

Photodegradation treatment of azo dye wastewater by UV/TiO₂ process

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Received 22 September 2004; received in revised form 11 November 2004; accepted 20 December 2004

Available online 2 April 2005

Abstract

In this study the photocatalytic decomposition of a synthetic dye, C. I. Acid Yellow 17, was investigated. The TiO₂ photocatalyst prepared by chemical vapor deposition (CVD) for UV/TiO₂ process was prepared by annealing at 550 °C for 24 h and anatase type crystalline (under XRD and SEM analysis) was obtained. The more important factors affecting the dye wastewater treatment in terms of dye removal ratio, color removal ratio, and mineralization ratio in this study were pH value of the solution, initial concentration of the dye wastewater, flow rate of the wastewater inflow and light intensity. Chloride and sulfate were detected in C. I. Acid Yellow 17 decomposition process while ammonium and nitrate were not detected.
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Keywords: Azo dye; Photodegradation; UV/TiO₂

1. Introduction

Dyestuff and dyeing industry have long been the important traditional industries in Taiwan. The wastewater that is characterized with high color, high chemical oxygen demand, low biodegradability and high variability has seriously polluted the drain water. Among the problems it causes, color is the most critical and dyestuff is the primary source of color. Most of dyestuffs are complicated aromatic compounds and are chemically stable. Though the wastewater possesses low BOD/COD ratio, the color, COD and residual dye level are still high even after traditional biological treatment or chemical coagulation treatment. Without further treatment, the wastewater will not meet the ever stricter environmental standards of discharged water.

The advanced oxidation process to oxidize the organic pollutants in wastewater with free radicals had been valued in recent years. There were some related articles published. Matthews [3] treated Methylene Blue, Rhodamine B, Methyl Orange and salicylic acid with fixed bed UV/TiO₂ process. The results indicated that the half-life of decomposition of the four compounds were around 21–22 min and the faster the flow rate of the wastewater circulation, the better the reaction. Shu et al. [5] treated the wastewater of Acid Red 1 and Acid Yellow 23 with UV/H₂O₂ and found that the color removal ratio reached 98% and 96% in 30 min with the initial concentration of 22.4 mmol/L and 23.5 mmol/L, respectively, at pH 5.7. Tang and An [6] investigated the treatment of five commercial dyes with suspended UV/TiO₂ photocatalytic process. The result showed that the color removal ratio varied a lot among those dyes at different pH values and suggested that the azo number in the dye molecules might be the factor related.

Most of the studies done on the wastewater treatment with TiO₂ photocatalyst or H₂O₂ addition to enhance the color removal effect used suspended TiO₂. However,

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suspension of TiO₂ requires further filtration or centrifugation to isolate TiO₂ from the solution, which added both costs and difficulties of the treatment technique. This study used fixed UV/TiO₂ photocatalytic treatment procedures for a batch experiment to investigate the parameters of solutions pH value, dye concentration, wastewater inflow rate and light intensity on the effects of dye wastewater treatment with photocatalytic decomposition. More than 50% of dyestuffs used in Taiwan textile and dyeing industrials are azo dyes. This study selected the widely used C. I. Acid Yellow 17 as the target of synthetic dye wastewater.

2. Methods

For the preparation of photocatalyst a chemical vapor deposition (CVD) method was used. Tetraisopropyl orthotitanate (Merck) and deionized water were put in two aeration bottles, respectively, heated up to 60 °C in a water bath, then induced to a pyrex glass tube (outer diameter of 3 cm, inner diameter of 2.6 cm, length of 70 cm) with nitrogen as the carrier gas. TiO₂ was deposited on the inner wall of the pyrex glass tube in the furnace, then the reactor was placed in a box furnace to eliminate impurities to purify the TiO₂ under proper annealing temperature for 24 h. The photocatalyst prepared was analyzed qualitatively with an X-ray diffractometer (XRD, Shimadzu, XD-5) and a scanning electron microscope (SEM, Topcon, ABT-150S).

