

Full Length Research Paper

Effect of chitosan biopolymer and UV/TiO₂ method for the de-coloration of acid blue 40 simulated textile wastewater

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The purpose for this study is to de-color C.I. Acid Blue 40 simulated textile wastewater using chitosan and UV/TiO₂ system. The methodology is to use chitosan biopolymer and UV/TiO₂ to degrade textile wastewater and to measure the color removal by UV-visible spectrophotometer. The operational parameters are chitosan, TiO₂, pH and reaction time. From the laboratory investigations, different efficiencies were observed according to different removal operating levels. Single chitosan of 2500 ppm dose was used to remove Acid Blue 40 textile wastewater and to obtain a better efficiency. TiO₂ alone with UV light was also used with the dose of 2500 ppm to obtain a better efficiency. In acidity, both chitosan and TiO₂ obtain better efficiencies under pH 4 operational condition. The best combination for UV/TiO₂ system to de-color the 50 ppm Acid Blue 40 textile wastewater was TiO₂ 2500 ppm concentration with UV illumination at pH 4. The result shows that the de-colorization efficiency reached 98.8% elimination after 210 min of reaction time.

Key words: Chitosan biopolymer, UV/TiO₂, Acid Blue 40, textile wastewater, spectrophotometer.

INTRODUCTION

During the period of economics growth, textiles contributed significantly to Taiwanese development. However, large textile wastewater is discharged which causes severe environmental issues that is tough to be treated (Cheng et al., 2003). The characteristics of textiles discharge are high toxicity and color. The color is still quite distinct when the concentration is only at ppm level (mg/l). Some innovative devices and studies have been developed to eliminate the color of textile wastewater, which may include ozonation method (Gharbani et al., 2008), chitosan reagent (Smith et al., 1993) and UV/TiO₂ photo-catalytic system (Kuo and Lin, 2009; Rezaee et al., 2009).

Chitosan, made from shrimp or crab shell after deacetylation and purification, is a natural polymer with some properties similar to coagulating agents. This biopolymer is also inexpensive, massive, nontoxic and stable. After mixing with surfactants, chitosan is used in

textiles to finish fabrics so as to enhance the color fastness and to fix dyeing (Yen, 2001; Najafi et al., 2009). Chitosan is also applied to treat wastewater (Annadurai et al., 2007) and the results show that a remarkable amount of metal ions is adsorbed from the water (Ho and McKay, 1999). In recent years, photochemical technologies had spread widely. The titanium dioxide photo-catalytic system can effectively decompose various contaminants and resolve environmental problems. Mechanism for the phenomena lies on the basis of high energy of ultraviolet (UV) illumination to induce the electron transformation and to produce the oxyhydrogen ($\cdot\text{OH}$) free radical simultaneously (Peill and Hoffmann, 1996; Aris et al., 2002). It can be used to kill micro-organisms, to cleave the organic bonds and to cause metal ions reduction. Either to treat organic contaminants alone (Sauer and Ollis, 1996), or to deal with organic contaminants and metal ions at the same time (Samarghandi et al., 2007), the approach of UV/TiO₂ system has acquired a very good reputation. Besides, nano titania holds many advantages such as cheap, easy to get, highly catalytic,

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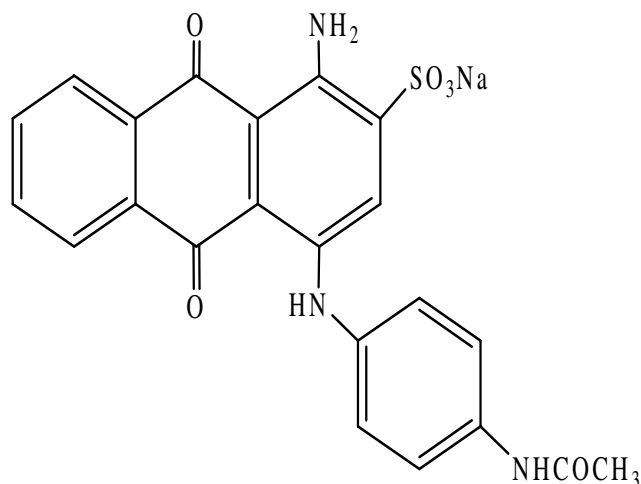


Figure 1. The molecular structure of C.I. Acid Blue 40 dye. Its molecular formula is $C_{22}H_{16}N_3NaO_6S$ and molecular weight is 473.43 g.

nontoxic and without secondary pollution.

