Photodegradation of methyl red by advanced and homogeneous photo-Fenton’s processes: A comparative study and kinetic approach

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The degradation of methyl red (MR), an azo dye, was carried out by the homogeneous photo-Fenton’s process (HPFP) and the advanced photo-Fenton’s process (APFP) using symmetrical peroxides such as hydrogen peroxide and ammonium persulphate (APS) as oxidants. The APFP showed higher efficiency than their homogeneous counterparts even at high dye concentrations due to the faster reduction of Fe²⁺ to Fe³⁺ ions on the iron surface. H₂O₂ proved to be a better oxidant for both the processes. However, APS efficiently inhibited the precipitation of iron oxy hydroxides at higher dosage of iron powder compared to H₂O₂ by providing excess acidity to the reaction medium. The rate constant for the kinetics of decolourisation by various oxidation processes is of the order: Fe²⁺/H₂O₂/UV > Fe²⁺/H₂O₂/dark > Fe²⁺/APS/UV > Fe²⁺/H₂O₂/UV > Fe²⁺/UV > Fe²⁺/APS/dark > Fe²⁺/dark = H₂O₂/UV > Fe²⁺/APS/UV > Fe²⁺/H₂O₂/dark > Fe²⁺/APS/dark = Fe²⁺/UV. The degradation reaction was followed by UV-visible and GC-MS spectroscopic techniques. Based on the intermediates obtained, probable degradation mechanisms have been proposed. It was found that the initial mechanism in the APFP involves the reduction of azo groups to amines while in the case of HPFP it leads to the formation of hydroxylated products due to the oxidation of azo groups.

1. Introduction

Azo dyes contain one or more nitrogen to nitrogen double bond (–N=N–) and they constitute almost 80% of the reactive dyes. Most of the azo dyes are not biodegradable by aerobic treatment processes.¹ However, azo dyes can be decolourised by anaerobic treatment,²³ but this leads to the production of toxic by-products such as aromatic amines.⁴ Advanced oxidation processes involving Fenton’s and photo-Fenton’s process for the degradation of organic dyes are extensively reported in the literature.⁵–¹⁰ The main advantage of photo-Fenton’s process are; reagents are easily available, cheap and cost effective. Further no scattering of light takes place, contact between the pollutants and the catalyst is high since the reaction is homogeneous. The disadvantage of a homogeneous process is the non-reusability of the catalyst which hinders its commercial application. Therefore, many researchers have investigated the applications of iron incorporated zeolites¹¹ and iron minerals¹² as catalytic material for the oxidation of organic pollutants. Lucking et al.¹³ tested the catalytic properties of iron powder, graphite and activated carbon for the oxidation of 4-chlorophenol in aqueous solution with hydrogen peroxide. They concluded that iron powder could be used to replace iron salts as a catalyst to the Fenton’s process. Zero Valent Metallic Iron (ZVMI) powder is an environmental friendly reducing agent which has been widely used for environmental remediation in recent years. In the present study, we compare the efficiency of the homogeneous photo-Fenton process (HPFP) with the Advanced photo-Fenton process (APFP) for the degradation of the azo dye—methyl red (MR). Though H₂O₂ is extensively used in Fenton’s process, few attempts have been made towards the use of peroxo disulfate as an oxidant. In view of this, the main focus is on the utilization of symmetrical peroxides like hydrogen peroxide and ammonium persulphate (APS) as the oxidants in the Fenton’s and photo-Fenton’s process.

2. Experimental section

2.1 Materials and methods

MR, methyl alcohol, APS, ferrous oxalate (FeC₂O₄), iron powder (electrolytic, 300 mesh size, 95% purity) and hydrogen peroxide (50%) were obtained from S. D. Fine Chemicals, Bombay, India and were used as received. The structure of the dye is shown in Scheme 1. The molecular formula of MR is C₁₅H₁₂N₃O₂ and the molecular weight is 269.

2.2 Experimental procedure

All the experiments were performed in a glass reactor of one litre capacity whose surface area is 176 cm². The light source used was a medium pressure mercury vapor lamp of 125 W. The photon flux of the light source was found to be 7.75 mW cm⁻² as determined by ferroxalate actinometry and the wave length emission is in the range of 350–400 nm. The experiments were performed in the presence of atmospheric oxygen using distilled water. In a typical experiment of HPFP, 200 ml of 10 ppm dye solution was taken along with iron ion solution and was exposed directly to the light. The pH of the solution reduces from 6.6 to 2.3 and it was adjusted to 3 using dilute NaOH. In APFP, pH of the dye solution after the addition of iron powder was found to