300 W, Oriel) was used as a light source and was converted into monochromatic light by a monochromator (Oriel). A solution containing 100 ppm TiO_2 and 20 ppm dye was added to a quartz cuvette (4 ml, Agilent). ITO glasses (Delta Technologies, Ltd., $R_s = 10 \pm 2\,\Omega$) were used as electrodes. A current meter (KEITHLEY 6517A) was used to induce a voltage between the ITO glasses and for current detection.

2.3. Photocatalytic degradation

The scheme for the reactor is shown in Fig. 1(b). A Xe arc lamp (300 W, Oriel) was used as a light source, and a UV filter (Oriel, cut off below 420 nm) was used to irradiate the visible light only. The solution of dye and TiO_2 was stirred vigorously by a magnetic stirrer. The reaction system was covered with aluminum foil for light reflection and to prevent the emission of light to surroundings. The cover was opened only for sampling the solution, and the electrode of the pH meter was immersed in the solution to check the initial pH and any change in pH.

2.4. Chemical analysis

The solution of TiO_2 and dye was filtered through a syringe filter (0.45 μm, Millipore) before checking the concentration of the dye by UV-Vis analysis (HP 8453). The absorbance at 510 nm of Acid Red 44 was used to calculate it's concentration and 270 nm was used for phenol. The components were more precisely analyzed by HPLC (WATERS 2487, 1525). The pH of the solutions was determined by a pH meter (Orion 940).

3. Results

The band gap energy of TiO_2 is known to be 3.0–3.2 eV [10]. After TiO_2 absorbs UV, the electrons of the balance band are excited to the conduction band. Dye-sensitized TiO_2 can excite electrons with visible light that has lower energy than UV. The dye absorbs visible light and the electrons of the dye are excited from the HOMO to the LUMO state. The excited electron of the dye is transferred to the conduction band of TiO_2 [2,11]. This dye-sensitization mechanism investigated in this study utilized a conventional, inexpensive dye which is used in the textile industry.

3.1. EFISPS result

To identify of photo-excitation of dye-sensitized TiO_2 under visible light, the EFISPS method was carried out. In the EFISPS method, the excited electrons of TiO_2 increase the conductivity of the TiO_2 solution. If the monochrome can excite the TiO_2, the current and conductivity of the solution increases. An out circuit potential is needed, because of the driving force of the ion and electron flow in the solution. The result (Fig. 2) shows an enhancement in the photo-excitation of the dye-sensitized TiO_2 under visible light compared with TiO_2 only. The photo-current of the dye-sensitized TiO_2 is higher and appeared over a more broad range of the visible light. An enhancement of approximately 3.7 times compared to a solution of TiO_2 was found.

3.2. Influence of pH on adsorption of dye

In the dye-sensitization mechanism, the adsorption of the dye to the TiO_2 surface is required because the association of dye with TiO_2 serves as the path of the electrons from the dye to the TiO_2 surface [12]. To increase the adsorption of the dye on the TiO_2 surface, the pH of the solution was adjusted as an environmental variable. The result (Fig. 3) shows that the optimum pH is 3.5 for dye adsorption. The zero point charge of TiO_2 is known to be 6.25. Above pH 6.25, the surface charge of TiO_2 is negative and below 6.25, it is positive [13]. Acid Red 44 is an acidic dye that has negative charge in solution. Conditions where the surface charge of TiO_2 is positive is favorable to adsorption of dye.