A quartz tube (outer diameter of 2 cm, inner diameter of 1.8 cm) was then put inside the TiO₂ deposited glass tube to make the circular tube reactor for this study. A UV light (Spectronics, BLE-8T365) was installed inside the tube as the light emitting source, and a UV light meter (I Light, IL 1700) was used to quantify the light intensity. The synthetic dye wastewater was prepared with C. I. Acid Yellow 17 (I-Hwa Co., purity of 75%), then poured into a pyrex cylinder tank (inner diameter of 11.6 cm, height of 14 cm, volume of 1.2 L) for thorough mixing, outer jacket was filled with water at a fixed temperature to control the temperature. A pH controller (Suntex, 102) was used for automatic control of the pH value of the dye wastewater. A peristaltic pump (Cole-Parmer, 7520-00) with variable rotation speed was used to control the flow rate of dye wastewater in the circular tube reactor for photocatalytic decomposition process. Samples were taken for analysis corresponding to proper time intervals.

For the absorbance measurement of C. I. Acid Yellow 17 solution a UV/visible spectrophotometer (Hitachi, UV-2001) to scan in the range of 190–800 nm was used. The color removal ratio was estimated by the ratio of absorbance of the sample vs. the original wastewater at the wavelength of maximum absorbance. HPLC (Waters, 510) was used to analyze the residual

level of C. I. Acid Yellow 17. Total organic carbon (TOC) was analyzed with a TOC analyzer (O.I. Analytical, 1010). COD and BOD were determined by the Standard Methods of APHA (Standard Methods, 19th Edition) while the concentration changes of chloride, sulfate, nitrate and ammonium ions were monitored by ion chromatography (IC, Dioney, 4500).

3. Results and discussion

3.1. Qualitative analysis of the catalyst

X-ray diffractometer was used to identify the quality and crystalline phase of the catalysts at various annealing temperatures (450 °C, 550 °C, 650 °C, 750 °C and 850 °C) and the results were compared with JCPDS database. It indicated that the TiO₂ crystal formed was of anatase type at 450–750 °C while rutile type appeared when the annealing temperature reached 850 °C. Zhang et al. [8] also found that anatase crystalline changed into rutile type at 600–1100 °C in the preparation of TiO₂ from TiCl₄. Furthermore, the SEM pictures revealed that the crystal nuclei grew larger as the annealing temperature increased, the particle size grew from 1.0–2.5 μm at 450 °C to 2.5–7.0 μm and the higher the temperature the smoother the particle surface. According to the quantitative analysis of TiO₂, the photocatalysts used in this study were prepared at 550 °C for 24 h with CVD method to obtain anatase with high purity for the photodecomposition reaction of dye wastewater.

3.2. Effect of pH value

Fig. 1 shows the dye removal ratio of C. I. Acid Yellow 17 at different pH values. During the 375 min of reaction time, the highest ratio reached was 70.6% at pH 3 while the lowest ratio 44.3% was observed at pH 11. As the zero point charge of TiO₂ is pH 6.4 and C. I.

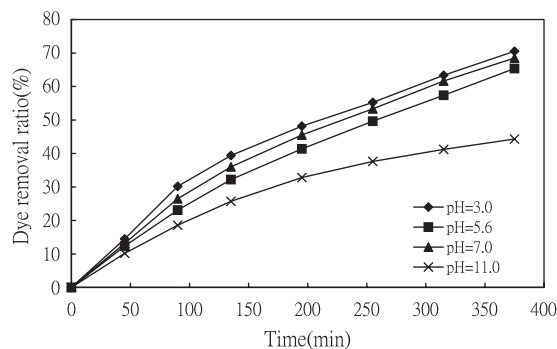


Fig. 1. The time change of dye removal ratio at various pH values (dye concentration 50 mg/L, temperature 25 °C, flow rate 0.82 cm/s, and light intensity 3.15 mW/cm²).

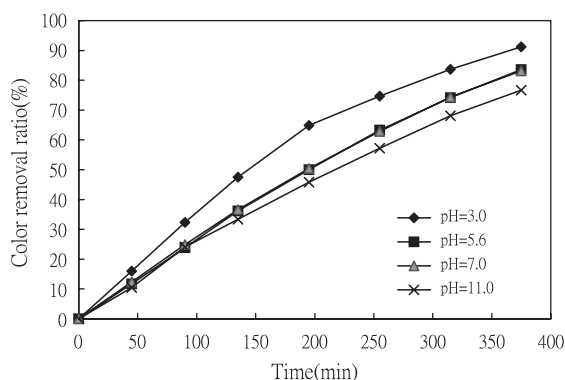


Fig. 2. The time change of color removal ratio at various pH values (dye concentration 50 mg/L, temperature 25 °C, flow rate 0.82 cm/s, and light intensity 3.15 mW/cm²).

