

Advanced oxidative decolourisation of Reactive Yellow 14 azo dye by UV/TiO₂, UV/H₂O₂, UV/H₂O₂/Fe²⁺ processes—a comparative study

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Abstract

The decolourisations of reactive azo dye, Reactive Yellow 14 (RY14), by three different advanced oxidation processes have been investigated. The dye is effectively decolourised by all these processes. The effects of dye adsorption, catalyst loading and dye concentration on the UV/TiO₂ process have been studied. These parameters influence the decolourisation rate. In UV/H₂O₂ and UV/H₂O₂/Fe²⁺ processes, H₂O₂, Fe²⁺ dosage and dye concentration have strong influence on the decolourisation. The kinetics of heterogeneous photocatalytic decolourisation is discussed in terms of Langmuir–Hinshelwood (L–H) kinetic model. The decolourisation rates observed are quite different for each system. The decolourisation efficiencies of these processes are in the following order UV/H₂O₂/Fe²⁺ > UV/TiO₂ > Fe²⁺/H₂O₂ > UV/H₂O₂.

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1. Introduction

High strength of coloured dye industry effluent inhibits light penetration and minimises the photosynthesis. The effluent has been found to be toxic and carcinogenic to aquatic environments [1]. Azo dyes are resistant to biodegradation and hence, conventional biological treatment methods are ineffective to decolourise the dye pollutants [2]. Reactive azo dyes are widely used in the dyeing industries because of its simple dyeing procedure. Unfortunately, there are no universally useful methods available for treatment of these dye wastes.

In recent years, advanced oxidation processes (AOPs) for wastewater treatment have drawn much attention. AOPs generate the highly reactive hydroxyl radical (•OH) to degrade recalcitrant chemicals present in wastewater. Production of

eco-friendly end product is the special feature of these processes. Heterogeneous photocatalysis using TiO₂ is one of the promising AOPs. Due to its high photocatalytic activity, TiO₂ was found to be an efficient photocatalyst for the removal of pollutants in wastewaters [3–8]. Homogeneous AOPs employing hydrogen peroxide with UV light (or) ferrous ion (or) both have been reported to be very effective in the degradation of pollutants [9–22]. Hydrogen peroxide alone cannot oxidise the pollutant effectively. But, it needs to be activated by means of UV light, ferrous (or) ferric salts.

For practical use of these processes in wastewater treatment, there is a need to determine the optimal conditions of experimental parameters for efficient removal. In our earlier work, we have reported the degradation of Reactive Orange 4 by advanced oxidation processes using UV and solar light [23–26]. In the present study, we have investigated the decolourisation of a reactive azo dye RY 14 by three different AOPs. Reactive Yellow 14 dye (C.I. No. 19,036, molecular weight = 669.0) is extensively used in the dyeing industries. The chemical structure and absorption spectrums of RY 14 are shown in Fig. 1.

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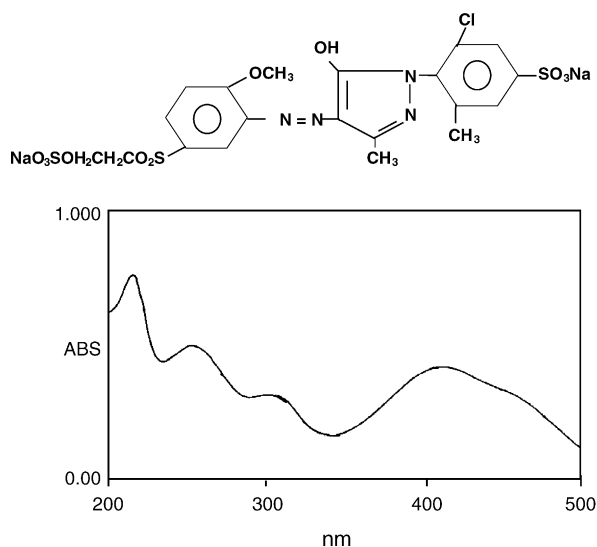


Fig. 1. UV absorption spectra and the structure of RY14 dye.

2. Materials and methods

2.1. Materials

The commercial azo dye Reactive Yellow 14 obtained from Colour Chem, Pondicherry was used as such. A gift sample of TiO_2 -P25 was obtained from Degussa (Germany). It has the particle size of 30 nm and BET specific surface area of $50 \text{ m}^2/\text{g}$. AnalaR-grade reagents H_2O_2 (30 %, w/w) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were used as received. The double distilled water was used to prepare experimental solutions. The pH of the solutions was adjusted using H_2SO_4 and NaOH.