3.3. Effect of pH as environmental variable on degradation of dye

The degradation of dye under visible light was investigated to verify the photo-catalytic activation of TiO_2 under visible light (Fig. 4). Under conditions of

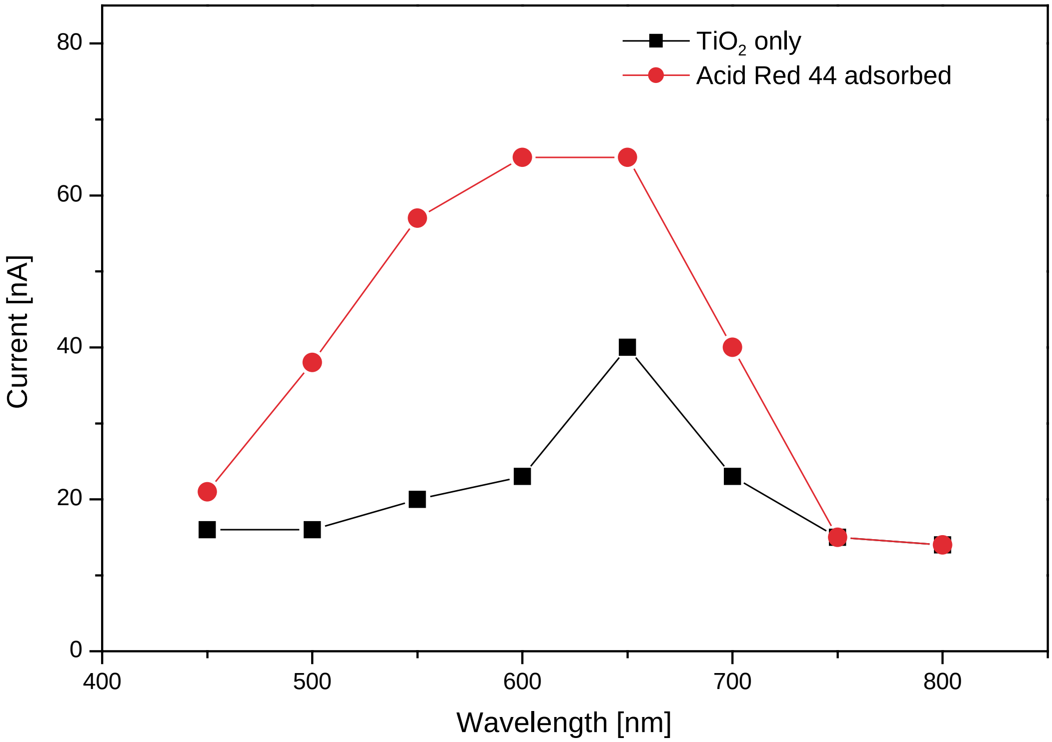


Fig. 2. Results of an EFISPS experiment in the visible light region.

visible light irradiation, the dye was not decomposed, and TiO_2 was found to have no photo-catalytic activity. However, in the dye mixed TiO_2 solution, the dye was decomposed as the result of dye-sensitization. Dye-sensitized TiO_2 has photo-catalytic activity under visible light and the dye is decomposed. In addition, the dependence of pH in dye degradation resembles that for adsorption. This indicates that the adsorption of dye is an important factor in dye-sensitization and pH is also important as an environmental variable. This dependance on pH was not apparent in dye degradation under UV (Fig. 5). From this result, the difference in degradation rate as a function of solution pH is negligible, except that the initial degradation rate for a high pH solution is relatively rapid. This indicates that pH is minor factor in photo-catalytic degradation under UV and that the role of pH is different than that for visible light.

pH change during the reaction was checked (Fig. 6(a) and (b)). The pH of the solution that was irradiated by UV decreased as the concentration of the dye decreased. However, the pH of the solution irradiated with the visible light remained unchanged, although the concentration decreased.

3.4. Decomposition of phenol by dye-sensitized TiO_2 under the visible light

This system was applied to the decomposition of a toxic organic compound, phenol. The result is shown in Fig. 7. The specific peak of phenol appeared at 270 nm, and the dye at 510 nm. The phenol peak disappeared more rapidly than the dye as the contact time increased. The intensity of the dye peak decreased after a long time had passed. This indicates that the dye-sensitized TiO_2 attacks phenol first, and the dye was attacked after the phenol had decomposed. The peak at which the range of absorbance was lower than 250 nm persisted after 20 h. This corresponds to the remaining organic compound as byproduct and the end-product of photocatalysis. After the dye was decomposed, dye-sensitization does not occur under visible light. This is a disadvantage of the system, but the energy saving is higher using UV only.

