



Decolourisation of Reactive Dyes by Modified Photo-Fenton Process Under Irradiation With Sunlight

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Key Words:

Reactive dyes
Decolourisation of dyes
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ABSTRACT

In a laboratory study, decolourisation of four reactive dyes (Cibacron Yellow C5G, Remazol Blue RGP, Remazol Red RGP and Remazol Golden Yellow RGP) by modified photo-Fenton (UV-vis/ferrioxalate/H₂O₂) process under irradiation with sunlight was examined. Over 90% decolourisation occurred in 90-120 min for dye concentrations of 20, 50 and 100 mg/L, indicating the effectiveness of ferrioxalate complexes in decolourisation of even strongly coloured solutions. The study has demonstrated that modified photo-Fenton process is an effective process for decolourisation of reactive dyes. The process is useful for treatment of dyehouse waste in tropical and equatorial regions where sunlight is abundant.

INTRODUCTION

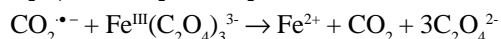
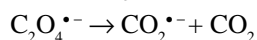
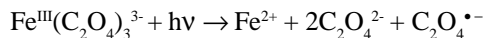
Reactive dyes are used to dye cellulosic fibres such as cotton. Due to growing worldwide use of cotton, the use of reactive dyes in the textile industry has increased rapidly. However, as a result of low dye fixation to the fabric, about 40% of the dye is unexhausted and remains in the spent dye bath waste, which is aesthetically objectionable and often toxic to aquatic life.

It is difficult to treat and decolourise textile dye waste containing reactive dyes by conventional chemical and biological methods. It has been demonstrated that semiconductor photocatalytic oxidation of organic substances can be an alternative to conventional methods of removal of organic pollutants from water (Ollis et al. 1991). An additional advantage of the photocatalytic process is its mild operating conditions and the fact that the semiconductor can be activated by sunlight (near UV), thus, reducing significantly the electric power requirement and, hence, the operating cost (Goswami 1995).

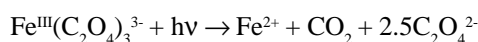
Titanium dioxide-mediated solar photocatalytic degradation of reactive dyes (Neppolian et al. 2003, Muruganandham et al. 2006, Muruganandham & Swaminathan 2007) and decolourisation of textile dye waste containing reactive dyes (Kanmani & Thanasekaran 2003, Reddy & Kotaiah 2005) have been studied. Zinc oxide-mediated solar photocatalytic degradation of reactive dye has also been studied (Roselin et al. 2002).

Titanium dioxide ($E_{bg} = 3.2$ eV) and zinc oxide ($E_{bg} = 3.2$ eV) absorb light up to $\lambda \cong 385$ nm (Mills et al. 1993), whereas ferrioxalate absorbs light strongly at longer wavelengths (up to $\lambda \cong 550$ nm) and generates hydroxyl radicals with high quantum yield (Safarzadeh-Amiri et al. 1997). Therefore, efficiency of oxidative decolourisation/degradation mediated by ferrioxalate under irradiation with sunlight ($\lambda \geq 320$ nm) – the modified photo-Fenton (UV-vis/ferrioxalate/H₂O₂) process – is expectedly higher than that by titanium dioxide or zinc oxide under irradiation with sunlight.

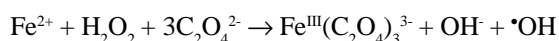
A simplified mechanism for the modified photo-Fenton (UV-vis/ferrioxalate/H₂O₂) process is outlined (Hislop & Bolton 1999). The ferrioxalate complex, Fe^{III}(C₂O₄)₃³⁻ is highly photosensitive, and reduction of Fe(III) to Fe(II) through a photoinduced ligand to metal charge transfer can occur over the ultraviolet and into the visible (out to λ ≅ 550 nm):



The reactions can be collapsed into one reaction, since the short lifetime of the oxyl radical C₂O₄^{•-} should preclude it from participation in other reactions, and its decarboxylation product, CO₂^{•-} is not involved in any other significant reactions:



There are no other significant photochemical reactions (e.g., H₂O₂ photolysis) because the molar extinction coefficients of the reactants are such that ferrioxalate is the predominant absorber. The Fe²⁺ produced then generates hydroxyl radical •OH via the Fenton reaction:



In presence of a sufficient excess of oxalate, Fe(III) will coordinate with either two or three oxalate ligands. As with the photo-Fenton reaction, iron cycles between oxidation states and so the production of hydroxyl radicals is limited only by the availability of light, H₂O₂ and oxalate, the latter two of which are depleted during the reaction.