Acid Yellow 17 is an anionic dye with good solubility, the sodium ion is easily dissociated in water and leaves the dye molecule with negative charges, so it makes it easier to be adsorbed on the surface of the catalyst to proceed reaction at lower pH value. Keiichi et al. [2] also found that positively charged TiO₂ surface adsorbed more Acid Orange 7 at lower pH value and more decomposition was achieved.

Fig. 2 shows the color removal ratio of dye wastewater at different pH values. Since the hydroxyl radical attacks the dye chromophore of dye in the photocatalytic reaction and causes the breakage of molecular bonds or functional groups, the color is resolved continuously and this turns to be faster than COD and TOC. The figure also indicates that the highest color removal is 91.2% reached at pH 3 and the lowest is 76.7% at pH 11, which is consistent with the findings in the dye removal ratio vs. pH value. Fig. 3 shows the effect of pH value on mineralization ratio. The dye molecule was broken into smaller pieces of intermediates in the initial stage then decomposed through carbon bond breakage, which resulted in TOC decrease in the latter period. The lowest TOC removal

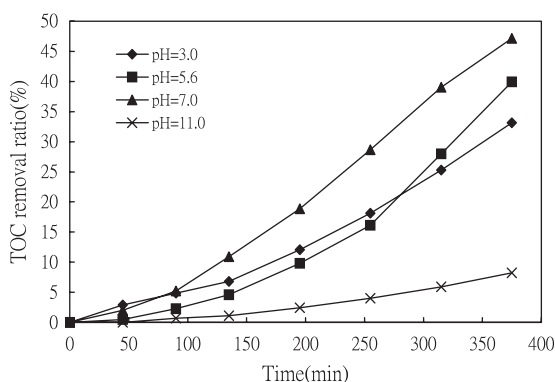


Fig. 3. The time change of TOC removal ratio at various pH values (dye concentration 50 mg/L, temperature 25 °C, flow rate 0.82 cm/s, and light intensity 3.15 mW/cm²).

ratio was 8.2% at pH 11 while reached the highest 47.2% at pH 7. This suggests that the photocatalytic degradation mechanism might be different under different pH values.

3.3. Effect of initial dye concentration

The dye removal ratio, color removal ratio and mineralization ratio were evaluated at different initial concentrations of C. I. Acid Yellow 17. Table 1 shows the results after 375 min of reaction time. Overall speaking, the removal ratio decreased as the initial concentration increased. The removal ratio of dye and TOC were only 5.6% and 0.2%, respectively, at initial concentration of 150 mg/L, which indicates that only dye molecules were decomposed at high initial concentration and hardly any mineralization reaction occurred. Tang and An [6] also found that the color removal ratio decreased as the initial concentration increased in the photocatalytic experiments with five different dyes. Davis et al. [1] investigated the real dyeing wastewater treatment and found the diluted wastewater reached higher color removal ratio than the original wastewater and the more diluted the better. The reason is that a high dye concentration shields the UV light thus the light triggered catalysts decreases.

3.4. Effect of flow rate

The flow rate affected the reaction time of dye molecules on the surface of catalyst. This study used a fixed TiO₂ system in combination of a recycled batch reaction system thus the flow rate is an important factor to control. Table 1 shows the final removal ratios of the dye, color and TOC at different flow rates (initial dye concentration 50 mg/L, pH 7, temperature 25 °C, light intensity 3.15 mW/cm²). The three removal ratios

