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Degradation of naphthylazo anionic dye by Fenton and Fenton-like processes: a comparative study with Fast sulphon black-F

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ABSTRACT

Wastewater effluent from industries using dyes and pigments contains high concentration of organics. This paper presents a method for degradation of Fast sulphon black-F (FSB), a naphthylazo anionic dye, using Fenton and Fenton-like reaction systems. The degradation of the FSB dye using a Fenton reagent varied with the molar ratios of the reactants ([Fe(II)]:[H_2O_2]) and pH. Removal of the dye was almost complete within 30 min and a maximum removal of ~99% was achieved with a molar ratio of 1:3.3 at pH 4.0. The degradation of the FSB dye was also carried out by the Fenton-like reaction system. Degradation of the FSB dye in the industrial wastewater sample by the Fenton reaction system was demonstrated by performing Jar tests. Magnetic iron(III) oxide was first prepared, followed by their characterization by X-ray diffraction and scanning electron microscopy techniques. A combination of magnetic iron(III) oxide and H_2O_2 (i.e., a Fenton-like reaction system) produced slower degradation of the dye initially than the Fenton reaction system, but was able to degrade the FSB dye completely within 30 min.

Keywords: Dye; Fenton reagent; Magnetic iron-oxide; Oxidation; Wastewater treatment

1. Introduction

Organic dyes are used extensively in various industries such as production of plastics, textiles, paper and leather tanning [1–3]. The widespread use of dyes and their discharge as collared wastewater results in environmental risk to the aquatic environment [4]. Dyes are generally toxic and non-biodegradable and influence photosynthetic activity and sustainability of life by blocking sunlight [5]. Removal of organic synthetic dyes from industrial wastewater is of utmost importance.

Numerous physical, biological and chemical methods have been reported to degrade dyes in wastewater and industrial effluents [6–9]. Among the chemical processes, advanced oxidation processes (AOPs) have been widely applied for removal, and mineralization of dyes [10–12]. AOPs include Fenton reaction system, electro-Fenton processes, and photocatalyzed oxidations. This process generates reactive oxygen species to cause degradation of dyes. For example, the hydroxyl radicals ($^{\bullet}OH$), produced in AOPs, react rapidly with moieties of dye and ultimately remove target compounds [13,14].

This paper focus on Fenton and Fenton-like reaction systems in which the dominated reactive $^{\bullet}OH$ radicals are usually generated to degrade organic contaminants [11,15–17]. In the current paper, degradation of Fast sulphon black-F (FSB-F), which is a naphthylazo anionic dye (1-hydroxy-8-(2-hydroxy-1-naphthylazo)-2-(4-sulfo-1-naphthylazo)-naphthalene-3,6-disulfonic acid, Fig. 1) was sought using the Fenton reaction systems. Surprisingly, no study was found in the literature that demonstrated removal of FSB-F using Fenton or Fenton-like reactions. In the present study, ferrous sulphate ($FeSO_4.7H_2O$) and iron(III) oxide were used as the source of iron in Fenton and Fenton-like reactions, respectively.

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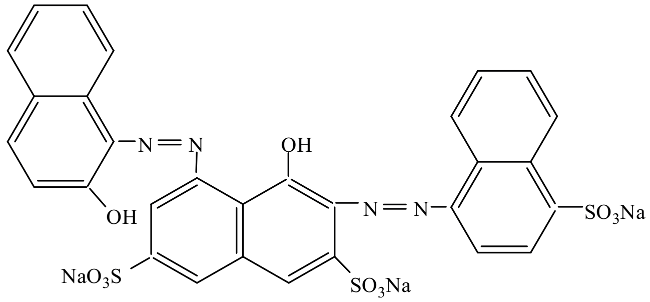

Fig. 1. Structure of Fast Sulphon Black-F.

The objectives of this research were to (i) degrade FSB dye using iron(II) and iron(III) oxide in Fenton reaction systems, (ii) optimize the conditions (molar ratio of Fe(II) and H_2O_2) as well as pH to remove FSB-F dye effectively, and (iii) demonstrate the removal of FSB dye from the plastic industry effluent by applying a Fenton reagent.

2. Experimental

2.1. Reagents

A solid FSB-F dye (C.I. 19185) and H_2O_2 (30% v/v) were purchased from Sigma Aldrich (St. Louis, Missouri, USA) and Merck (Mumbai, India), respectively. Source of Fe(II) was ferrous sulphate heptahydrate ($FeSO_4.7H_2O$), which was obtained from Merck (Mumbai, India). All solutions were prepared in doubly distilled deionised water. A stock solution of H_2O_2 (30%) was standardized with $KMnO_4$ in acidic medium. An industrial wastewater sample was obtained from the washing water of polymer recycling industry (Surya Plastic, Raipur, Chhattisgarh, India). The pH and chemical oxygen demand (COD) of this industrial wastewater sample were 12.0 and 900 mg/L, respectively.

