



Photo degradation of Methyl Orange an azo dye by Advanced Fenton Process using zero valent metallic iron: Influence of various reaction parameters and its degradation mechanism

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ARTICLE INFO

Article history:

Received 3 May 2008

Received in revised form 29 July 2008

Accepted 9 August 2008

Available online 15 August 2008

Keywords:

Photo Fenton process

Fenton process

Zero valent iron powder

Methyl Orange

ABSTRACT

Advanced Fenton process (AFP) using zero valent metallic iron (ZVMI) is studied as a potential technique to degrade the azo dye in the aqueous medium. The influence of various reaction parameters like effect of iron dosage, concentration of H_2O_2 /ammonium per sulfate (APS), initial dye concentration, effect of pH and the influence of radical scavenger are studied and optimum conditions are reported. The degradation rate decreased at higher iron dosages and also at higher oxidant concentrations due to the surface precipitation which deactivates the iron surface. The rate constant for the processes Fe^0/UV and $\text{Fe}^0/\text{APS}/\text{UV}$ is twice compared to their respective Fe^0/dark and $\text{Fe}^0/\text{APS}/\text{dark}$ processes. The rate constant for $\text{Fe}^0/\text{H}_2\text{O}_2/\text{UV}$ process is four times higher than $\text{Fe}^0/\text{H}_2\text{O}_2/\text{dark}$ process. The increase in the efficiency of Fe^0/UV process is attributed to the cleavage of stable iron complexes which produces Fe^{2+} ions that participates in cyclic Fenton mechanism for the generation of hydroxyl radicals. The increase in the efficiency of $\text{Fe}^0/\text{APS}/\text{UV}$ or H_2O_2 compared to dark process is due to continuous generation of hydroxyl radicals and also due to the frequent photo reduction of Fe^{3+} ions to Fe^{2+} ions. Though H_2O_2 is a better oxidant than APS in all respects, but it is more susceptible to deactivation by hydroxyl radical scavengers. The decrease in the rate constant in the presence of hydroxyl radical scavenger is more for H_2O_2 than APS. Iron powder retains its recycling efficiency better in the presence of H_2O_2 than APS. The decrease in the degradation rate in the presence of APS as an oxidant is due to the fact that generation of free radicals on iron surface is slower compared to H_2O_2 . Also, the excess acidity provided by APS retards the degradation rate as excess H^+ ions acts as hydroxyl radical scavenger. The degradation of Methyl Orange (MO) using Fe^0 is an acid driven process shows higher efficiency at pH 3. The efficiency of various processes for the de colorization of MO dye is of the following order: $\text{Fe}^0/\text{H}_2\text{O}_2/\text{UV} > \text{Fe}^0/\text{H}_2\text{O}_2/\text{dark} > \text{Fe}^0/\text{APS}/\text{UV} > \text{Fe}^0/\text{UV} > \text{Fe}^0/\text{APS}/\text{dark} > \text{H}_2\text{O}_2/\text{UV} \approx \text{Fe}^0/\text{dark} > \text{APS}/\text{UV}$. Dye resisted to degradation in the presence of oxidizing agent in dark. The degradation process was followed by UV-vis and GC-MS spectroscopic techniques. Based on the intermediates obtained probable degradation mechanism has been proposed. The result suggests that complete degradation of the dye was achieved in the presence of oxidizing agent when the system was amended with iron powder under UV light illumination. The concentration of Fe^{2+} ions leached at the end of the optimized degradation experiment is found to be 2.78×10^{-3} M. With optimization, the degradation using Fe^0 can be effective way to treat azo dyes in aqueous solution.