The purpose of this study is for the color elimination of 50 ppm C.I. Acid Blue 40 simulated textile wastewater on laboratory operations by chitosan and UV/TiO₂ system. By addition of a variety of doses of reagents, we investigated the relationship between reaction time and removal efficiency under different operational conditions. Among those operations, we selected an appropriate parameter to achieve the best efficiency. Thus, the best condition in a laboratory scale could be applied in industrial treatment system for textiles discharge (Laszlo, 1994).

METHODS

Reagents

The chemical structure of C.I. Acid Blue 40 is shown in Figure 1 and its characteristics are presented in Table 1. The C.I. Acid Blue 40 was obtained from Everlight Chemical Co. (Taiwan) with Everacid Blue A2G. Chitosan with 95% deacetylation which was dissolved in 2% acetic acid to form pH 6 solution was obtained from Ohka Enterprises Co. (Taiwan). Titanium dioxide (TiO₂) with average diameter (30 nm) was obtained from Ming Yuh Scientific Co. (Taiwan).

Instruments and analysis

The instruments used are micro-analytical balance (Sartorius CP 4235), magnetic stirrer with heater (Globallab glhps-gs/50), UV-visible spectrophotometer (JASCO V-530) and UV lamp T5-8W (8W and 60 Hz). After tested by the spectrophotometer, the C.I. Acid Blue 40 was determined to get the maximum absorption wavelength at 618 nm. Color removal percentage was calculated by the following equation:

$$R\% = [(A_0 - A) / A_0] \times 100\%$$

Where, A₀ is the pre-treatment absorbance of textile wastewater and A is the post-treatment absorbance of textile wastewater.

Table 1. Physical and chemical properties of C.I. Acid Blue 40 dye.

Properties	Description
Physical state	Brownish blue powder
Solubility in water	30 (g/l) at 100 °C
pH at water	6 (weak acid)
Strength	150 - 160%
Dyeing	Dip-dyeing
Fastness	Light (5), Washing (4 - 5)
Application	Wool, silk and nylon

Experiments

Since the discharge color was very obvious even at the ppm level (mg/l), the concentration of the simulated textile wastewater was thus set at 50 ppm which was 0.01 g acid blue dye plus water up to 200 ml. Five doses of chitosan including 500, 1000, 1500, 2000, and 2500 ppm, respectively, were used. Doses of nano-particle TiO₂ used in this investigation included 500, 750, 1000, 1500, 2000, and 2500 ppm. The pH conditions were 2, 4, 6, 8, and 10, respectively. Single reaction was operated within 70 min for an operational parameter alone and sampled every 10 min to measure the absorbance. The combination was operated within 210 min under some better operational parameters and sampled every 30 min to measure the maximum absorbance so as to investigate the best removal efficiency. The textile wastewater was set at 25 °C (room temperature in Taiwan) during the operations.

RESULTS AND DISCUSSION

Effect of chitosan

The chitosan doses mixed up with 50 ppm Acid Blue 40 synthetic wastewater were 500, 1000, 1500, 2000 and 2500 ppm. The absorbance was measured every 10 min by a spectrophotometer, and then, the removal percentage was calculated. The experimental results of 70 min chitosan operation are shown in Figure 2. From the operation curves in Figure 2, it can be seen that, the color removal was based on reaction time in a fixed chitosan dose. 2500 ppm had the best operation curve because the 30 min reaction could reach 94% de-coloration.

