



A comparative study of the azo dye reactive black 5 degradation by UV/TiO₂ and photo-fenton processes

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ABSTRACT

The decolorization of the azo dye Reactive Black 5 in aqueous solution has been studied using UV/TiO₂ and photo-Fenton processes. The effects of operating parameters, such as pH, H₂O₂ dosage, TiO₂ dosage, Fe²⁺ dosage and the initial dye concentration, were investigated. The optimal conditions for each of the processes were obtained. The kinetics data in both the cases fitted well to the first-order equation. A comparison of the results under the optimal conditions showed that the azo dye Reactive Black 5 was found to undergo substantial and rapid decoloration by both the method. However, the decoloration of the azo dye by the photo-Fenton processes was much more efficient.

Key words: Reactive Black 5; UV/TiO₂; Photo-Fenton; Comparative

INTRODUCTION

Wastewater from textile and dye industries[1] are highly polluted by suspended solids, high chemical oxygen demand values, high biochemical oxygen demand values, heat, acidity, basicity and other soluble substances. Most of pollutants, except color, can be reduced by chemical, physical or biological methods. Therefore, the color problem of some textile wastewater caused by the residual dyes during the dyeing process needs more effort to be studied and investigated. Color removal from textile wastewater has also been a matter of considerable interest during the last two decades, not only because of the potential toxicity of certain dyes but often due to their visibility in recipient waters [2].

Reactive azo dyes are the largest group of organic dyes with -N=N- group as a chromophore in the molecular structure and represent more than a half of the global dye production specially because of their wide usage in dyeing industries due to the simple dyeing procedure[3]. These reactive dyes belong mostly to the non-biodegradable and recalcitrant type of water pollutants, which make activated sludge treatment methods inadequate. A long residence time for microorganisms to degrade such a pollutant is required, because they are affected by organic pollutant toxicity. More intense physical/chemical conditions are needed in order to remove dyes from the wastewater [4,5]. Physical treatment of colored wastewater requires a post-treatment to remove newly secondary waste. The chemical oxidation of toxic and hazardous organic pollutants, which are frequently present in surface waters and wastewaters, is often carried out by using single oxidants such as ozone, hydrogen peroxide, potassium permanganate, chlorine, etc. Among chemical methods, especially advanced oxidation process, such as photocatalytic oxidation, photo-Fenton, electro-Fenton, UV/ H₂O₂, and ozonation processes seem to be more promising[6-9]. These processes base on generation of powerfully oxidizing radicals (especially •OH). Degradation of azo dye by Fenton type processes could be significantly accelerated in the presence of UV irradiation, resulting with complete mineralization of the azo dye [10]. The use of TiO₂ as semiconductor photocatalysts for environmental clean up promises increasing attention because of its low cost, non-toxic, insoluble, highly reactive nature and relatively high chemical stability of TiO₂, especially when sunlight is used as the source of irradiation[11]. Photocatalytic methods with catalysts was

successfully applied to the decomposition of many organic contaminants, i.e. including azo dyes [12-16].

The main objective of this study is to analyse the decolorization of Reactive Black 5 by UV/TiO₂ and photo-Fenton processes. The effects of operating parameters, such as pH, H₂O₂ dosage, TiO₂ dosage, Fe²⁺ dosage and the initial dye concentration, were also investigated.

EXPERIMENTAL SECTION

2.1 Material

The azo dye, Reactive Black 5 was obtained from Shanghai and used without any purification. Molecular structure of Reactive Black 5 is illustrated in Fig. 1.

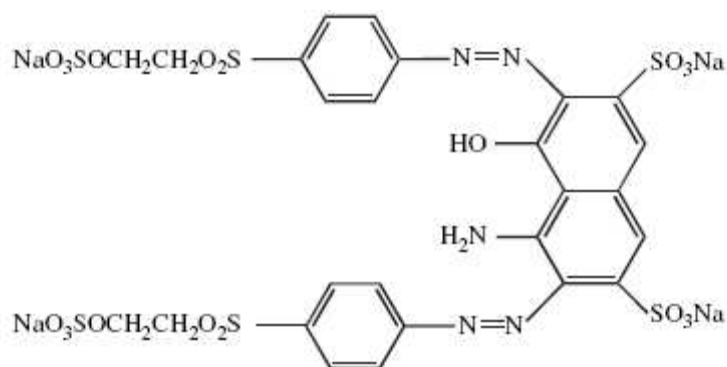


Fig.1 Chemical structure of Reactive Black 5

2.2 Photodegradation experiments

All experiments were carried out in a batch waterjacketed photoreactor with the total capacity of 800mL. The irradiation source was a mercury lamp 125W(UV-C, 254nm), which was placed in the inner quartz tube of the reactor as it was described elsewhere[17-19]. The incident UV-light flux at 254nm, 7.36×10^{-6} Einstein s⁻¹, was calculated on the basis of hydrogen peroxide actinometry measurements.