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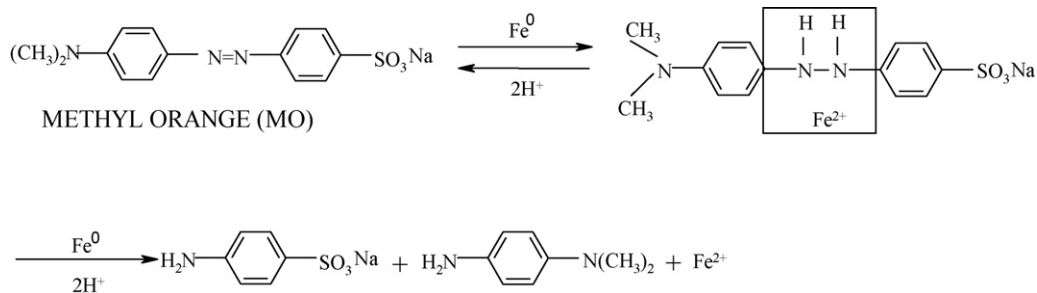
1. Introduction

The presence of low concentration of synthetic dyes is a major obstacle to the use and reuse of water streams. Colorants are widely used in different branches of industry, i.e. textile, painting, leather, printing, photography, etc. Significant losses of these dyes can occur

during the dyeing and finishing operations and are released as textile effluents. Dyes in waste water create aesthetic problems, limit the possible use of the water and reduce the efficacy of microbial waste water treatment because they may be toxic to micro organisms. Dyes absorb and scatter sunlight which is essential for algae growth. These effluents are threat to the ecosystems due to its toxicity and resistance to destruction by biological treatment methods. Particularly azo dyes which contain one or more nitrogen to nitrogen double bonds ($-\text{N}=\text{N}-$) constitutes a significant portion that are widely used in industries today. The products of the degradation

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Scheme 1.

can be mutagenic and carcinogenic causing long-term health concerns. Traditional methods such as carbon adsorption, flocculation, coagulation, etc., mainly transfer the contaminants from waste water to secondary waste. Azo dyes are not biodegradable by aerobic treatment processes [1]. Under anaerobic condition they are reduced to potentially carcinogenic aromatic amines [2,3]. In recent years, Advanced Oxidation Processes (AOPs) have drawn considerable attention for the destruction of these dyes. AOPs are based on the generation of highly reactive hydroxyl radicals which have one unpaired electron and are very strong oxidizing agent. They are non-selective, extreme potent oxidant only second to elemental fluorine. Fenton's oxidation generates hydroxyl radicals from Fenton's reagent. In this paper, degradation of azo dye using heterogeneous photo Fenton process is investigated. Though homogeneous photo Fenton process is efficient in removing these azo dyes [4–9], the removal of sludge containing iron ions at the end of the treatment is costly and requires large amount of chemicals and man power. The non-reusability of catalyst indeed hinders its further application. A great deal of interest has been developed in the degradation of these azo dyes over the prospects of new treatment strategies by zero valent metallic iron (ZVMI). Therefore many researchers have investigated the applications of iron incorporated zeolites (sodium-alumino silicates) [10], ferrihydrite, crystalline goethite [11] and semi crystalline Iron oxide [12] 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 reaction. Zero valent metallic iron powder is an environmental friendly reducing agent which has been widely studied for environmental remediation in recent years [14–26]. Among the various pollutants, azo dyes are easier for the degradation using iron powder. The initial degradation mechanism of azo dyes on the surface of ZVMI is illustrated in Scheme 1. The disadvantage of using iron metal is that: (i) it requires acidic conditions; (ii) higher dosage of iron powder generates significant levels of Fe^{2+} ions which may cause secondary pollution; (iii) surface precipitation over the course of extended operation. To overcome these drawbacks the present research work aims at the use of low iron dosage and the experiments were designed for the complete mineralization of Methyl Orange (MO) dye in the desired time and the surface precipitation of the catalyst is thus avoided. The objective of the present research is to investigate the effectiveness of Fenton's oxidation of the dye with Fe^0 as a source for the production of Fe^{2+} ions as catalyst. Effective operating conditions and recycling efficiency of iron powder are reported. The present research work focuses mainly on the effect of oxidants concentration, catalyst loading, effect of pH, influence of hydroxyl radical scavenger and the initial concentration of the dye on the degradation. With the usage of iron powder incorporation of various inorganic anions (like sulfate, chloride, nitrate, etc.) is avoided and further concentration of Fe^{2+} ions after the photo degradation process is lowered.

