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Photoassisted Fenton mineralisation of Acid Violet 7 by heterogeneous Fe(III)–Al_2O_3 catalyst

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Abstract

Photoassisted Fenton mineralisation of an azo dye Acid Violet 7 was studied in detail using a Fe(III) loaded Al_2O_3 as a heterogeneous catalyst in the presence of H_2O_2 and UV-A light. The catalyst ferrioxalate–Al_2O_3 is more efficient than ferricnitrate–Al_2O_3. 35% Fe^{3+} loaded Al_2O_3 shows maximum efficiency in the degradation. The effects of reaction parameters such as catalyst loading, H_2O_2 concentration, initial solution pH and initial dye concentration on photodegradation were investigated and the optimum conditions are reported.

Keywords: Heterogeneous photo-Fenton; Acid Violet 7; Wastewater treatment; Ferrioxalate; Al_2O_3

1. Introduction

Although Fenton reactions were known for more than a century [1], it was reported as a method for wastewater treatment since 1990s [2–5]. The photochemically enhanced Fenton reactions are considered most promising for the remediation of wastewater containing a variety of toxic chemicals [6–10]. The higher efficiency of photo-Fenton reaction is due to the efficient recycling of Fe^{2+} than the thermal process [11]. Therefore, the photo-Fenton reaction may be carried out using either Fe(II) or Fe(III) as initial reactant. However, the use of Fe(II)/Fe(III) as a homogeneous catalyst has a significant disadvantage.

The removal of sludge containing Fe ions at the end of wastewater treatment is costly and needs large amount of chemicals and manpower. In this context, the photocatalytic degradation of organic contaminants using heterogeneous photo-Fenton catalyst will be more preferred. A number of heterogeneous catalysts developed by immobilizing Fe(II)/Fe(III) ions on various supports had been reported in the literature [12–17].

We had investigated the photocatalytic degradation of various dyes using advanced oxidation process and developed some modified semiconductor photocatalysts for AOPs [6,18–21]. In this paper, we report the preparation of Fe(III) loaded Al_2O_3 as heterogeneous catalyst and the photodegradation of Acid Violet 7 (AV 7) using this catalyst in the presence of H_2O_2 and UV light.

2. Experimental

2.1. Materials and chemicals

Acid Violet 7 (C.I. 18055) was obtained from s.d fine chemicals. Potassium ferrioxalate was prepared [22] and purified. Ferricnitrate from s.d fine, Al_2O_3 (neutral) from Loba chemicals (particle size 70–230 mesh), H_2SO_4, NaOH and H_2O_2 (30% w/w) from Qualigens were used as received. All the solutions were prepared with deionized water.

2.2. Preparation of catalyst

The preparation of the modified heterogeneous catalyst Fe^{3+}–Al_2O_3 is given below. Five grams of Al_2O_3 and required percentage of potassium ferrioxalate or ferricni-

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trate were added to ethanol/water mixture (60:40). The suspension was stirred for 3–4 h. Then the pale yellowish coloured Fe^{3+} loaded Al_2O_3 catalyst was filtered and dried. This Fe^{3+} loaded Al_2O_3 catalyst obtained by adding potassium ferrioxalate or ferricnitrate were tested for their degradation efficiencies under the same conditions. The percentages of degradation by these two catalysts are shown in Fig. 1. The initial adsorption of dye by ferricnitrate–Al_2O_3 was about 22% in dark and hence the degradation by this catalyst starts from 78%. But the adsorption by ferrioxalate–Al_2O_3 was not significant. About 95% degradation was observed with ferrioxalate–Al_2O_3 process at the time of 60 min whereas ferricnitrate–Al_2O_3 produced only 23% degradation.

Since ferrioxalate–Al_2O_3 gives maximum degradation than the ferricnitrate–Al_2O_3 catalyst, we have chosen ferrioxalate–Al_2O_3 catalyst for further study.

2.3. Apparatus

Heber multilamp photoreactor model HML-MP 88 (Fig. 2) was used for photoreaction. This model consists of eight medium pressure mercury vapour lamps of 8 W set in parallel. The lamp emits in a broad spectrum with 365 nm of peak wavelength. It has a reaction chamber with specially designed reflectors made of highly polished aluminium and built-in cooling fan at the bottom. It is provided with a 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 total radiation exposure length of 330 mm. The irradiation was carried out using four parallel medium pressure mercury lamps (32 W) in open-air condition. The light intensity was measured using ferrioxalate actinometer and it is found to be 1.381×10^{-6} einstein $L^{-1}\,s^{-1}$. The solution with Fe^{3+}–Al_2O_3 with H_2O_2 and dye was continuously aerated by a pump to provide oxygen and for complete mixing of the reaction medium.