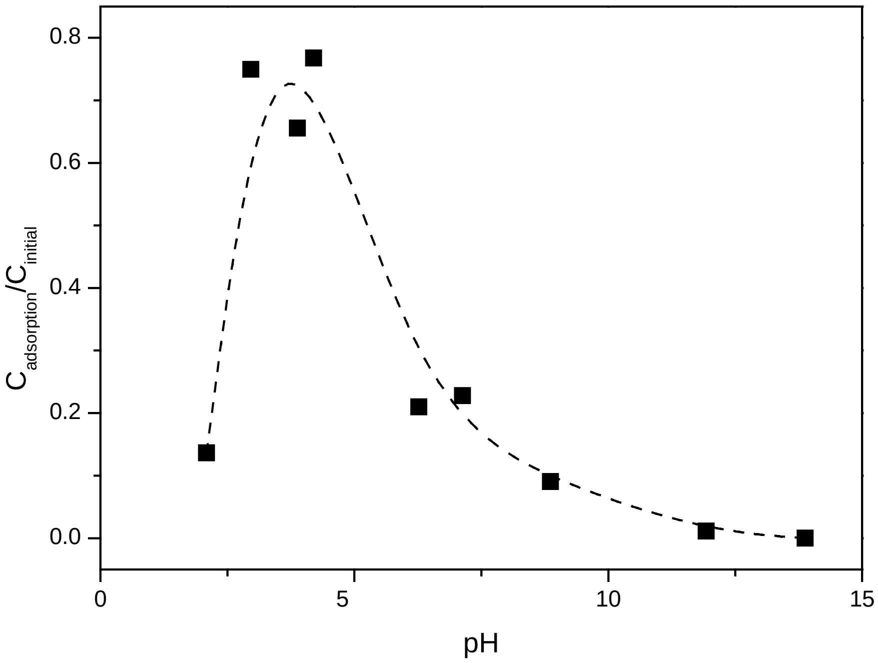


Fig. 3. Influence of pH on the amount of dye (Acid Red 44) adsorbed.

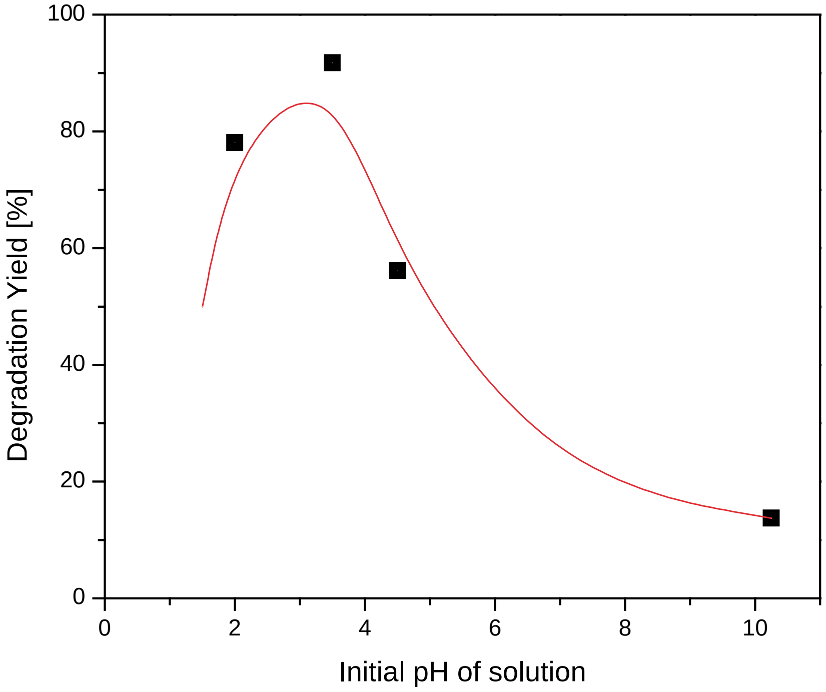


Fig. 4. Dye degradation results under visible light ($\lambda > 420$ nm) in different initial pH ($pH_i = 2$, 3.5, 4.5 and 10.3). The experimental conditions were: $[TiO_2] = 5$ g/l, $[dye]_i = 10$ ppm, total volume of the solution was 40 ml, the reaction time was 3 h.