2.2. Photoreactor

Heber multilamp photoreactor model HML-MP 88 (Fig. 2) was used for photoreaction. This model consists of eight medium-pressure mercury vapour lamps (8 W) set in parallel and emitting 365 nm of peak wavelength. It has a reaction chamber with specially designed reflectors made of highly polished aluminum and built in cooling fan at the bottom. It is provided with the magnetic stirrer at the centre. Open borosilicate glass tube of 50 ml capacity, 40 cm height and 20 mm diameter was used as a reaction vessel with the total light exposure length of 330 mm. The irradiation was carried out using four parallel medium-pressure mercury lamps in open-air condition. The light intensity was measured using ferrioxalate actinometer and the intensity was found to be $1.381 \mu\text{einsteins}/\text{min}$. The solution with TiO_2 and dye was continuously aerated by a pump to provide oxygen and for complete mixing of reaction solution.

2.3. Methods

2.3.1. Procedure

A 50 ml of the dye solution containing appropriate quantity of the TiO_2 suspensions was used. The suspension was

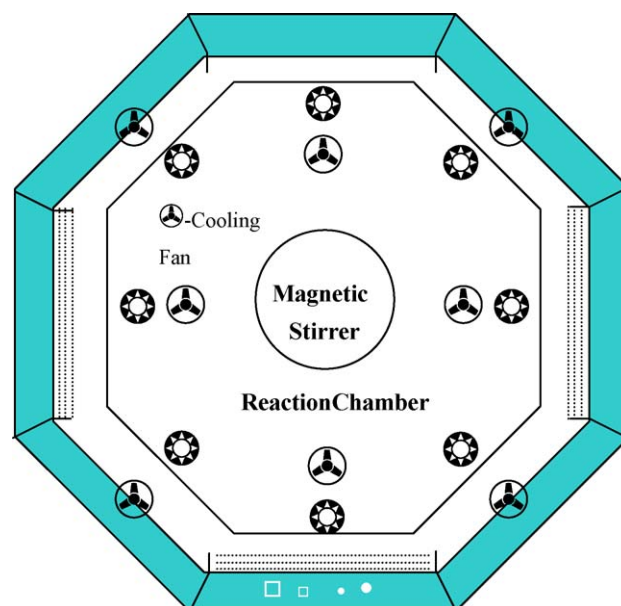


Fig. 2. Schematic diagram of photoreactor.

stirred for 30 min in dark for the attainment of adsorption equilibrium. At specific time intervals, 2 ml of the sample was withdrawn and centrifuged to separate the catalyst. 1 ml of the centrifugate was diluted to 10 ml and its absorbance at 410 nm was measured. The absorbance at 410 nm ($n \rightarrow \pi^*$ transition of $\text{N}=\text{N}$ group) is due to the colour of the dye solution and it is used to monitor the decolourisation of dye. Natural pH of dye solution is 5.5. For UV/ H_2O_2 process, a desired molar ratio of dye/ H_2O_2 at pH 3 was prepared freshly before the experiments. For Fenton and photo-Fenton process, a desired molar ratio of dye/ Fe^{2+} / H_2O_2 solution were freshly prepared from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and the dye stock solution. The pH of the solution was adjusted to 3.0 (for Fenton process, the mixture was kept in dark). After irradiation, the absorbance was measured immediately to avoid further reaction. The pH of the solution was adjusted to 5.5 before taking the concentration measurements. The interference by Ferrous ions in the UV region was negligible in the concentration range used for the present study.

2.3.2. Adsorption experiments

The adsorption experiments have been performed with the dye solutions at different pH and different dye concentrations. A 50 ml of aqueous dye solution was made to contact with 200 mg of TiO_2 for overnight at 20°C using mechanical shaker. In order to avoid the photoreaction of TiO_2 , the samples were kept in dark for the entire period of the experiment. After adsorption, the solutions were centrifuged to separate the catalyst. The concentration of the dye solution was determined from its absorbance at 410 nm. The amount of dye adsorbed on the catalyst was calculated by mass balance. This equilibrium was reached in 30 min. UV spectral analysis was done using Hitachi U-2001 spectrophotometer. The pH of the solution was

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