2.3 Analytical methods

The UV-vis spectra of Reactive Black 5 solution were recorded from 200 to 800nm using a UV/Vis spectrophotometer with a spectrometric quartz cell (UV752, China). The maximum absorbance wavelength of Reactive Black 5 was found at 598 nm. In the whole reaction process, it was found that the measure of concentration of Reactive Black 5 is not interfered by the decolorization products. Therefore, the concentration of Reactive Black 5 in reaction mixture at different reaction times was determined by measuring the absorption intensity of solution at 598 nm and using a calibration curve.

The decolorization efficiency of Reactive Black 5 was defined as follows:

$$\text{Decolorization efficiency} = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \quad (1)$$

Where C₀ is the initial concentration of Reactive Black 5, and C_t is the concentration of Reactive Black 5 at reaction time t (minute).

RESULTS AND DISCUSSION

3.1 Comparison of UV/TiO₂ and photo-Fenton oxidations

A comparison of the dye decolorization of Reactive Black 5 with photo-Fenton and UV/TiO₂ was investigated at 50 mg/L[dye], 0.05 mmol/L [Fe²⁺] or 0.05 mmol/L [TiO₂], 2.0mmol/L [H₂O₂], pH3.5 and 298 K.

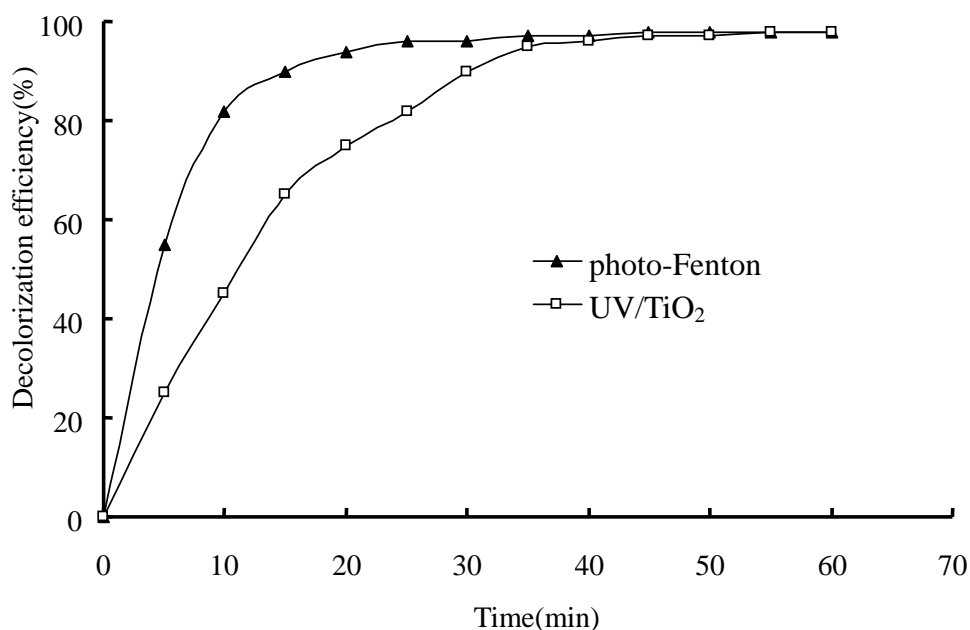


Fig.2 A comparison of the decolorization efficiency of Reactive Black 5 with photo-Fenton and UV/TiO₂ reaction

As seen from Fig.2, it was showed that both photo-Fenton and UV/TiO₂ oxidations were effective in dye decolorization. The decolorization efficiency was 97% after 45min. However, the decolorization efficiency exhibited different rates for the photo-Fenton and UV/TiO₂ oxidations. The decolorization efficiency in photo-Fenton oxidation was much faster than that of the UV/TiO₂ oxidation in the initial stages and the decolorization efficiency was similar for both systems after 45min.