The present study examined decolourisation of four reactive dyes by modified photo-Fenton (UV-vis/ferrioxalate/H₂O₂) process under irradiation with sunlight (λ ≥ 320 nm).

MATERIALS AND METHODS

Reactive dye, Cibacron Yellow C5G was obtained from the Arab-Malaysian Development Bhd., Taiping, Perak, Malaysia, and Remazol Blue RGP, Remazol Red RGP and Remazol Golden Yellow RGP from the Kamunting Textile Industries Sdn. Bhd., Kamunting, Taiping, Perak, Malaysia. Concentration of dye (colour) was determined by measuring the absorbance at the wavelength of maximum absorbance (Cibacron Yellow C5G: 410 nm; Remazol Blue RGB: 605 nm; Remazol Red RGP: 525 nm; and Remazol Golden Yellow RGP: 410 nm) against a standard curve.

To study decolourisation by the modified photo-Fenton process, concentration of the dye was chosen as 20, 50 and 100 mg/L. Two hundred and fifty millilitres of the dye solution were taken in a 500 mL borosilicate glass beaker, pH was adjusted with sodium hydroxide or sulphuric acid to a predetermined value, and different preselected dosages of Fe(III), oxalic acid and hydrogen peroxide were added. The mixture was kept stirred by a magnetic stirrer to ensure a homogenous mixture and aeration, and exposed to sunlight. Aliquots were withdrawn at 30 min intervals and filtered through a 0.45 μm membrane filter for measurement of colour. Sunlight intensity was measured in kW/m² by a pyranometer at 30 min intervals. Based on the pattern of decolourisation, optimum process conditions (pH, dosages of Fe(III), oxalic acid and hydrogen peroxide) for decolourisation were selected.

RESULTS AND DISCUSSION

To determine the optimum pH and irradiation time for decolourisation, a test was conducted with excess dosages of Fe(III) (40 mg/L), oxalic acid (H₂C₂O₄) (275 mg/L) and hydrogen peroxide (H₂O₂)

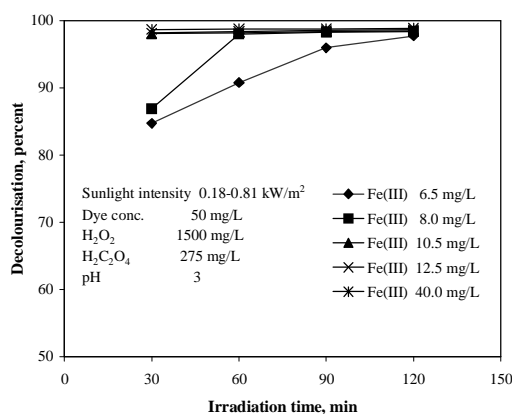
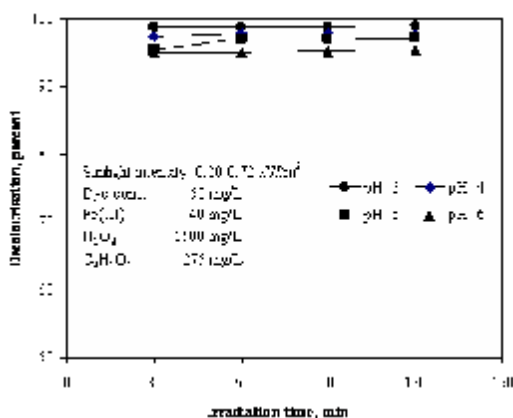


Fig. 1: Effect of pH and irradiation time on decolourisation of cibacron yellow CSG.

