Advanced oxidation process-photocatalyzed degradation of a textile dye using titanium dioxide

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ABSTRACT

Visible light-assisted photocatalyzed degradation of a textile dye, acid red 88(AR88) was carried out. The kinetics of disappearance of the dye was followed spectrophotometrically. Effect of various experimental parameters such as the initial dye concentration, amount of photocatalyst and the addition of oxidants such as peroxomonosulphate (PMS) and peroxodisulphate(PDS) on the photocatalyzed degradation of AR88 was studied. In the presence of oxidants, a significant enhancement in the degradation rate was observed. A detailed mechanism of degradation of the dye in the presence and absence of oxidants has been proposed.
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INTRODUCTION

In recent years, advanced oxidation processes (AOPs) are gaining significant attention in the field of environmental remediation. Among the AOPs, titanium dioxide assisted photocatalysis is widely used for sterilization, disinfection, air and water purification, self-cleaning and antifogging surfaces[1]. Water purification by photocatalysis is a suitable process as it guarantees complete mineralization of pollutants, which other conventional treatment technologies like adsorption, flocculation, biological oxidation etc., fail to assure. Photogenerated $^\bullet$OH radical formed on TiO_2 surface is believed to be the reactive radical species responsible for the photocatalyzed degradation of pollutants[2-4].

Degradation of acid red 88 (AR88) by various methods[5-9] like biological degradation involving Spingomonas sp strain 1CX, adsorption by neutral alumina, photocatalytic oxidation and ozonation were found to be less effective. So, the focus of the present investigation is to apply peroxomonosulphate and peroxodisulphate as oxidants, thereby to enhance the photocatalytic degradation rates of AR88 under visible light irradiation and compare the degradation efficiency of these oxidants.

MATERIALS AND METHODS

Acid red 88, the textile dye with the molecular formula $C_{20}H_{13}N_2O_4SNa$ which absorbs in the visible

region(λ_{max}=506nm), is used as the substrate. TiO_2 photocatalyst (Degussa P25, Germany) having a specific surface area of $57m^2g^{-1}$ is used. Potassium peroxomono sulphate, a triple salt with the composition $2KHSO_5$. $KHSO_4.K_2SO_4$ from Janssen Chimica, Belgium and potassium peroxodisulphate(Merck) were used as received. When preparing the molar solutions of oxone, the fact that 1mol of oxone gives 2mol of peroxomono sulphate was considered as shown by its chemical formula. All the experiments were carried out at natural pH except for the experiments involving pH variation in which case the pH of the medium was adjusted using sodium hydroxide/perchloric acid.

Experimental procedure and analysis

The photoreactor employed in this study is discussed elsewhere[10]. A typical experimental procedure adopted in the present investigation is described below. By dissolving the appropriate amount of the dye in 70ml of double distilled water in a photoreactor vessel, the desired concentration of the dye was maintained. A known amount of the photocatalyst, viz., TiO_2, was then added to the dye solution and prior to irradiation the aqueous suspension was mixed continuously in dark for 45min to ensure adsorption/desorption equilibrium. The concentration of the dye in bulk solution under this condition was treated as the initial concentration for further kinetic analysis of the photodegradation process. During the irradiation, 5ml aliquots were withdrawn at appropriate time intervals and the photocatalyst was removed immediately by centrifugation and filtration through a syringe filter(0.45μm, Sartorius). The decrease in the concentration of the dye was determined spectrophotometrically using the UV-VIS spectrophotometer (Shimadzu, model: UV-1601) by following the absorbance of the clear dye solution at its λ_{max} (506nm).

RESULTS AND DISCUSSION

Preliminary experimental results showed no appreciable change in the concentration of the dye with (a) dye in light (b) dye and catalyst in dark. Irradiation of the dye in the presence of TiO_2 photocatalyst leped to the enhanced decolorisation of the dye confirming the photocatalytic process.

A straight line passing through origin on plotting log OD vs.L irradiation time for various initial concentrations of AR88, confined to first-order kinetics and from the slopes of these plots, the first order rate constants, $k'(s^{-1})$, were calculated.