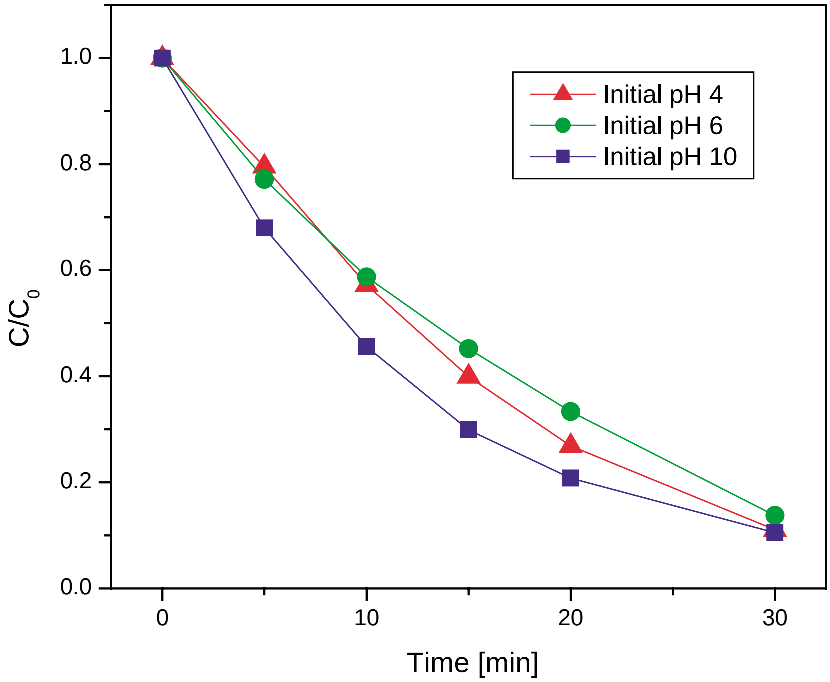


Fig. 5. Dye degradation results under UV in different initial pH ($pH_i = 4$, 6 and 10). The experimental conditions were: $[TiO_2] = 0.4$ g/l, $[dye]_i = 20$ ppm, total volume of the solution was 160 ml.

4. Discussion

4.1. *Effect of the pH of the solution on the adsorption of dye to TiO_2 surface*

Acid Red 44 is an acidic dye and is adsorbed to TiO_2. This adsorption is due to electrostatic forces. Desorption of the dye also occurred when the pH of solution was adjusted to 10.5. The rate of adsorption and desorption was very rapid and most of the adsorbed dye was desorbed within 2 h. These adsorption and desorption mechanisms can be attributed to a combination of chemical reactions. The reactions are shown below:

$>\text{Ti–OH} + \text{H}^+ \Leftrightarrow >\text{Ti–OH}_2{}^+$,
(+) charge ($\text{p}K_{\text{a1}} = 4.5$)

$>\text{Ti–OH} + \text{OH} \Leftrightarrow >\text{Ti–O}^- + \text{H}_2\text{O}$,
(−) charge ($\text{p}K_{\text{a2}} = 8.0$)

$\text{HA} \Leftrightarrow \text{H}^+ + \text{A}$, dye ($\text{p}K_{\text{dye}}$)

$>\text{Ti–OH}_2{}^+ + \text{A} \Leftrightarrow >\text{Ti–OH}_2{}^+ \cdots \text{A}^-$,
adsorption ($\text{p}K_{\text{ads}}$)