Table 1

List of dye, color and TOC removal ratios at various dye concentrations, flow rates and light intensities after 375 min of reaction time

| Initial concentration (mg/L) | Flow rate (cm/s) | Light intensity (mW/cm ²) | Removal ratio | | |
|------------------------------|------------------|---------------------------------------|---------------|-------|------|
| | | | Dye | Color | TOC |
| 25 | 1.70 | 3.15 | 71.2 | 88.4 | 70.9 |
| 50 | | | 68.5 | 83.2 | 47.2 |
| 100 | | | 51.0 | 54.9 | 35.0 |
| 150 | | | 5.6 | 16.5 | 0.2 |
| 50 | 0.63 | 3.15 | 67.2 | 81.2 | 43.3 |
| | 0.82 | | 68.5 | 83.2 | 47.2 |
| | 1.41 | | 71.0 | 87.3 | 49.8 |
| | 1.70 | | 72.2 | 88.1 | 53.2 |
| | 2.51 | | 70.5 | 87.6 | 46.8 |
| 50 | 1.70 | 1.24 | 24.8 | 50.3 | 5.1 |
| | | 2.04 | 54.7 | 80.4 | 31.4 |
| | | 3.15 | 72.2 | 88.1 | 53.2 |

exhibit identical trends in 375 min of reaction time. The photocatalytic reaction rate might be controlled by mass transfer at lower flow rate therefore the increase of flow rate before 1.7 cm/s and makes the dye solution mix well thus the removal ratios increase. However, the removal ratios started to lower down as the flow rate exceeded 1.7 cm/s. The reaction rate might change the surface reaction control at high flow rate and it might cause incomplete reaction of the dye molecules or adsorption of the intermediates on the TiO_2 surface.

3.5. Effect of light intensity

The final removal ratios of the dye, color and TOC at different light intensities are listed in Table 1 (initial dye concentration 50 mg/L, pH 7, temperature 25 °C, flow rate 1.70 cm/s). It indicates that the increase of light intensity also increases the dye removal ratio evidently, and the effect is stronger at low light intensity. Similar results are obtained at color removal ratio and mineralization ratio. Comparing the three ratios, it is found that light intensity affects the mineralization the most followed by dye removal ratio while affects color removal ratio the least. The research done by Ollis et al. [4] found that there are more photons per unit time and unit area at higher light intensity thus the chances of photon activation on catalyst surface increases too, therefore the photocatalytic power is stronger. However, as the light intensity increases, the number of activation sites remains the same thus the reaction rate only reaches a certain level even when the light intensity continues to increase.

3.6. Results of full spectrum scan

Fig. 4 shows the full spectrum scanning of C. I. Acid Yellow 17 with time in 9 h of reaction. The primary absorption peaks of the original dye solution are 223, 243 and 403 nm in the range of 190–800 nm. As the reaction time increases the three peaks disappear gradually and the full spectrum scanning pattern

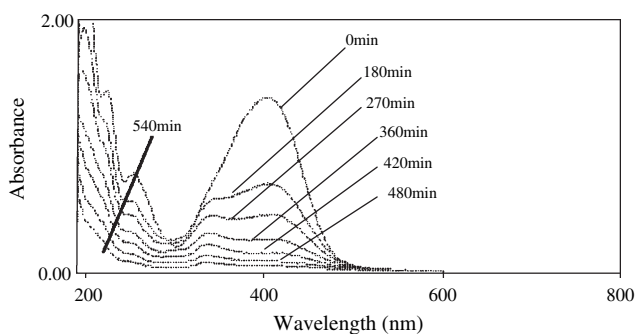


Fig. 4. The full spectrum scanning of Acid Yellow 17 in 9 h of reaction time.

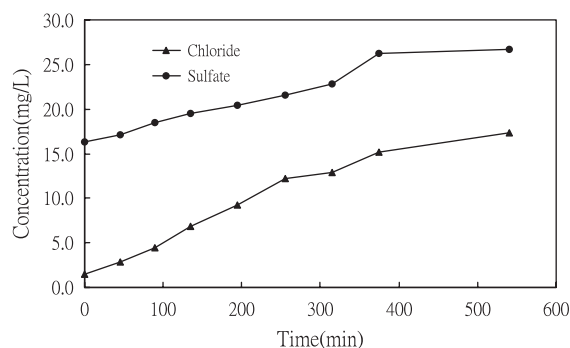


Fig. 5. The time change of chloride and sulfate concentrations in 9 h of reaction (dye concentration 50 mg/L, pH 7, temperature 25 °C, flow rate 1.70 cm/s, and light intensity 3.15 mW/cm²).

changes obviously after 180 min. A single peak of 300 nm–500 nm at 0 min run time seemed to break into two peaks at this range of wavelength during the run. This may be the evidence of the intermediate by-product. At the end of the 540 min of reaction time, there is no evident absorption peak observed. It indicates that the main chromophores in the original dye solution are destroyed with the photocatalytic reaction and proves that C. I. Acid Yellow 17 is decomposed in the UV/ TiO_2 system.