2.2. Synthesis and characterization of iron(III) oxide

Iron(III) oxide was prepared by a co-precipitation method [18]. It was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. XRD measurements were carried out with a PANalyticalX'Pert PRO instrument (CoK_α radiation), which was equipped with an X'Celerator detector and programmable divergence and anti-scatter slits. SEM analysis was performed on the JEOL (JSM-6490LAA, analysis station, USA) that was interface with computer controlled to acquire images.

2.3. Experiments on degradation of dye

A Fenton reaction study was carried by adding H_2O_2 into solution containing dye and $FeSO_4$ in sulphuric acid. The amounts of the reactants in the mixed solution were varied to achieve different molar ratios of Fe(II) and H_2O_2 at constant pH 4.0. The progress of the reaction was monitored by carrying out absorbance measurements of FSB dye every 5 seconds. The absorbance was measured at 510 nm, an absorption maximum of the FSB dye. Removal of the FSB dye from an industrial wastewater sample was performed using the Jar test method. In this method, the pH of the mixed solution was 4. The stirrer speed was 350 rpm for the first 3 min and was then 2,000 rpm for the next 27 min. After the treatment of FSB by the Fenton reaction, sedimentation period was 15 min.

3. Results and discussion

Initially, degradation of the FSB dye was sought by the Fenton reaction system using concentrations of Fe(II) and H_2O_2 at 1.00 mM and 0.33 mM, respectively, ([Fe(II)]:[H_2O_2] = 1:3.3) at pH 4.0. The spectrum of the dye is given in the inset of Fig. 2. Fig. 2 gives the ratio of initial concentration ($[FSB]_0$) and concentration of the dye at different time intervals ($[FSB]_t$). The FSB was degraded completely within 30 min (Fig. 2). The hydroxyl radicals ($^\bullet OH$) which were generated from the Fenton reaction ($Fe^{II} + H_2O_2 \rightarrow Fe^{III} + OH^- + {}^\bullet OH$) caused the decomposition of the dye. Azo dyes have shown high reactivity with $^\bullet OH$, for example, Direct Orange 61 and Acid Orange 7 dyes containing N=N, $-NH_2$, and –OH moieties have second-order rate constants of the order of 10^{10} $M^{-1}s^{-1}$ [19]. Because the FSB dye has similar moieties (see Fig. 1), $^\bullet OH$ radicals were able to degrade the FSB dye.

Next, a Fenton-like reaction was used to determine the extent of FSB dye degradation by this method. Fe(III) oxide in these experiments was first characterized by surface techniques (Fig. 3). The XRD technique gave a scattering peak of iron(III) oxide. Fig. 3(a) suggests the prepared iron oxide was in crystalline phase. The SEM image suggests that morphology of iron oxide particles (Fig. 3(b)). In the Fenton-like reaction, the amounts of Fe(III) and H_2O_2 were 7.9 mg/L and 0.33 mM, respectively, at pH 4.0. Decay of the dye under this system is demonstrated in Fig. 2. With this reaction, the initial decay of the dye was slower than the decay by the Fenton reaction (Fig. 2). Significantly, the Fenton-like reaction was also able to degrade the FSB dye almost completely within 30 min (Fig. 2). In the Fenton-like system (Fe^{III} and H_2O_2), the reactive $^\bullet OH$ is not directly produced. This system first generates Fe^{II} ($Fe^{III} + H_2O_2 \rightarrow Fe^{III} + HO_2^\bullet$ and $Fe^{III} + HO_2^\bullet \rightarrow Fe^{2+} + O_2 + H^+$), which subsequently reacts with H_2O_2 to yield $^\bullet OH$ [1,20,21]. The delayed formation of the

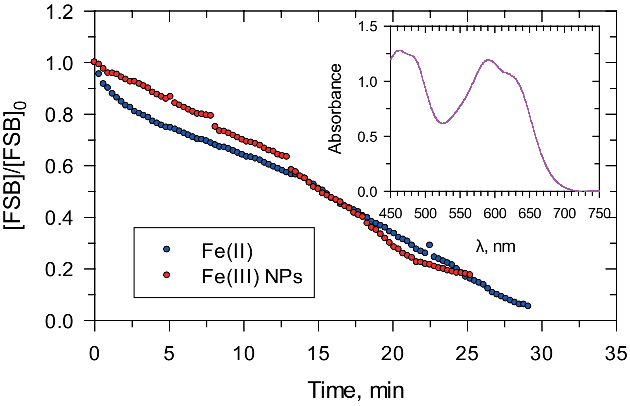

Fig. 2. Degradation of FSB-F: (a) Fenton reaction [Fe^{2+}] = 1.00 mM, [H_2O_2] = 0.33 mM, pH = 4; (b) Fenton-like reaction using iron oxide: [Fe^{3+}] = 1.00 mM, [H_2O_2] = 0.33 mM, pH 4.0. Inset: Spectra of FSB-F at different times during the Fenton reaction.