The surface of the TiO_2 is changed positive by the first reaction, and negative by the second reaction. Acidic dye is usually ionized as in the third reaction. The negative form of the dye is adsorbed on the positive surface of the TiO_2 in the fourth reaction. The kinetics of the reactions are shown below as numerical expressions:

$$\frac{\theta}{>\text{Ti–OH}_2{}^+}\quad \frac{1-\theta-\delta}{>\text{Ti–OH}}\quad \frac{\delta}{>\text{Ti–O}^-},$$

$$[A^-] = \frac{[HA]_0 \cdot K_{\text{dye}}}{[H^+] + K_{\text{dye}}},$$

$$K_{\text{a1}} = \frac{\theta}{(1-\theta-\delta)[H^+]},$$

$$K_{\text{a2}} = \frac{\delta}{(1-\theta-\delta)[\text{OH}^-]},\qquad K_{\text{ads}} = \frac{S_{\text{ads}}}{S \cdot \theta \cdot [A^-]}$$

where $0 < \theta, \delta, 1-\theta-\delta < 1$ and S the total surface area.

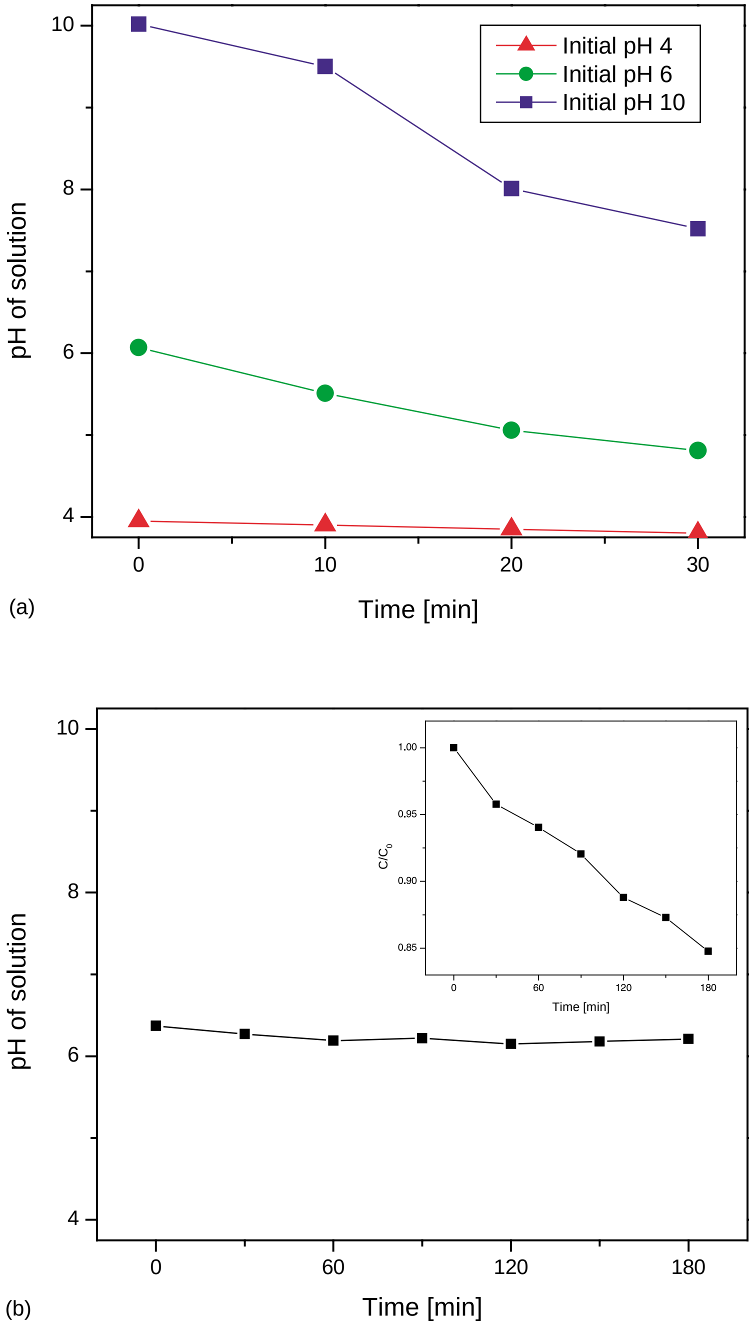


Fig. 6. pH changes of solutions as dyes are decomposed by TiO_2 (a) under UV and (b) under visible light. In the inset, the decrease of dye concentration is shown although the pH of the solution was almost unchanged.