Effect of TiO₂

The TiO₂ doses mixed up with 50 ppm Acid Blue 40 synthetic wastewater were 500, 750, 1000, 1500, 2000 and 2500 ppm. TiO₂ followed UV illumination so as to carry out the photo-catalytic effect. The absorbance was measured every 10 min and then the removal percentage was calculated. The experimental results of 70 min TiO₂ operation are shown in Figure 3. From Figure 3, it can be seen that 2500 ppm TiO₂ with UV irradiation had the best operation curve to eliminate the color.

In order to excite TiO₂, a UV lamp with wavelength around

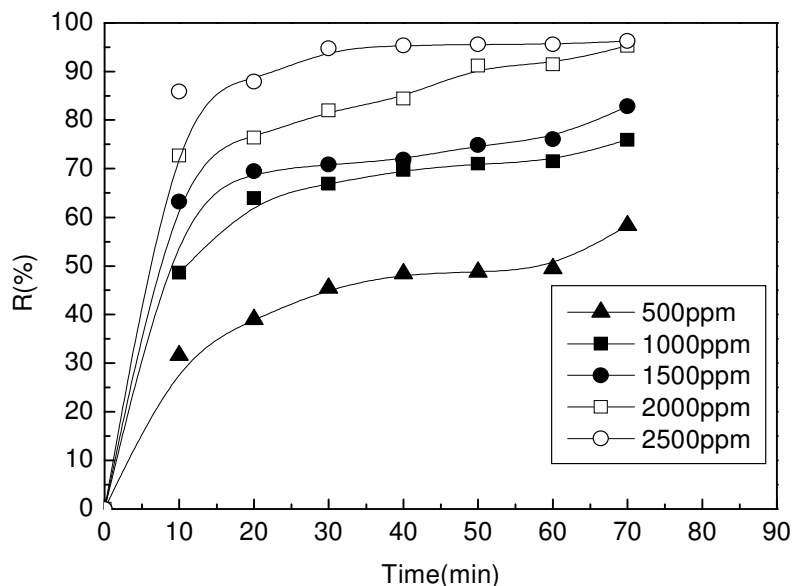


Figure 2. Effect of chitosan concentration on color removal within 70 min reaction at 25°C. The simulated textile wastewater was 50 ppm.

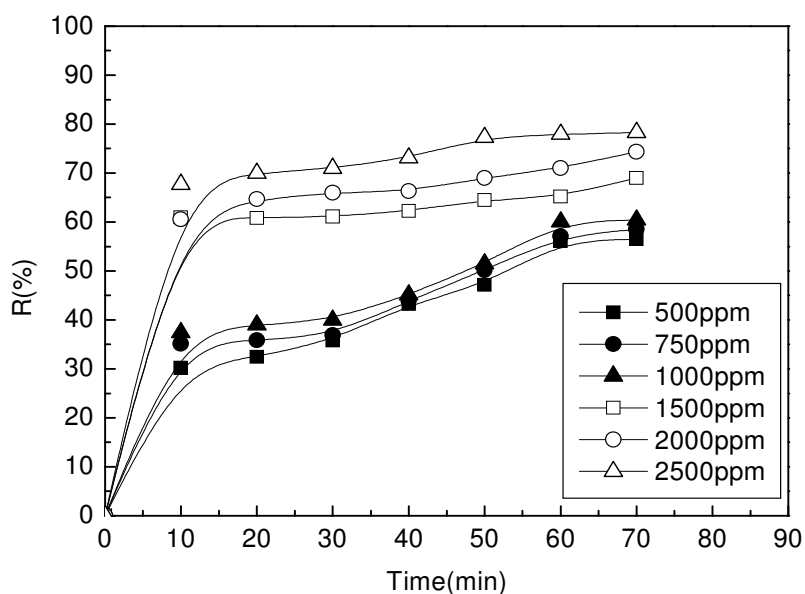


Figure 3. Effect of TiO_2 concentration with UV illumination on color removal within 70 min reaction at 25°C. The simulated textile wastewater was 50 ppm.