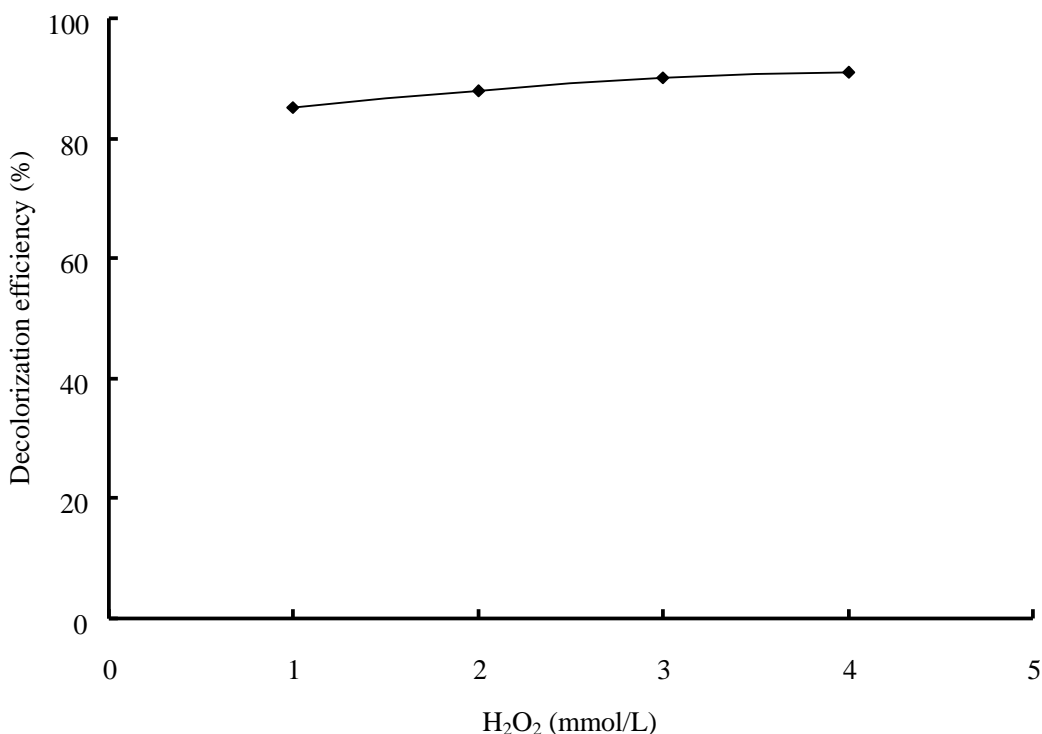


Fig.3 Effect of initial H₂O₂ concentration on decolorization of Reactive Black 5 by photo-Fenton reaction

3.2 Effect of H₂O₂ concentration

The effect of H₂O₂ was studied by varying the amount of H₂O₂ used for the experiment from 1.0mmol/L to 4.0mmol/L with 0.05mmol/L of [Fe²⁺], 50mg/L of dye solution, pH₀=3.5, reaction time of 20minutes and 298 K.

Fig.3 shows the relationship between decolorization of the dye at different initial concentrations.

As seen from Fig.3, it indicated that the decolorization of the dye increased with increasing H_2O_2 concentration. When the H_2O_2 concentration increased to 2mmol/L, in the photo-Fenton reaction the decolorization efficiency could reach to 94% after 20minutes. H_2O_2 concentration above 2mmol/L would not induce significant change in decolorization efficiency.

3.3 Effect of TiO_2 concentration

The effect of TiO_2 was studied by varying the amount of TiO_2 used for the experiment from 1.0mmol/L to 4.0mmol/L with 50mg/L of dye solution, $\text{pH}_0=3.5$, reaction time of 20minutes and 298 K. Fig.4 shows the relationship between decolorization of the dye at different initial concentrations. In UV/ TiO_2 reaction, 75% of decolorization efficiency could be achieved after 20minutes when the TiO_2 concentration was 2mmol/L.