Effect of photocatalyst amount

Experiments were carried out with various amounts of catalyst powder, C_{TiO_2},(0.286-1.143g/l) at constant C_{AR88}(5×10^{-5}M) and pH. The corresponding k' values obtained under these experimental conditions are shown in figure 1. It can be seen that the rate constant for the degradation of AR88 increased up to 0.857g/l and it decreased on further increase in catalyst amount. The increase in the decolorisation rate in the former case may due to the increase in effective surface area of the catalyst that resulted in the decomposition of more number of AR88 molecules. However, decrease of rate constant above 0.857g/l may be attributed to the scattering of light on TiO_2 particles[11,12]. Hence, an optimum titanium dioxide amount of 0.857g/l was used for all studies.
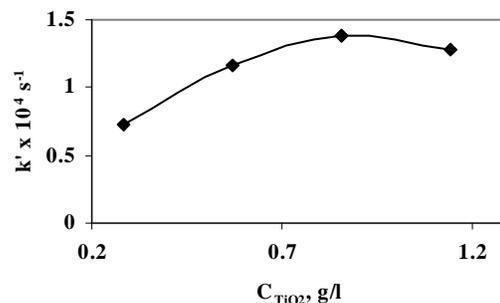
Figure 1: Effect of titanium dioxide amount on the degradation rate of acid red 88; C_{AR88} = 5×10^{-5}M
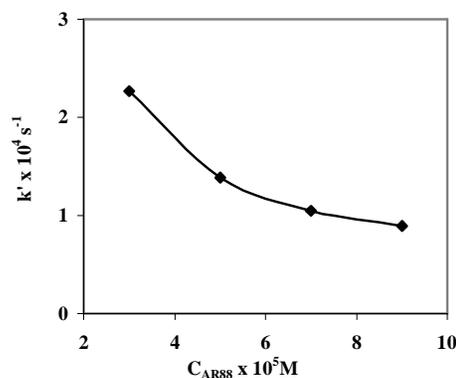
Figure 2 : Rate constants for the photcatalysed degradation of acid red 88 at different dye concentrations. C_{TiO_2}= 0.857g/l

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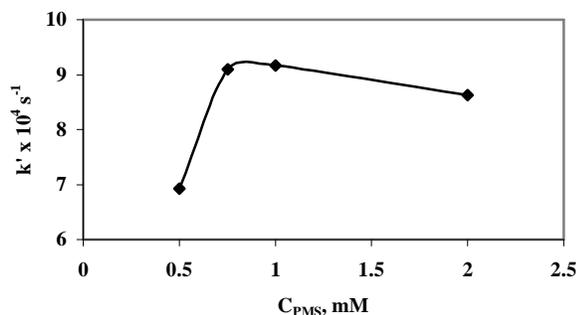
Figure 3 : Effect of C_{PMS} on the degradation rate of acid red 88; C_{AR88}= 5×10⁻⁵M; C_{TiO2}=0.857g/l
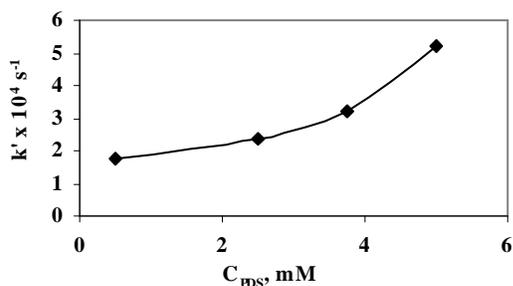
Figure 4 : Effect of C_{PDS} on the degradation rate of acid red 88; C_{AR88}= 5×10⁻⁵M; C_{TiO2}= 0.857g/l

Effect of initial concentrations of AR88

Photocatalytic experiments were carried out at various initial concentrations of AR88($3×10^{-5}$–$9×10^{-5}$M) and at constant C_{TiO2}(0.857g/l) at natural pH(~6.2). The plot of rate constant (k') vs.C_{AR88} for various initial concentrations of acid red 88 is shown in figure 2. These results show that the rate constants decreased with increase in the initial dye concentrations and this trend can be explained by considering the formation of hydroxyl radicals on the TiO_2 surface. As the dye concentration increases, the formation of $^{\bullet}OH$ from TiO_2 surface decreased since it is the dye that absorbs the entering photon than the photocatalyst and in low dye concentration, the reverse effect was observed[13-15]. Hence, the number of hydroxyl radicals formed on the TiO_2 surface determines the decolorisation rate of the dye.

