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## Peroxomonosulphate, an efficient oxidant for the photocatalysed degradation of a textile dye, acid red 88

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#### Abstract

Visible light-assisted degradation of a mono azo textile dye acid red 88 (AR88) was carried out in presence of titanium dioxide photocatalyst. Various operational parameters such as variation of the initial dye concentration, photocatalyst and pH on the photocatalytic degradation rate were studied. Effect of the amount of oxidants such as peroxomonosulphate (PMS) and peroxodisulphate (PDS) and the ratio of concentration of oxidant to the concentration of dye ( $C_{\text{oxidant}}/C_{\text{dye}}$ ) on the photocatalysed degradation rate were also investigated. Though the rate of photodegradation of the dye decreased with increase in dye concentration, the rate increased with  $C_{\text{oxidant}}/C_{\text{dye}}$  ratio. Total organic carbon (TOC) analysis revealed a rapid mineralisation of AR88 in the presence of PMS. A suitable mechanism explaining the observed enhanced decolorisation and mineralisation rate of the dye with PMS is presented.

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Keywords: Photocatalysis; Acid red 88; Peroxomonosulphate; Peroxodisulphate; Visible light

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#### 1. Introduction

The rapid industrialisation, besides its benefit, has resulted in hazardous effects of chemicals on the environment. For example, effluents released from pulp and paper industries and petrochemical, textile and dyeing industries discharge different types of pollutants that are toxic, carcinogenic, and mutagenic to the aquatic lives as well as human beings. Several stringent legislations are being imposed world wide to protect the environment from pollution and the advanced oxidation processes (AOPs) are currently gaining significant importance [1-3] to meet the limitations of the current legislations.

AOPs mainly involve the generation of very powerful and non-selective oxidising agent, the hydroxyl radical ('OH), [4–6] which is produced by different combinations of ozone, hydrogen peroxide, UV radiation and titanium dioxide and also by the combination of hydrogen peroxide with ferrous ions in the so-called Fenton's reagent, for the destruction of hazardous pollutants in air and water [7,8]. AOPs are especially attractive because they hold out the promise of completely mineralising the target pollutant and hence are useful complement to the conventional treatment methods like flocculation, carbon adsorption, air stripping, reverse osmosis, aerobic biological oxidation, etc [9].

Heterogeneous photocatalysis is a viable method for waste water treatment as it completely mineralises the organic pollutants. Among the semiconductor photocatalysts available [10–12], TiO<sub>2</sub> is widely used owing to its properties like resistance to photocorrosion, less expensive, nontoxic and the use of it at ambient conditions. Irradiation of TiO<sub>2</sub> ( $E_g = 3.2 \text{ eV}$ ) with light energy  $\geq E_g$ , causes valence-band electrons to be excited to the conduction band creating holes in the valence band. The conduction band electrons ( $e_{CB}^-$ ) and valence band holes ( $h_{VB}^+$ ) migrate to the surface and participate in interfacial oxidation–reduction reactions.

$$\begin{split} \text{TiO}_2 &\xrightarrow{h\nu} \text{TiO}_2(e^-, h^+) \\ \text{TiO}_2(h^+) + \text{H}_2\text{O} &\rightarrow \text{TiO}_2 + \text{OH}^{\bullet-} + \text{H}^+ \\ \text{TiO}_2(e^-) + \text{O}_2 &\rightarrow \text{TiO}_2 + \text{O}_2^{\bullet-} \end{split}$$

The superoxide radical anion generated is ultimately converted into 'OH [13] that degrades the dye further.

The recombination of the  $e_{CB}^-$  and  $h_{VB}^+$  is undesirable for the efficient degradation of the pollutants and the addition of oxidants like  $H_2O_2$ ,  $K_2S_2O_8$ , KHSO<sub>5</sub>, KBrO<sub>3</sub> etc., avoids the recombination process by rapid reaction with the conduction band electrons generating very reactive oxidizing radicals, thus increasing the efficiency of photocatalysts.

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{\bullet-} + SO_4^{2-}$$

$$HSO_5^- + e^- \rightarrow SO_4^{\bullet-} + OH^-$$

For efficient degradation of pollutants these oxidants should (a) readily accept the conduction band electrons (b) rapidly dissociate into harmless products and (c) lead to the formation of 'OH or other radicals which are highly reactive [14]. Although, many Refs. [15–18] are available for the photocatalysed degradation of organic pollutants using peroxodisulphate (PDS) as an oxidant, the literature involving peroxomonosulphate (PMS) as oxidant is limited. Al-Ekabi et al. [14] carried out the photocatalysed degradation

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