300 - 350 nm was adopted in the laboratory. At the stage, UV light provided energy to promote TiO_2 onto an excitement energy state. It caused electron transfer and oxyhydrogen (OH) dissociation from water molecule (H_2O) and meanwhile it produced the $\cdot\text{OH}$ free radical. This free radical was the catalyst for photo-decomposition and the driving force for color elimination.

The higher the TiO_2 dose, the higher the $\cdot\text{OH}$ free radical that was released. Therefore, the color removal of textiles

discharge should be more potent. That is the reason why the operation curves below 2500 ppm TiO_2 could not catch up with the 2500 ppm dose operation curve in Figure 3.

Effect of pH

For chitosan, 2500 ppm dose was better than the others

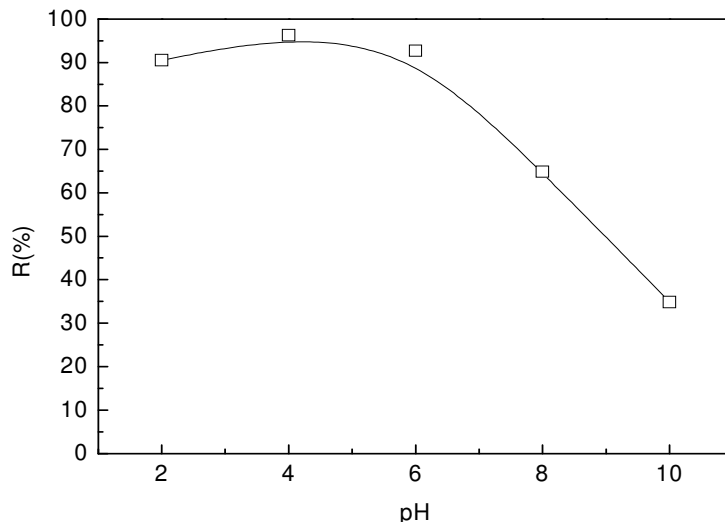


Figure 4. Effect of pH varied on simulated textile wastewater color removal at 25°C. The wastewater was 50 ppm and chitosan was 2500 ppm.

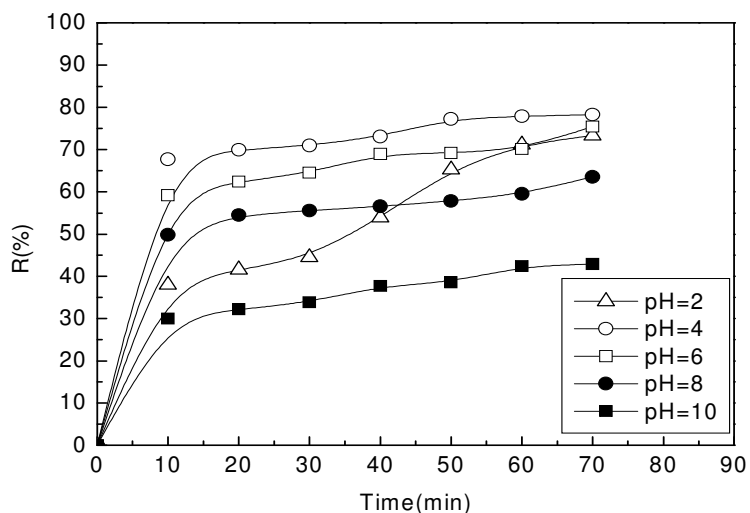


Figure 5. Effect of pH varied on simulated textile wastewater color removal within 70 min reaction at 25°C. The wastewater was 50 ppm and TiO_2 was 2500 ppm.

to de-color Acid Blue 40 synthetic wastewater as shown in Figure 2. Hence we varied pH conditions when we operated with fixed chitosan concentration at 2500 ppm. The effect of pH in this wastewater treatment is shown in Figure 4. From the observations, the important points can be made: To eliminate the color of Acid Blue 40 wastewater, chitosan is an acidophilic reagent since the removal efficiency in the acid conditions (pH 2, 4 and 6) was better than those in the base conditions (pH 8 and 10), Although the removal efficiency was quite different, it is not in accordance with the pH variation and the de-coloration peak occurred at pH 4.