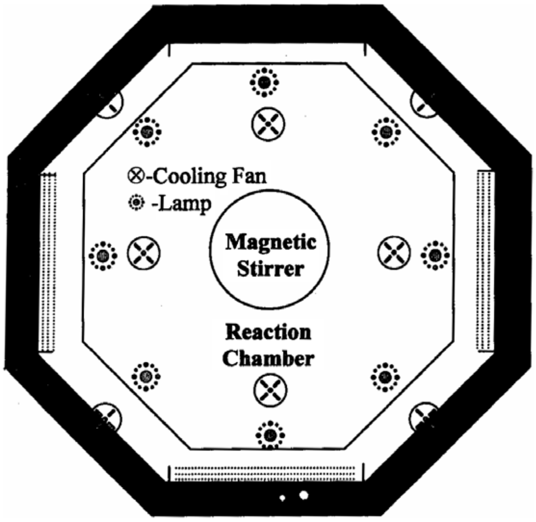


Fig. 2. Schematic diagram of photoreactor.

2.4. Procedure

In all cases, 50 mL of the dye solution containing appropriate quantity of the Fe^{3+}–Al_2O_3 and H_2O_2 suspensions were used. The suspension was stirred for a few minutes in the dark for the attainment of equilibrium and then it was irradiated. At specific time interval, 2 mL of the sample was withdrawn and centrifuged to separate the catalyst. One millilitre of the centrifugate was diluted to 10 mL and its absorbances at 306 nm and 522.5 nm were measured. The evolution of CO_2 has been tested by the formation of $CaCO_3$ when the gas evolved during the reaction is passed into limewater. The absorbance at 522.5 nm is due to colour of the dye solution and it is used to monitor the decolourisation of the dye.

The absorbance at 306 nm represents the aromatic content of AV 7 and the decrease of absorbance at 306 nm indicates the degradation of aromatic ring. The structure and UV–Vis spectral changes of AV 7 are given in Fig. 3.

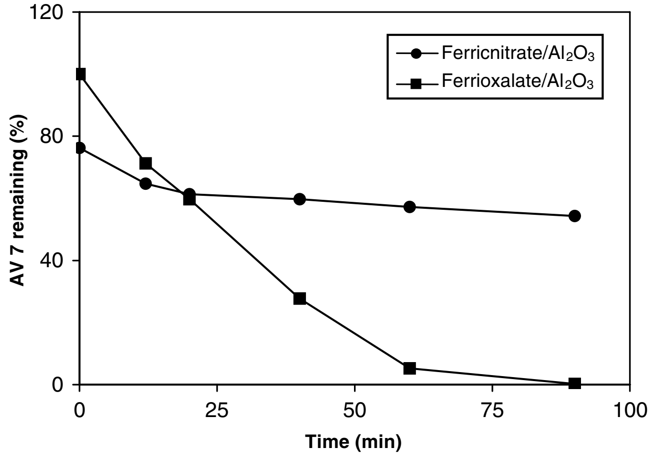
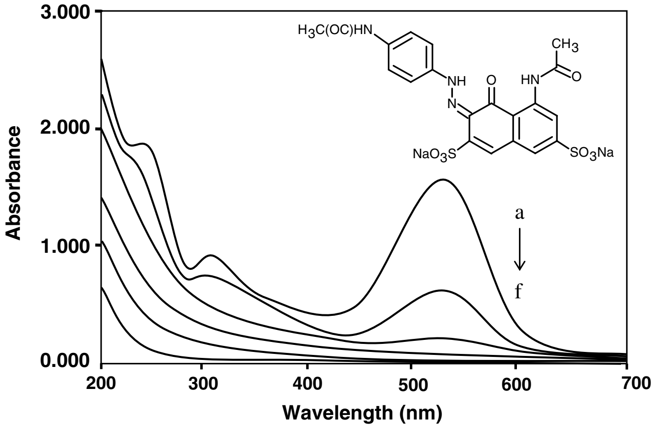


Fig. 1. Comparison of ferricnitrate–Al_2O_3 and ferrioxalate–Al_2O_3: [AV 7] = 5×10^{-4} M; catalyst suspended = 1 g L^{-1}; H_2O_2 = 10 mmol; airflow rate = 8.1 mL s^{-1}; pH 3 ± 0.1; $I_0 = 1.381 \times 10^{-6}$ einstein $L^{-1}\,s^{-1}$.



a – 0 min; **b** – 10 min; **c** – 20 min; **d** – 40 min; **e** – 60 min; **f** – 90 min

Fig. 3. The structure and UV–Vis spectral changes of AV 7: [AV 7] = 5×10^{-4} M; catalyst suspended = 1 g L^{-1}; H_2O_2 = 10 mmol; airflow rate = 8.1 mL s^{-1}; pH 3 ± 0.1; $I_0 = 1.381 \times 10^{-6}$ einstein $L^{-1}\,s^{-1}$.