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Kinetics of degradation of acid red 88 in the presence of Co^{2+}-ion/peroxomonosulphate reagent

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ABSTRACT

Visible light-assisted photo-Fenton-like oxidation of a mono-azo textile dye, acid red 88 (AR88), has been carried out in the presence of Co^{2+} as the catalyst and peroxomonosulphate (PMS) as the oxidant. Decolorization of AR88 in the Co^{2+}/PMS system was observed to follow zero-order kinetics with respect to the dye. It was also found that the decolorization of AR88 increased as the concentration of cobalt ions was increased. The rate of abatement of the acid red 88 was found to be independent of the concentrations of dye and oxidant (PMS). Mineralization studies were also carried out by monitoring the reduction in total organic carbon (TOC) content during the course of the reaction and a suitable mechanism has been proposed.

1. Introduction

Contamination of soil and groundwater, due to discharges of industrial wastewaters into the ecosystem, leads to a serious health and environmental problems. Recently, the advanced oxidation processes (AOPs) have attracted much attention in the area of wastewater treatment and other environmental applications [1–3]. Advanced oxidation technologies involve the generation of highly reactive radical species by several processes that include photocatalysis using semiconductors, photo-Fenton reaction ($h\nu/Fe^{2+}/H_2O_2$), ozonation, and UV photolysis of oxidants such as hydrogen peroxide and persulphate [4–10].

Fenton's reagent is a mixture of hydrogen peroxide and ferrous ions that produces $^{\bullet}OH$ radicals. However, it requires acidic pH (3.0) and is reported to be slow and of poor mineralization (less than 60%). In order to overcome the limitations of the Fenton's reagent and to find suitable oxidation processes, several attempts were made and those modified Fenton reactions are called Fenton-like reactions. Recent studies by Fernandez et al. [11] showed that the use of Co^{2+}-ions in combination with peroxomonosulphate in homogeneous medium led to the generation of sulphate radicals which had greater efficiencies than and several operational advantages over the conventional Fenton's reagent. It was also supported from the experimental results carried out to find the favorable metal(s) for the decomposition of potassium peroxomonosulphate ($KHSO_5$) by Ag(I), Ce(III), Co(II), Fe(II), Fe(III), Mn(II), Ni(II), Ru(III) and V(III) [12]. The results showed that cobalt(II) was the best catalyst for the activation of peroxomonosulphate due to its oxidation potential (1.82 eV) being slightly higher than that of the couple Co^{3+}/Co^{2+} (1.80 eV) which drives the reaction to Co^{3+} from the initial Co^{2+}-ion upon PMS addition in solution [13]. The potential applicability of Co^{2+}/PMS reagent either in homogeneous [13,14] or heterogeneous form [15,16] for the pollutant degradation is also reported recently.

Some of the advantages of using Co^{2+}/PMS reagent for the photocatalytic degradation organic pollutants in industrial wastewaters are:

(a) Co^{2+}/PMS reagent can be applied over a wide range of pH, which is evidenced from the Co^{2+}/PMS catalyzed degradation of 2,4-dichlorophenol in the pH range 2.0–8.0 [17]. While Fenton's reagent has failed to exhibit its catalytic activity when the pH exceeded 3.0, Co^{2+}/PMS reagent showed higher efficiency at neutral pH, which is a significant advantage since the pH of most of the contaminated natural waters falls in the range of 6.0–8.0.
(b) Co^{2+}/PMS reagent shows higher mineralization of pollutants; >90% mineralization was reported for the mineralization of Orange II [13] and 2,4-dichlorophenol [17].

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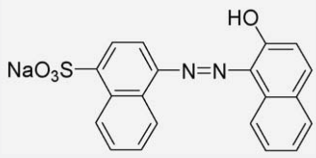
Table 1
Chemical structure and absorption maximum of acid red 88.

Dye	Chemical structure	λ_{max} (nm)
Acid red 88 (C.I. 15620)		505

(c) Co^{2+}/PMS reagent is cost-effective as it avoids the costs due to post-neutralization and sludge treatment and it is operative at low metal concentrations.

In the present investigation the kinetics of decolorization of acid red 88 in the presence of Co^{2+}/PMS reagent is dealt with in detail. The factors influencing the mineralization of AR88 are also studied.

2. Experimental

2.1. Materials

Acid red 88, $C_{20}H_{13}N_2O_4SNa$ (Table 1), a textile dye that absorbs in the visible region (λ_{max} = 506 nm), was a gift from Atul Ltd, India. Co^{2+}-ion solution was prepared from analytical grade samples of $CoSO_4 \cdot 7H_2O$ (E-Merck). Oxone, the commercial name of potassium peroxomonosulphate, is a triple salt with the composition $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ from Janssen Chimica (Belgium); it was used as received. When preparing the molar solutions, we took the fact that 1 mol of oxone gives 2 mol of peroxomonosulphate as shown by its chemical formula. Sodium nitrite (E-Merck, India) was used as the quenching agent for both sulphate and hydroxyl radicals. Unless otherwise specified, all reagents were of analytical grade and the solutions were prepared using double distilled water.