Fig. 2: Effect of Fe(III) dosage on decolourisation of cibacron yellow CSG.

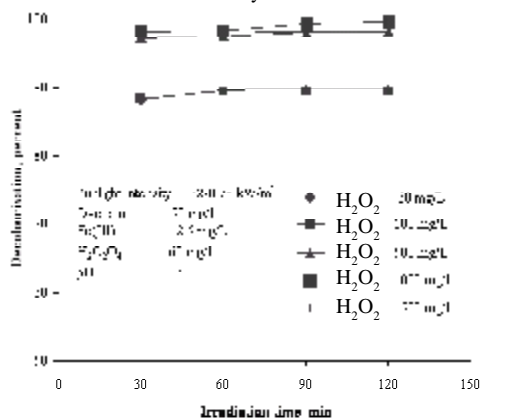
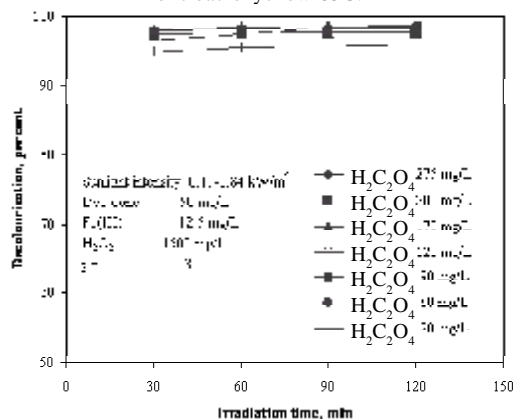


Fig. 3: Effect of oxalic acid dosage on decolourisation of Cibacron Yellow CSG.

Fig. 4: Effect of hydrogen peroxide dosage on decolourisation of Cibacron Yellow CSG.

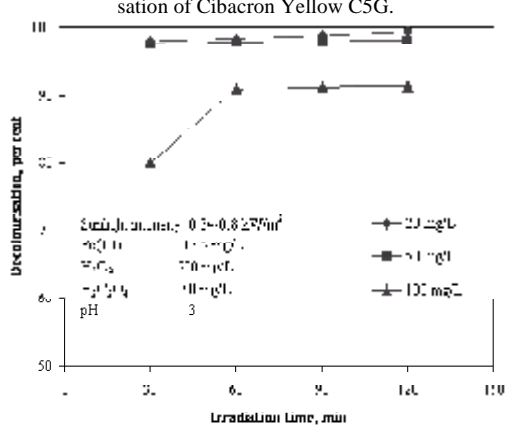
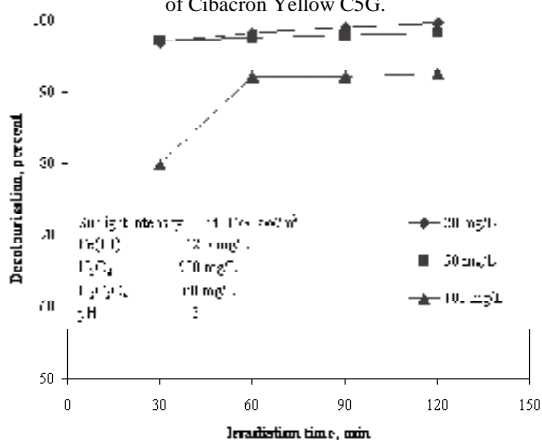


Fig. 5: Effect of dye concentration on decolourisation of Cibacron Yellow CSG.

Fig. 6: Effect of dye concentration on decolourisation of Remazol Blue RGP.