2. Experimental

2.1. Materials and methods

H_2O_2 (50%) and CH_3OH were supplied from Merck. Methyl Orange and ammonium per sulfate (APS) is obtained from BDH and used without further purifications. The other synonymous names for MO are *p*-(*p*-dimethyl amino phenyl azo)-benzene sulfonate of Sodium, Helanthine B, Orange III, gold orange, tropacoline D. The chemical formula is $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{NNC}_6\text{H}_4\text{SO}_3\text{Na}$ and the formula weight is 327 and has a λ_{max} of 460–480 nm. It is an orange yellow powder soluble in water and insoluble in alcohol. The MO dye is red colored in acid medium and yellow orange colored in the alkaline medium. The structure of the MO is shown in Scheme 1. Iron powder (electrolytic, 300 mesh size and nominal purity is 95.0%) was supplied from SD Fine CHEM, Mumbai and was used without any further treatment.

2.1.1. Experimental procedure

Fenton's experiments are conducted using the following different reaction conditions (i) variation of oxidants concentration (H_2O_2 from 2 ppm to 20 ppm and APS from 10 ppm to 50 ppm), (ii) Variation of iron dosage from 10 mg to 200 mg, (iii) Variation of pH from 2.0 to 9.2. These experiments were planned in order to determine optimum condition for the dye degradation. Artificial light source of 125 W medium pressure mercury vapor lamp with the photon flux of 7.75 mW/cm^2 (as determined by ferrioxalate actinometry) whose wavelength peaks around 350–400 nm is used. Pyrex glass reactor of size (150 mm × 75 mm) with 1 l capacity whose surface area is 176 cm^2 is directly exposed to the light source in open air condition. The entire photo reactor system is maintained at 25°C using thermostat (Fig. 1). The pH variation of the solution is

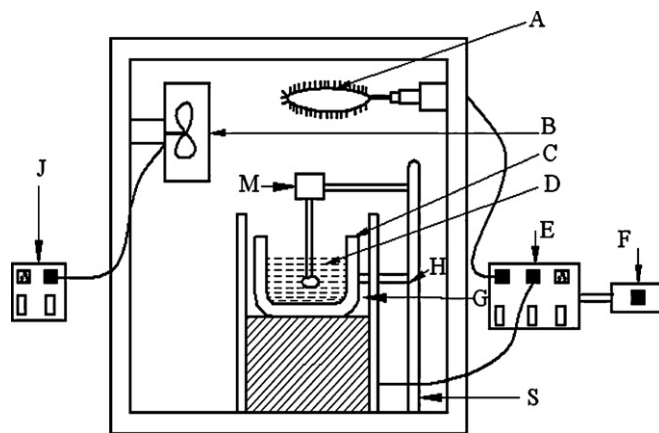


Fig. 1. Schematic diagram of the experimental set-up: (A) mercury vapor lamp; (B) fan; (C) Pyrex glass reactor; (D) experimental solution; (E) stabilizer; (F and J) switch box; (G) thermostat; (H) clamp; (M) motor; (S) stand.

adjusted either by adding dilute NaOH or dilute H₂SO₄. In a typical experiment, 200 ml of 10 ppm dye solution was used along with desired amount of iron powder. The reaction mixture is stirred in dark for 5 min. The light is focused on the solution at a distance of 29 cm and required amount oxidant is added. Most of the experiments were conducted thrice in identical conditions and difference in the error between consecutive experiments was less than 3%.

2.1.2. Analytical methods

The change in pH of the reaction solution was measured using systronics digital pH meter 335. The solution is taken out from the reactor at desired time intervals and was centrifuged. The centrifugate were analyzed by UV–vis spectroscopy using Shimadzu UV-1700 Pharmaspec UV–vis spectrophotometer. The concentration of the dye was calculated from the standard calibration for the characteristic λ_{max} of MO dye. The centrifugates were extracted into non-aqueous ether medium and were subjected to GC–MS analysis using GC–MS–QP 5000 Shimadzu mass spectrometer to identify the photo products during the course of the reaction.