2.2. Dark decolorization studies

Since the decolorization under light irradiation is very fast, we could not measure it in the present investigation. The decolorization of the dye in the dark was analyzed using the 'kinetics mode' available in the Shimadzu UV–vis spectrophotometer (UV 1601). All dark experiments were carried out in a quartz cuvette (5 ml capacity) provided along with the spectrophotometer. The desired concentrations of all the solutions were made up for 3 ml and the order followed in mixing the additives was as follows: dye, cobalt(II)-ion and oxone.

2.3. Photocatalytic reactor and light source for photomineralization studies

A 100 ml capacity borosilicate glass with an opening at the top to facilitate periodical removal of the sample was used as the photochemical reactor. Light irradiation was carried out by means of a solar box designed in our laboratory which consists of three 250 W tungsten–halogen lamps (Philips, India) inside a rectangular box fitted with two exhaust fans to considerably lower the temperature within the solar box during irradiation. The short wavelength radiations ($\lambda < 310$ nm) were removed by the walls of the reaction vessel.

2.4. Kinetic studies

The treatment efficiency was measured from the plot of concentration of the dye (which is calculated from the absorbance) vs. time. The straight-line obtained in the concentration of the dye (C_{AR88}) vs. time plot suggested that the decolorization of AR88 follows zero-order kinetics with respect to the dye.

$$C = k'_0 t + C_0 \qquad (1)$$

where C_0 and C are the initial dye concentration and the concentration of the dye at any time 't' respectively. In this paper, the term 'C' is represented as C_{AR88}. k'_0 is the pseudo zero-order rate constant which can be calculated from the C_{AR88} vs. time plot.

3. Results and discussion

3.1. Dark decolorization studies

The following preliminary experiments were performed to check the feasibility of the catalytic degradation of the dye using Co^{2+}/PMS reagent, (i) AR88 + Co^{2+}, (ii) AR88 + PMS, (iii) AR88 + Co^{2+} + PMS and the results are shown in Fig. 1. It was clearly seen that no appreciable dye decolorization was observed when either Co^{2+}-ion or PMS was added alone whereas a faster and nearly complete decolorization was obtained within 8 min when Co^{2+}-ion in conjunction with PMS was used. That is, the decolorization of the dye was observed only after the conjunction of Co^{2+}-ion with PMS, which clearly proved the efficiency of the Co^{2+}/PMS reagent taken in the present investigation.

It was also observed that there is no change in the absorption spectrum of the dye during the addition of Co^{2+}-ion into the dye solution which ruled out the possibility of any complex formation between the Co^{2+}-ion with AR88.

3.1.1. Effect of concentration of the dye

Experiments were carried out with various concentrations of the dye, $C_{AR88} = (3–9) \times 10^{-5}$ M keeping the other experimental parameters, viz., C_{PMS} = 5 mM and $C_{Co^{2+}} = 0.025$ mM as constants. Fig. 2 (inset) shows the linear decrease in the concentration of acid red 88 with time for different initial concentrations of acid red 88 used. The obtained dark decolorization rate constant (k'_0) values for the variations in C_{AR88} are also presented in Fig. 2. As expected

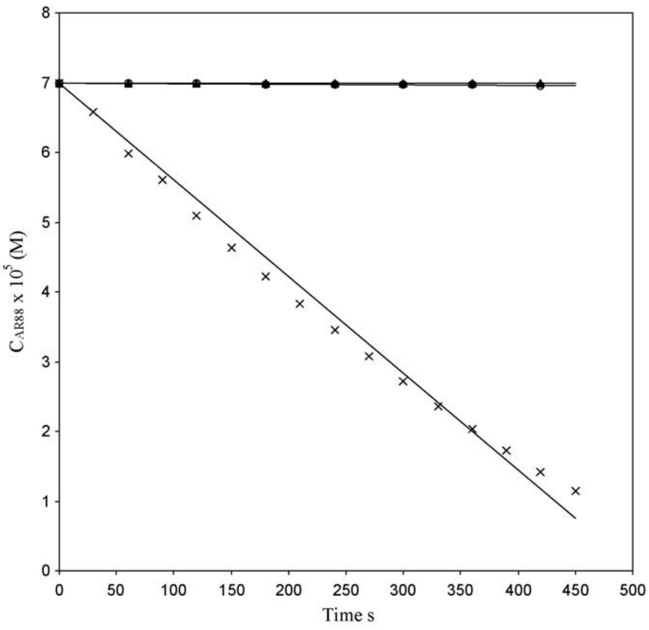


Fig. 1. Preliminary experiments for the decolorization of acid red 88 in the dark using Co^{2+}/PMS reagent.
(○) — AR88 + Co^{2+}-ion; (▲)— AR88 + PMS; (×)— AR88 + Co^{2+}-ion + PMS; $C_{AR88} = 5 \times 10^{-5}$M; $C_{Co^{2+}} = 0.025$ mM; C_{PMS} = 5 mM.