3.7. Fate of chlorine, sulfur and nitrogen atoms in the dye molecule

To further understand if there are inorganic ions released to reach mineralization in the UV/ TiO_2 process of C. I. Acid Yellow 17 decomposition, ion chromatography is utilized to monitor the levels of inorganic ions during the reaction process. The result shows in Fig. 5 that there were no ammoniums or nitrates detected while chloride and sulfate levels increase as the reaction time increases. The pH value decreased in the photocatalytic

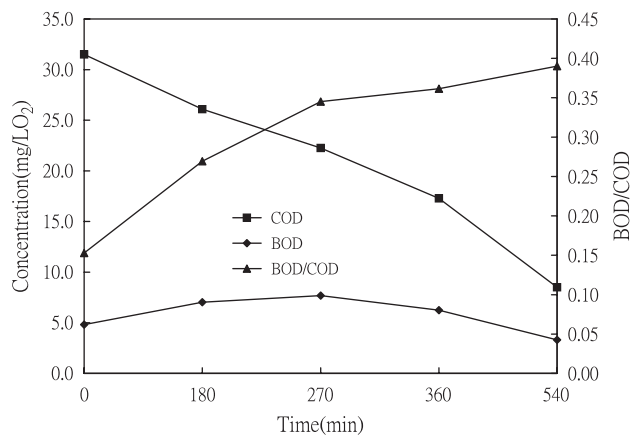


Fig. 6. The time change of BOD and COD levels and BOD/COD ratio in 9 h of reaction (dye concentration 50 mg/L, pH 7, temperature 25 °C, flow rate 1.70 cm/s, and light intensity 3.15 mW/cm²).

decomposition reaction of C. I. Acid Yellow 17, which indicates that there might be mineralized acids like HCl and H₂SO₄ and some organic acid intermediates produced in the process. While the nitrogen atoms in the dye molecule existed in the form of organic intermediates, chlorine and sulfur atoms were partially mineralized and were released in the forms of inorganic ions. Wang [7] proposed that the chlorine atom would break from the dye molecule and be released in the solution in dependence on the bonding position in the study of eight dyes with sunlight photocatalytic treatment. The chlorine would break most easily if it is bonded in straight chain of the dye molecule followed by the site bonded in benzene ring; the chemical stability of the chlorine bonding structure is the key.

3.8. Investigation on biodegradability

Fig. 6 shows the COD and BOD levels and BOD/COD ratio in the 9 h of reaction time. The COD level decreased from the initial concentration 31.5 mg/L to 8.5 mg/L, BOD level increased gradually from the initial concentration 4.8 mg/L to 7.7 mg/L then dropped to 3.3 mg/L, BOD/COD ratio increased rapidly from the initial level 0.16 then increased slowly to 0.39 after 270 min of reaction time. The data indicate that the non-biodegradable organic part of the dye molecule was destroyed, decomposed and even mineralized in the photocatalytic process during the initial 270 min of reaction time and that BOD changed little and remained in low level in the whole reaction process, which indicates that there were less organic compounds which were difficult to biodegrade after the decomposition of C. I. Acid Yellow 17.

4. Conclusions

In the preparation of TiO₂ photocatalyst with chemical vapor deposition, anatase crystalline was obtained by annealing at 550 °C for 24 h. To obtain

maximum dye removal, color removal and mineralization ratios, low pH value, high light intensity and low initial concentration are required. The full spectrum scanning results indicate that C. I. Acid Yellow 17 is decomposed in this reaction system and chloride and sulfate are detected too. In the 9 h of reaction time, the COD level of original wastewater lowered down significantly while the BOD/COD ratio was elevated significantly, which indicates that some non-biodegradable organic materials are also removed in the C. I. Acid Yellow 17 decomposition process.

Acknowledgements

This work was supported by the research grant no. NSC89-2211-E-005-005 from the National Science Council in Taiwan.

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