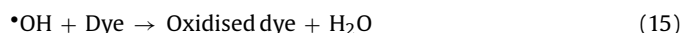
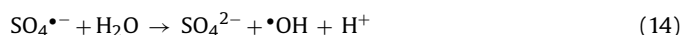
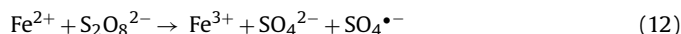
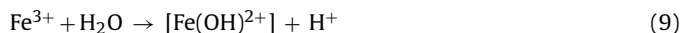
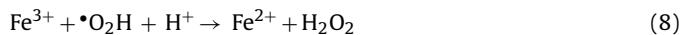
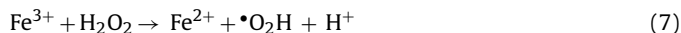
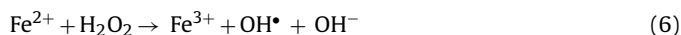
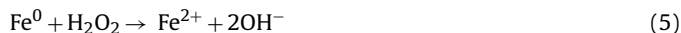
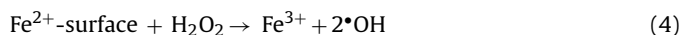
The concentration of Fe²⁺ ions generated on the iron surface at the end of degradation was quantitatively analyzed by a colorimetric method using *o*-phenanthroline as a reagent. The absorbance of Fe(II)-phenanthroline complex was measured at 510 nm. The concentration of photo generated Fe²⁺ ions were estimated by the standard calibration curve.

3. Results and discussions

The classical Fenton process is characterized by the reaction of aqueous Fe(II) ions with H₂O₂ to generate hydroxyl radicals which then degrade recalcitrant organic pollutants. The application of this process is limited by the amount of ferrous ion in the solution and the ability of the system to regenerate ferrous ions. The present research focuses on the generation of hydroxyl radicals that differs from classical Fenton process by taking ZVMI. This application is referred to as Advanced Fenton Process (AFP), which utilizes metallic iron surfaces to generate Fe²⁺ and gives rise to potent Fenton type reactions. The oxidized Fe²⁺ is further oxidized to Fe³⁺ in the presence of oxidizing agents. The reduction of Fe³⁺ ion to Fe²⁺ is faster at the iron surface compared to the homogeneous Fenton process as shown in Eq. (1). These factors attribute the potential application of modified Fenton process [27].



Zero valent iron metal is readily oxidized to Fe²⁺ ion in the presence of oxidants. In the aqueous systems this phenomenon leads to the dissolution of solid which is the primary cause of metal corrosion. The various possible reactions of iron powder with H₂O₂/APS is shown in Eqs. (2)–(15).



3.1. Effect of pH

It was anticipated that changes in pH will influence the degradation of the dye in two ways (i) direct involvement of H⁺ in the reaction at lower pH (ii) mass transport limitations imposed by the precipitation of a passive film on the metal surface at higher pH. Fe⁰ oxidizes to Fe²⁺ in aqueous acidic conditions due to the dissolution at lower pH as shown in Eq. (2). Fe²⁺ present in the solution decomposes H₂O₂/APS to generate hydroxyl and other free radicals as shown in Eqs. (4), (6), (7), (10), (12)–(14). This supports the fact that Fenton process is effective in the acid medium. To investigate the influence of pH on the degradation process, the experiments were conducted at a range of 2.0–9.2 pHs. In the lower acidic condition of pH 2.0 the bands in the visible region disappears completely in 20 min indicating the complete discoloration of the dye. A new peak at 302 nm with high intensity is obtained confirming the formation of stable intermediate which did not disappear even after 30 min of irradiation. It was assigned to amine substituted benzene sulfonic acid. The slower rate of degradation is also due to the excess H⁺ ions present in the solution acting as hydroxyl radical scavenger as shown in Eq. (16) [6,22].