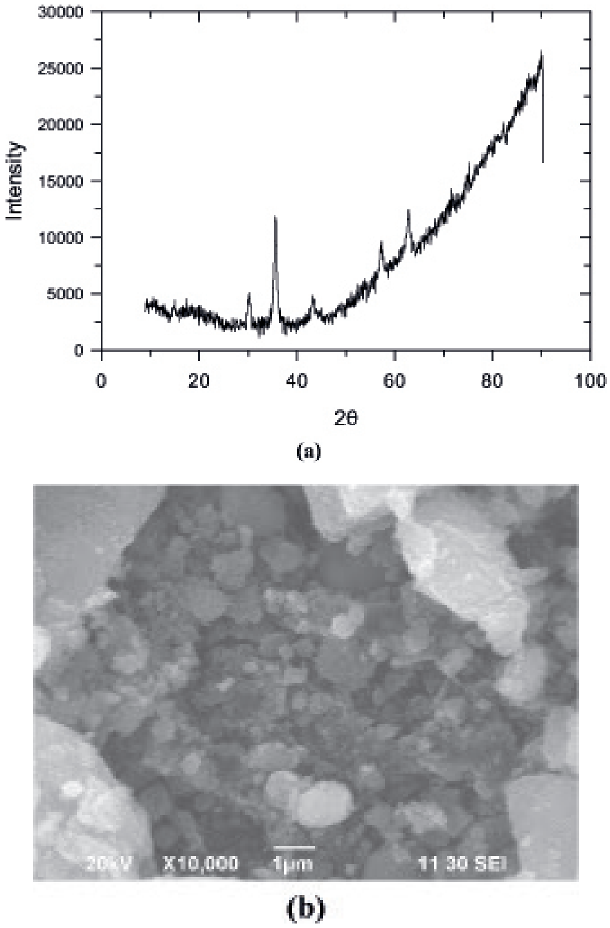

Fig. 3. Characterization of iron(III) oxide: (a) X-ray diffraction spectra and (b) scanning electron microscopy (SEM) image.

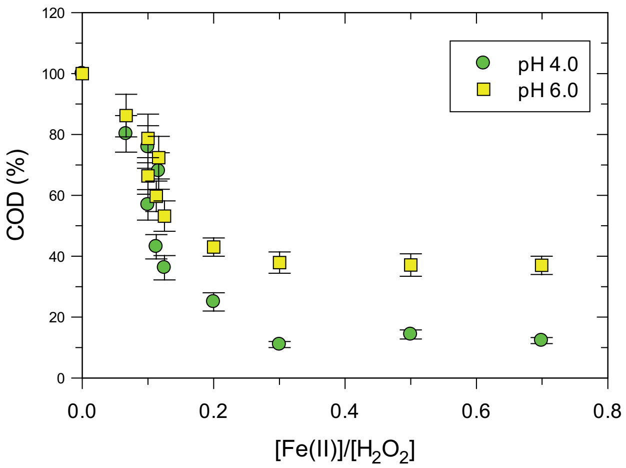

Fig. 4. Decrease in chemical oxygen demand (COD) as a function of the molar ratios of Fe^{2+} to H_2O_2 at pH 4.0 and 6.0 during the oxidation by Fenton reaction system.

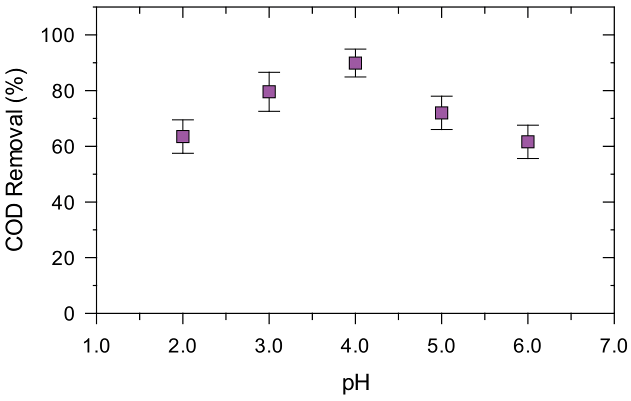

Fig. 5. Chemical oxygen demand (COD) removal (%) at different pH value during the Fenton reagent: [Fe(II)] = 1.0 mM, $[H_2O_2]$ = 0.33 mM.

$^{\bullet}$OH radicals may result in the initially sluggish degradation of the FSB dye in the Fenton-like reaction compared with the Fenton reaction (Fig. 2).