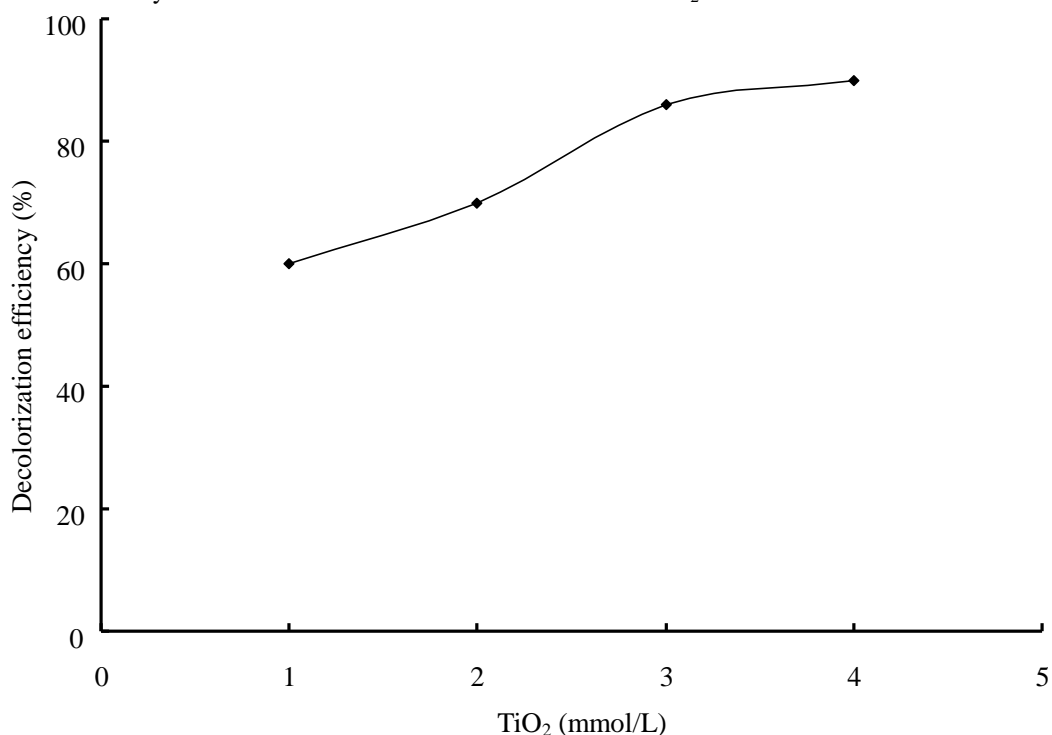


Fig.4 Effect of initial TiO_2 concentration on decolorization of Reactive Black 5 by UV/ TiO_2 reaction

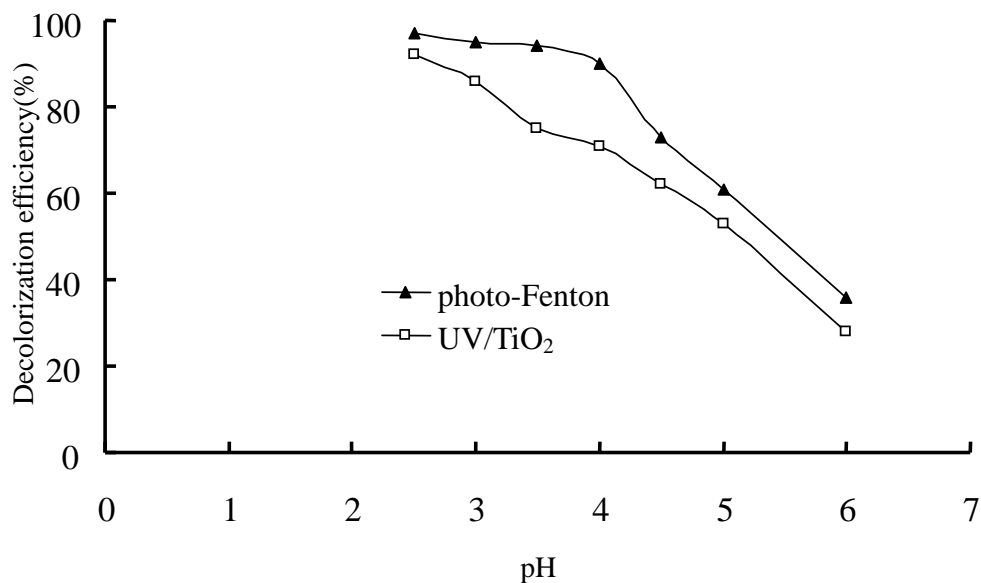


Fig.5 Effect of initial pH on decolorization of dye by photo-Fenton and UV/ TiO_2 reaction

3.4 Effect of initial pH

The effect of initial pH was studied by varying pH in the solution from 2.5 to 6.0 with 0.05mmol/L of $[\text{Fe}^{2+}]$ or 0.05mmol/L of $[\text{TiO}_2]$, 40mg/L of dye solution, 2.0mmol/L $[\text{H}_2\text{O}_2]$, $\text{pH}_0=3.5$, reaction time of 20minutes and 298 K.