When the pH of the medium is increased to 3.0, the bands in the visible region disappears completely in 15 min of irradiation and only one peak at 198 nm is observed which is attributed to benzene. When the pH of the medium was further increased from 4 to 9.2, the discoloration of the dye could not be achieved even after 1 h of irradiation (Fig. 2). In the pH range of 4–6, substituted amines and benzene was the minor product where as in the higher pH at 9.2 aniline was the major product. At alkaline conditions the rate of mineralization of the dye is low [22]. Moreover at higher pH, the process of hydrolysis of iron ions dominates the other reaction process. This leads to the deposition of precipitated iron

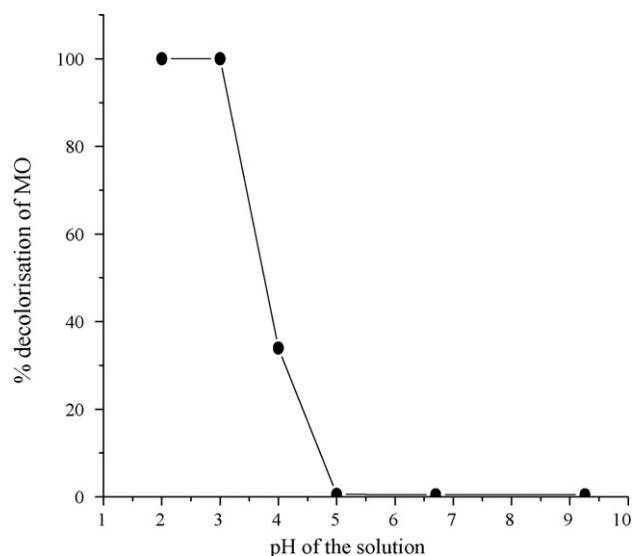


Fig. 2. %Decolorization of MO at different pH (iron dosage = 10 mg, H₂O₂ = 10 ppm and dye concentration = 10 ppm).

hydroxides on Fe⁰ surface which blocks the further electron transfer process between Fe⁰ and MO which further reduces the generation of hydroxyl radicals in the solution. Therefore optimized standard condition for conducting the Advanced photo Fenton's experiments is found be pH 3.

3.1.1. Effect of iron dosage

Increase in the dosage of Fe⁰ from 10 mg to 200 mg has pronounced effect on the efficiency of AFP. The influence of iron dosage on the degradation of MO dye was monitored by maintaining H₂O₂ (10 ppm)/APS (40 ppm) concentration constant. At lower iron dosages of 10–30 mg, rapid discoloration of the dye was achieved with H₂O₂ as oxidant which is implied by the disappearance of λ_{max} band in 15 min. With increase in the iron dosage to 50 mg, the λ_{max} in the visible region still persists even after 30 min of irradiation. On further increase of Fe⁰ dosage up to 200 mg degradation rate decreases drastically. This is due to the inhibition effect shown by the iron ions. These results are in accordance with the classical Fenton reaction where in excess Fe²⁺ ions (in the present case Fe²⁺ is generated by AFP) acts as hydroxyl radical scavenger as shown in Eq. (17) [6,22].



During the course of the reaction it was observed that, at lower iron dosage (10 mg) the reaction solution was almost transparent. With increase in the dosage up to 30 mg, turbidity in the reaction mixture was observed which is due to the precipitation of hydroxides of iron. With further increase of iron dosage from 50 mg to 200 mg the precipitate separated from the solution. This clearly indicates that higher dosage of iron powder is undesirable as the precipitation of excess iron as iron hydroxide takes place. This can be explained by the fact that, at lower iron dosage the final pH of the solution after degradation reached a value of 3.72 which is acidic in nature. With higher dosage of iron final pH of the solution is 5.1 which is less acidic. Under these conditions the precipitation of iron hydroxide takes place. These results were further confirmed by the experiments conducted at pH 5 (with low iron dosage) showing slower degradation rate. This indicates that the modified Fenton process also works better in acidic pH range of 3.0–3.5. Hence the presence of excessive iron powder could be detrimental since the final pH of the system Fe⁰:H₂O₂/Fe⁰:APS could reach higher values thereby decreasing the degradation rate. The concentration of Fe²⁺ ions leached at the end of the optimized degradation experiment is found to be 2.78×10^{-3} M.