In next set of experiments, the conditions of the Fenton reaction system were optimized in order to achieve maximum removal of the FSB dye. The molar ratios of Fe(II) to H_2O_2 were changed by varying the concentration of H_2O_2 from 0.04 mM to 0.7 mM, while keeping the Fe(II) concentration at 1.0 mM. The removal of dye was examined by determining values of COD and the study was carried out at pH 4.0 and 6.0. The results are shown in Fig. 4. Initially, a growth in the ratio of the reactants increased the degradation of the dye and no further rising in removal was found at the molar ratio of $[Fe(II)]/[H_2O_2] \geq 3.3$. The maximum removals were ~90% and ~62 % at pH 4.0 and pH 6.0, respectively (Fig. 4). The enhanced removal efficiency at lower pH was not surprising because the Fenton reaction is known to have high efficiency under acidic conditions (~pH 3-4), which produce $^{\bullet}$OH efficiently [15,22].

The optimum pH for removing FSB dye was also investigated by varying the pH of the reaction using a molar ratio of 1.0:3.3 mM ($[Fe(II)]:[H_2O_2]$). Again, this study was performed by carrying out COD measurements, and the results are shown in Fig. 5. The maximum COD removal was ~90% at pH 4.0. It appears that the remaining small organic molecules (e.g., aliphatic acids), yielded from the decomposition of the dye, contributed to the residual COD after the 30-min treatment using the Fenton reaction process. Previous studies using Fenton reactions have also given similar results in which simple organic acids were not consumed efficiently by the $^{\bullet}$OH radicals efficiently [11].

Finally, a test was conducted to assess the removal of the FSB dye from an industrial wastewater sample using a reaction ratio of 1.0:3.3 mM ($[Fe(II)]:[H_2O_2]$) at pH 4.0. The water quality parameters of the industrial wastewater are given in Table 1. The results shown in Fig. 6, clearly demonstrated the fading of the dye colour of the dye with time. The final colour of the reaction solution had almost no traces of dye colour. The yellowish colour of the final solution was due to the Fe(III) generated by the Fenton reaction.

Table 1
Characteristics of industrial wastewater

Parameters	Unit	
pH	—	12.0
Conductivity	μS/m	9,230
TDS	ppm	6,160
Temperature	°C	30
COD	mg/L	900
BOD	mg/L	36
DO	mg/L	9.2
Turbidity	NTU	110

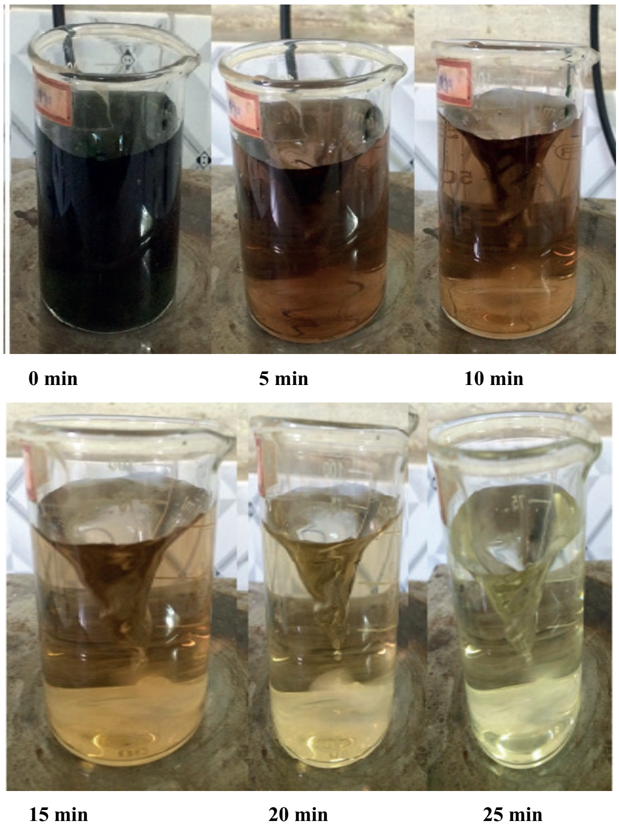

Fig. 6. Degradation of dye during the Jar test Fenton reaction system: $[Fe^{3+}] = 1.00$ mM, $[H_2O_2] = 0.33$ mM; pH = 4.

4. Conclusion

Both the Fenton reaction and the Fenton-like reactions were able to degrade the FSB dye. The ratio of the reactants and the pH were important parameters to achieve effective removal of the dye by the Fenton reaction system. The Fenton reaction creates Fe(III) sludge, which requires disposal. As such, the application of the Fenton-like system using iron(III) oxide may be preferable because used iron(III) oxide can be filtered and recycled. Magnetic separation of iron(III) oxide nanoparticles is another possibility. This will allow reusing the iron(III) oxide. Removal of the studied azo dye from the industrial wastewater was clearly seen using the Fenton reaction.

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