Fig.5 shows the relationship between decolorization of the dye at different initial concentrations.

Fig.5 shows that lower pH resulted in higher rates of dye decolorization. For the photo-Fenton reaction, 94% of decolorization was achieved in 20minutes at a $\text{pH}<3.5$ and when the pH was further decreased, the decolorization efficiency was similar. However, in the UV/ TiO_2 reaction, 75% of decolorization efficiency was obtained after 20minutes at $\text{pH}<3.5$.

3.5 Effect of the initial dye concentration

The effect of the initial dye concentration on photo-Fenton and UV/ TiO_2 processes was investigated with $\text{pH}_0=3.5$, 0.05mmol/L of $[\text{Fe}^{2+}]$ or 0.05mmol/L of $[\text{TiO}_2]$, 2.0mmol/L of $[\text{H}_2\text{O}_2]$, reaction time of 20minutes and 298 K. The influence of the dye concentration is shown in Fig.6.

It was observed that higher the initial dye concentration, lower the decolorization efficiency of dye by photo-Fenton and UV/ TiO_2 reaction. This means that with constant $[\text{H}_2\text{O}_2]_0$ and $[\text{TiO}_2]_0$, more hydrogen peroxide was consumed because of a higher dye concentration.

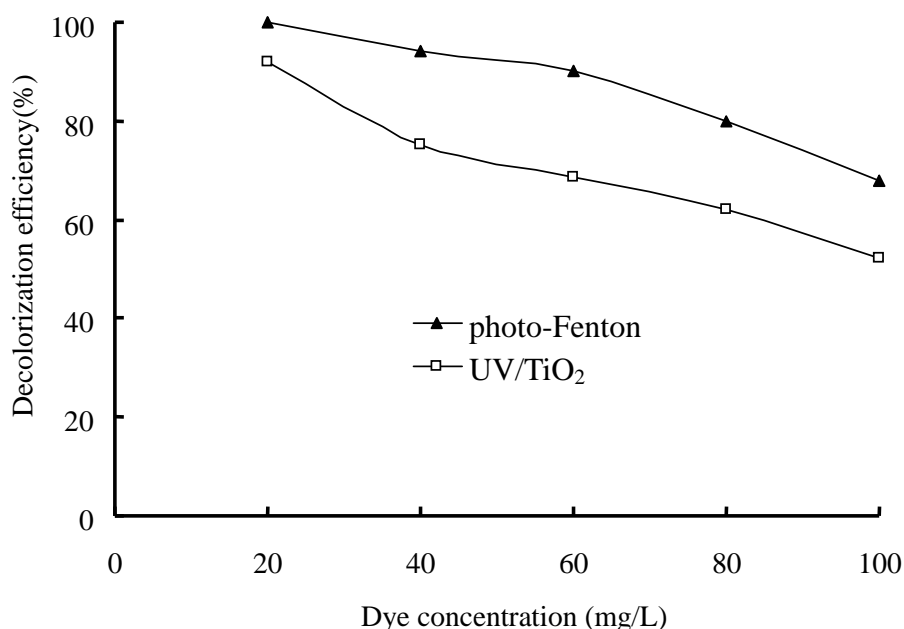


Fig.6 Effect of the initial dye concentration on the decolorization of dye by photo-Fenton and UV/ TiO_2 reaction

CONCLUSION

The photo-Fenton and UV/ TiO_2 oxidation can effectively decolorize Reactive Black 5 in aqueous solution under neutral conditions. The decolorization efficiency in photo-Fenton oxidation was much faster than that of the UV/ TiO_2 oxidation in the initial stages and the decolorization efficiency was similar for both systems after 45min. For the two oxidation systems, the decolorization efficiency of Reactive Black 5 depends on $[\text{Dye}]_0$, $[\text{Fe}^{2+}]_0$ or $[\text{TiO}_2]_0$, $[\text{H}_2\text{O}_2]_0$ and pH.

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