3.1.2. Effect of oxidants

The present study investigates the application of H₂O₂ and APS which posses symmetrical peroxide structures and the use of these oxidants in the light induced processes are explored. Effect of oxidants at different concentration is studied. Per sulfate anion is the most powerful oxidant of the per oxygen family of compounds and one of the strongest oxidants used in remediation.



The standard oxidation–reduction potential for the above reaction is 2.1 V compared to 1.8 V for H₂O₂ and 1.4 V for peroxy monosulfate anion (HSO₃⁻). This potential is higher than the redox potential of the permanganate anion (1.7 V), but slightly lower than that of ozone (2.2 V). In addition to direct oxidation per sulfate can be induced to form sulfate radicals, there by providing free radical reaction mechanisms similar to the hydroxyl radical pathways generated by Fenton's chemistry as shown in Eq. (19).

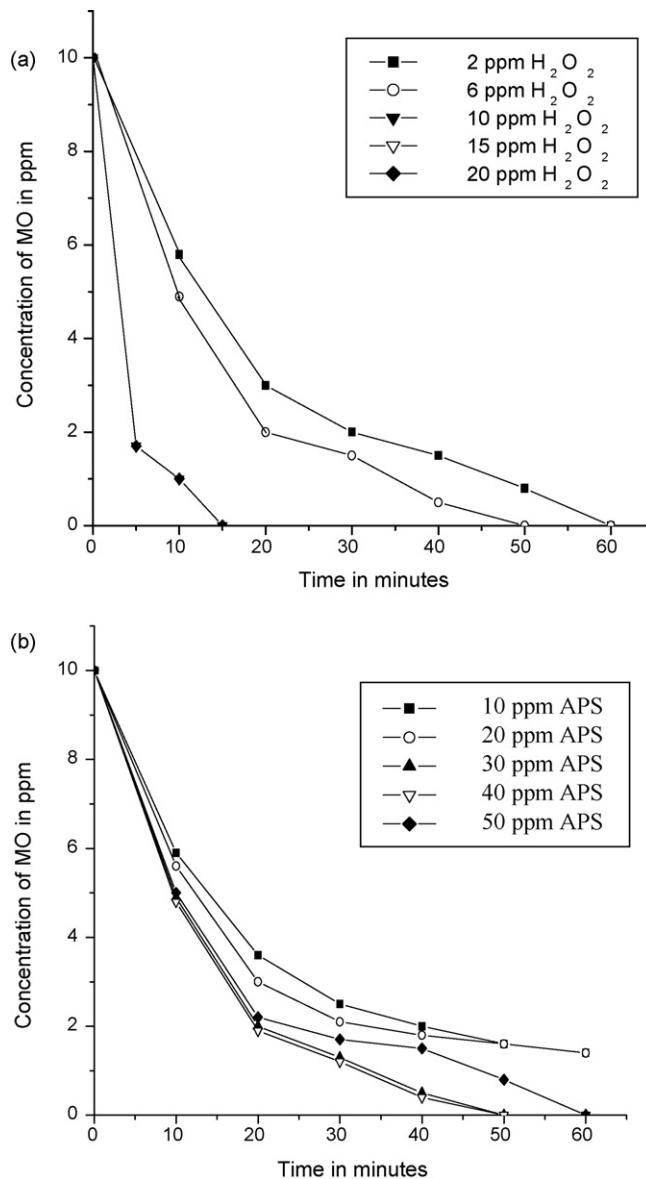
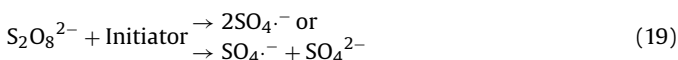


Fig. 3. (a) Effect of concentration of H₂O₂ on the degradation of MO (iron dosage = 10 mg, pH 3 and dye concentration = 10 ppm); (b) effect of concentration of APS on the degradation of MO (iron dosage = 10 mg, pH 3 and dye concentration = 10 ppm).