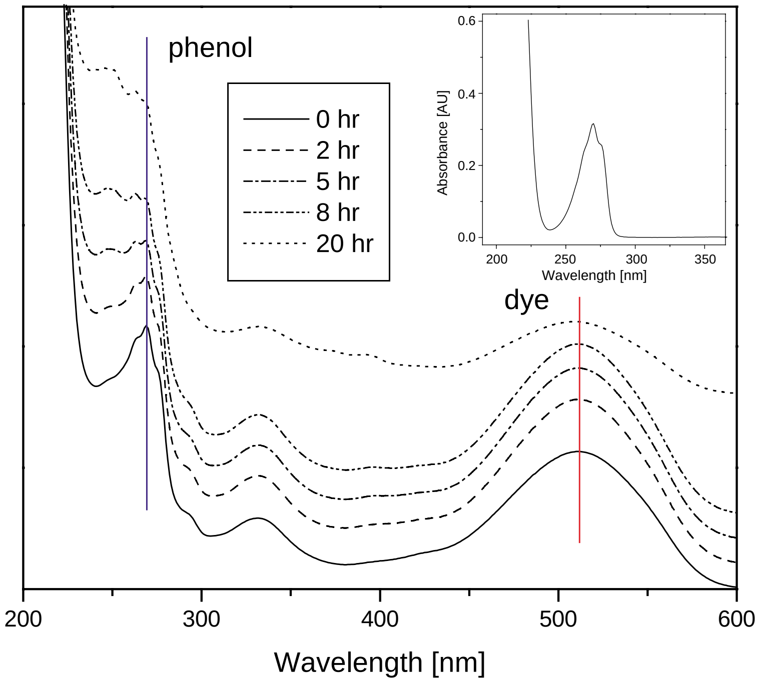


Fig. 7. Decomposition of phenol by TiO_2 under visible light. The experimental conditions were: $[TiO_2] = 6.7$ g/l, $[dye]_i = 50$ ppm, $[phenol]_i = 20$ ppm total volume of solution is 150 ml, and visible light ($\lambda > 420$ nm) was used. In the inset, only a phenol solution; $[phenol] = 20$ ppm.

In these chemical equations, the amount of adsorption is pH dependant, and the optimum pH for maximizing adsorption is determined by initial concentration of the dye and the equilibrium constant of dye, K_{dye}. The optimum pH of Acid Red 44 was 3.5 in this study.

4.2. Effect of pH on degradation of dye

The photocatalytic activity of dye-sensitized TiO_2 was maximized by adjustment of the pH to 3.5. This is the optimum pH for the adsorption of dye to the TiO_2. This result shows that dye adsorption is an important factor in dye-sensitization and that the photocatalytic activity of TiO_2 under visible light can be increased with increasing extent of dye adsorption. Adjustment of the pH was the environment variable for increasing the extent of adsorption in this study. However, under conditions of UV irradiation, this dependence follows different trend. The initial degradation rate for a basic solution was relatively rapid. This indicates that the photocatalytic activation mechanism for TiO_2 under conditions of UV is different from that under visible light. The mechanisms are shown in Fig. 8. Under UV irradiated conditions, TiO_2 excites an electron from the valance band to the conduction band. The positive hole and electron is then separated, and this electron and hole participates in a red-ox reaction with chemicals that diffuse from the outside. Usually in water, oxygen is reduced to a super-oxide radical and a hydroxyl ion is oxidized to a hydroxyl radical. Some times organic compounds participate in red-ox reactions. However, under visible light irradiated conditions, TiO_2 only, does not function as a photocatalyst, but dye-sensitization induces photocatalytic activation. The adsorption of the dye is required for this sensitization. The excited electron of the dye is transferred to the conduction band of TiO_2 through the adsorption bridge. In this case the electron induces photocatalytic activation. No positive hole exists. The positive hole consumes the hydroxyl ion of the solution to give a hydroxyl radical, and the pH of solution then changes. The experimentally observed pH decreases under UV irradiated