These results are explainable by some phenomena. Once chitosan gets dissolved in water, it becomes a charged molecule. The repulsion between these molecules keeps chitosan at a uniform dispersion. At pH 2, 4 and 6, better dispersion, cause better interaction effect that consequently improved the elimination. The best acidity level for chitosan to de-color wastewater was pH 4.

In the case of TiO_2 , 2500 ppm dose was better than other doses that de-colored the Acid Blue 40 wastewater shown in Figure 3. TiO_2 was fixed at 2500 ppm, pH and reaction time conditions were varied. The effect of pH in this TiO_2 experiment is shown in Figure 5. The best pH

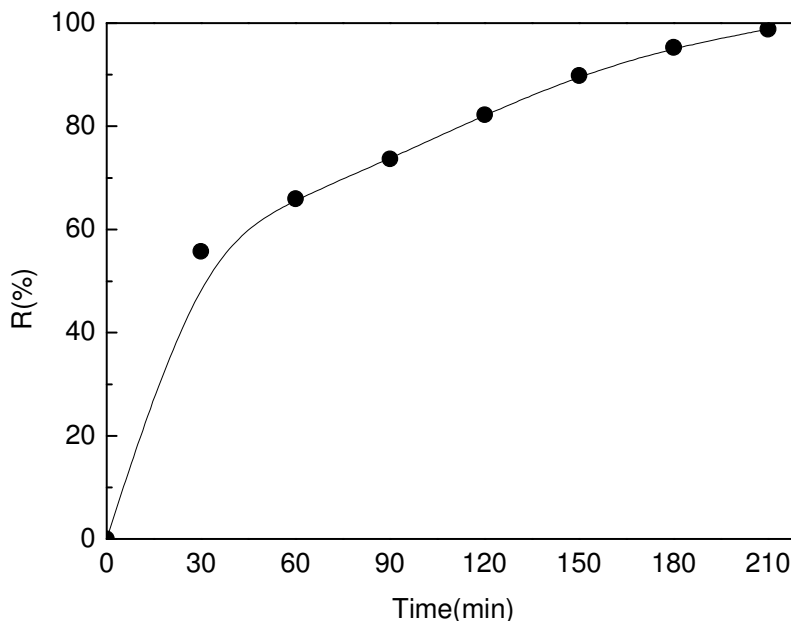


Figure 6. The color removal within 210 min reaction time on 50 ppm simulated textile wastewater at 25°C. The UV/TiO₂ operation system was 2500 ppm TiO₂ with UV illumination and pH 4.

condition for color removal was also at pH 4.

The UV/TiO₂ combination system

To sum up the parameters above, the best condition for UV/TiO₂ combination are TiO₂ dose 2500 ppm with UV illumination and at pH 4 operation system. From Figure 6, the removal efficiency quite correlated with the reaction time, which means the longer the reaction, the better the efficiency. The ultimate operation time is 210 min in the laboratory. At that time, the de-coloration efficiency was as high as 98.8%.

Conclusions

The dose and pH level of both chitosan and TiO₂ for the de-coloration of C.I. Acid Blue 40 simulated textile wastewater are 2500 ppm and pH 4, respectively, to obtain better removal efficiency. At 2500 ppm TiO₂ dose, pH 4 for the UV/TiO₂ combination system with ultraviolet illumination and after 160 min operation could reach 90% removal efficiency. When the reaction time was increased to 210 min which is the optimal time in this investigation, the elimination efficiency was 98.8%. Based on economic consideration (cost and efficiency) in an engineering point of view, we found that the system can spend only 150 - 180 min (2.5 - 3.0 h) to achieve almost 90% effectiveness. It is practicable for this system to be applied to industrial operation.

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