Effect of pH

Semiconductors show different surface properties with different pH. Since the heterogeneous photocatalysis is a surface phenomenon, study of the effect of pH of the reaction medium is quite essential to know

optimum pH at which highest degradation of the dye is possible. By maintaining other experimental parameters constant (C_{AR88} = $5×10^{-5}$M and C_{TiO2}=0.857g/l), the pH of the dye solution was varied between 3.0 and 11.0. We obtained a similar trend that was reported by Saquib and co-workers[7]. At pH=1.5, the dye was completely adsorbed on the photocatalyst surface and prevents the photocatalytic degradation process[16].

Variation of PMS

PMS is a powerful oxidising agent(E°=1.84V)[17] similar to peroxodisulphate and undergoes radiolytic and photolytic reactions[18,19]. In order to understand the effect of PMS on the photocatalytic degradation of acid red 88, the concentration of PMS (C_{PMS}) was varied from 0.5 to 2.0mM, keeping the concentration of the dye($5×10^{-5}$M) and amount of TiO_2 (0.857g/l) constant. The plot of k' vs.C_{PMS} for the addition of various concentrations of peroxomonosulphate is shown in figure 3. It can be seen that the rate constant increased with increase in C_{PMS} upto 0.75mM and attained a plateau on further increase in C_{PMS} to 1.0mM and then decreased for added concentration to 2.0mM C_{PMS}. The increase of dye degradation 0.75mM is due to the increased formation of $^{\bullet}OH$ and $SO_4^{\bullet-}$ radicals that attacks the dye effectively. The decrease of k' values above 1.0mM might be due to the quenching reaction (Eqn. 1) of $^{\bullet}OH$ or $SO_4^{\bullet-}$ by peroxomonosulphate itself which results in the formation of less reactive $SO_5^{\bullet-}$.

$$HSO_5^- + {}^{\bullet}OH \ or \ SO_4^{\bullet-} \longrightarrow SO_5^{\bullet-} + OH^- \ or \ SO_4^{2-} + H^+ \ (1)$$
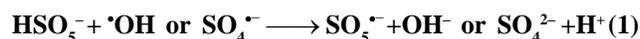
Variation of PDS

Peroxodisulphate ($S_2O_8^{2-}$), which can be decomposed to SO_4^{2-} by UV light ($\lambda \leq 250$ nm)[20-24] and by e^-_{aq} [25], was found to undergo light induced photocatalytic decomposition in presence of TiO_2 and ZnO powders with concomitant oxygen evolution.

The effect of PDS on the photocatalytic degradation of the dye was studied at various concentrations of PDS, C_{PDS},(0.5–5.0mM) keeping C_{AR88}($5×10^{-5}$M) and amount of TiO_2 constant. It is observed that the rate constant increases with increase in C_{PDS}(Figure 4). It is also noted that the rate of mineralization of the dye was less than that in the presence of PMS, for all the variation in C_{PDS}.

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The mechanism of mineralization of the dye by PMS may be given as follows:

$$HOOSO_3^- + e^-_{CB} \begin{cases} SO_4^{\bullet-} + OH^- \\ SO_4^{2-} + OH^{\bullet} \end{cases} \quad (2)$$

$$HOOSO_3^- + h^+_{VB} \xrightarrow{H_2O} SO_5^{\bullet-} + H^+ \quad (3)$$

$$2(SO_3^{\bullet-}) \rightarrow 2HSO_4^- + O_2 \quad (4)$$
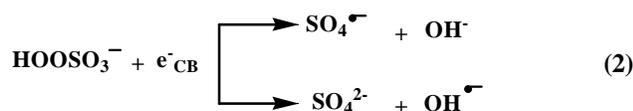
The mechanism involving $S_2O_8^{2-}$ for the mineralization of the dye is:

$$S_2O_8^{2-} + e^-_{CB} \longrightarrow SO_4^{2-} + SO_4^{\bullet-} \quad (5)$$

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