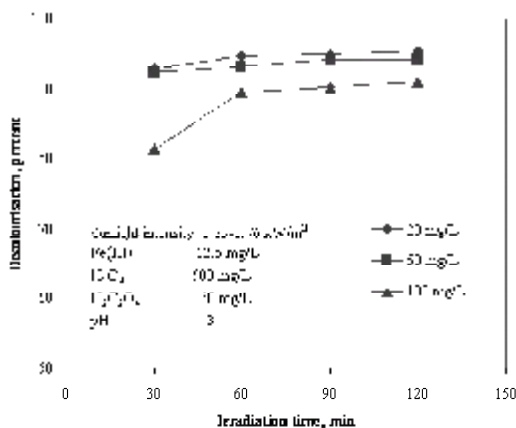


Fig. 7: Effect of dye concentration on decolourisation of Remazol Red RGP.

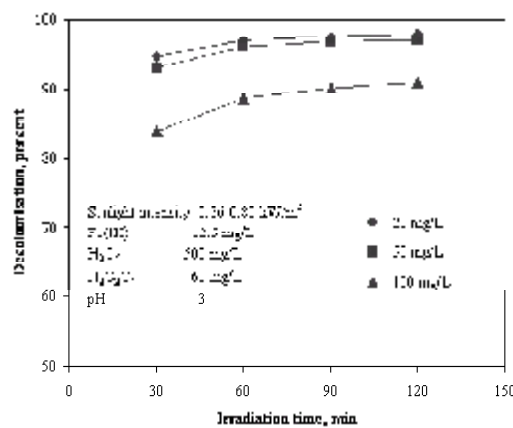


Fig. 8: Effect of dye concentration on decolourisation of Remazol Golden Yellow RGP.

(1500 mg/L), and at different pH (3-6). Fig. 1 shows that rapid decolourisation occurred in about 30 min and decolourisation remained constant after 60 min. Decolourisation (98.8%) was the highest at pH 3. All the subsequent tests were conducted at pH 3.

The dependence of decolourisation on Fe(III) dosage was studied by employing different dosages of Fe(III) (6.5, 8.0, 10.5, 12.5 and 40.0 mg/L) with 275 mg/L of $H_2C_2O_4$ and 1500 mg/L of H_2O_2 (Fig. 2). Decolourisation rate increased with increasing Fe(III) dose and maximum decolourisation (98.8%) occurred with Fe(III) dosages of 12.5 and 40 mg/L.

To determine the effect of oxalic acid dosage on decolourisation, Fe(III) and H_2O_2 dosages were held at 12.5 and 1500 mg/L, respectively and $H_2C_2O_4$ dose was varied (20-275 mg/L). The results presented in Fig. 3 show that decolourisation (98.5-98.6%) was similar for $H_2C_2O_4$ dosages of 60-275 mg/L. It may be noted that the ferrioxalate complex is relatively unreactive with hydroxyl radical, OH (Aplin et al. 2001) and, hence, increased oxalate concentration did not significantly affect decolourisation.

Fig. 4 shows decolourisation of the dye at pH 3 with Fe(III) and $H_2C_2O_4$ dosage of 12.5 and 60 mg/L, respectively and H_2O_2 dosages of 60-1500 mg/L. Greater than 98.5% decolourisation occurred with H_2O_2 dosages of 500-1500 mg/L. The selected process conditions for decolourisation were pH 3, Fe(III) dose 12.5 mg/L, $H_2C_2O_4$ dose 60 mg/L and H_2O_2 dose of 500 mg/L.

To examine the effect of dye concentration on decolourisation, dye solutions of Cibacron Yellow C5G, Remazol Blue RGP, Remazol Red RGP and Remazol Golden Yellow RGP of different concentrations (20, 50 and 100 mg/L) were irradiated under selected process conditions (Figs. 5-8). Over 90% decolourisation occurred in 90-120 min for all dye concentrations, indicating the effectiveness of ferrioxalate complexes in decolourisation of even strongly coloured solutions.

Modified photo-Fenton (UV-vis/ferrioxalate/ H_2O_2) is an effective process for decolourisation of reactive dyes. High (over 90%) decolourisation is achieved under irradiation with sunlight. The process can also be used under irradiation with incandescent lamp (Tripathi & Chaudhuri 2004). The process is useful for treatment of dyehouse waste in tropical and equatorial regions where sunlight is abundant. In the absence of sunlight, irradiation with incandescent lamp is equally effective.

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