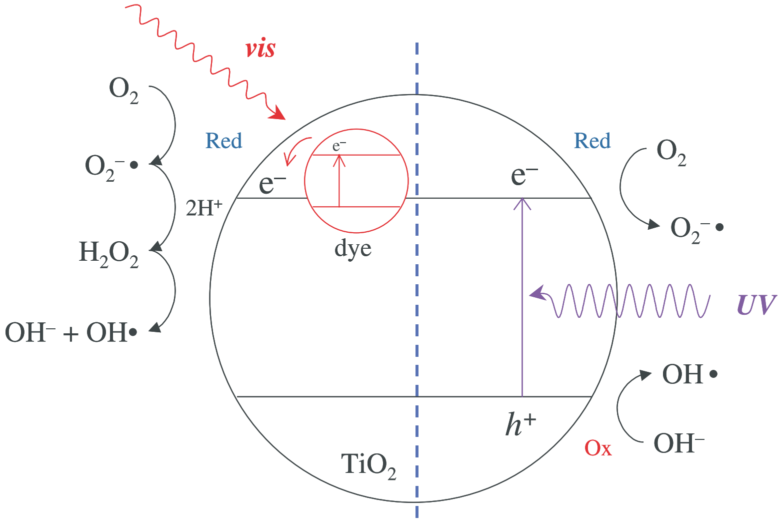
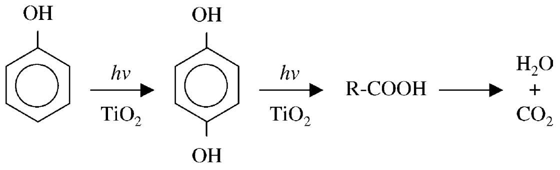


Fig. 8. The photoactivation mechanism of TiO_2 under UV (right side) and the dye-sensitized activation mechanism under visible light (left side).

conditions but no pH change occurs under the visible light irradiated conditions. The initial rate of degradation in basic solution under UV is more rapid than under other pH conditions. This suggests that the hydroxyl ion in the basic solution acts as a precursor of hydroxyl radicals. The hydroxyl radical has very active potential for decomposing organic compounds. This is one reason why photocatalytic activity under UV is higher than that under visible light condition.

4.3. Decomposition of phenol by dye-sensitized TiO_2 under the visible light

Phenol is decomposed by photocatalysis by the pathway shown below [14,15]. In this research, the pH of solution was decreased because organic acid was generated by photocatalysis. So the initial pH was not adjusted to 3.5 but 4.5 for maintaining proper pH condition:



More hydrophobic compounds are attacked with difficulty by hydroxyl radical and super-oxide radicals in photocatalysis [16]. In this research, phenol is more soluble in water than the dye, Acid Red 44. The dye is more bulky and contains more benzene rings than phenol. Phenol which is a small and hydrophilic organic compound might be easily attacked by radicals.

5. Conclusions

We conclude that the adsorption of a dye onto the TiO_2 surface is an important factor in the photosensitization by a dye under visible light. In addition, differences in the photocatalytic activation mechanism under visible irradiated conditions with that of UV irradiated condition are proposed. This concept was applied to the decomposition of phenol, a toxic chemical that is used in industry and discharged into steams of waste water. These results show that a conventional dye can be used for the photosensitizer of TiO_2 functioning under visible light.

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