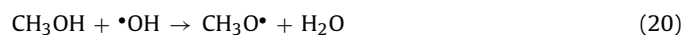
The sulfate radical is one of the strong aqueous oxidizing species with a redox potential of 2.6 V similar to that of hydroxyl radical 2.8 V. In addition to its oxidizing strength, per sulfate and sulfate radicals have several advantages over other oxidant systems. First, it is kinetically fast, second sulfate radical is more stable than the hydroxyl radical and thus capable to transport greater distances in the sub-surface level. These attributes combine to make per sulfate a viable option for the chemical oxidation of broad range of contaminants.

When the concentration of H₂O₂ was varied from 2 ppm to 6 ppm, the λ_{max} in the visible region decreased in its intensity and disappears in 60 min. When the concentration of H₂O₂ was increased from 10 ppm to 20 ppm, the λ_{max} in the visible region disappears in 15 min which results in the discoloration (Fig. 3a). The final pH of the solution after discoloration remains in the range of 3.56–3.67 for all the concentrations of H₂O₂ for 10 mg of Fe⁰ dosage. Similar experiments were carried out using APS as an oxidant in the

concentration range of 10–50 ppm (Fig. 3b). The optimum concentration of APS is found to be 40 ppm. The reaction proceeds at a slower rate for APS in comparison with H_2O_2 which may be due to the difference in the reactivity of APS at the surface of iron powder. Secondly sulfate radical being more stable than hydroxyl radical, its kinetics in attacking the organic molecule is slower compared to hydroxyl radical. Further the excess acidity provided by APS can retard the Fenton process. Hydroxyl radical generation from H_2O_2 is either due to direct photolysis of H_2O_2 or due to interaction with Fe^0 -surface which is a one step process. But in the case of APS the reaction of persulfate radicals with iron powder results in sulfate radicals and subsequent reactions of these radicals with water leads to the formation of hydroxyl radicals which is a two-step process. The kinetics of the later reaction is slow and more over sulfate radicals being more acidic in nature further lowers the pH of the medium. Though the number of free radicals generated is more for APS, their kinetics of attacking the organic molecules is slower compared to hydroxyl radicals.

3.1.3. Role of scavenger on oxidizing agents

Hydroxyl radicals play a significant role in the oxidation of azo dye by photo Fenton process. To investigate the role of hydroxyl radicals, the degradation process was carried out in the presence of hydroxyl radical scavenger like methyl alcohol. Methyl alcohol is capable of deactivating the hydroxyl radicals and its derivatives. Methanol reacts with hydroxyl radical and to a lesser extent with hydrogen radical with second order rate constants $9.7 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$ and $2.6 \times 10^6 \text{ mol}^{-1} \text{ s}^{-1}$, respectively as shown in Eqs. (20)–(21).



Though methanol is able to quench hydroxyl radical but the extent of quenching is different for different oxidizing agents. When the H_2O_2 was used as an oxidizing agent, the rate decreased from $48.0 \times 10^{-3} \text{ min}^{-1}$ to $2.20 \times 10^{-3} \text{ min}^{-1}$ in the presence of methyl alcohol. In the case of APS as an oxidant, the rate of the reaction decreased from $17.5 \times 10^{-3} \text{ min}^{-1}$ to $4.4 \times 10^{-3} \text{ min}^{-1}$. Though the initial step of quenching is same for both the oxidants the rate constant decreased drastically in the case of H_2O_2 compared to APS. The dye degradation is 33% in the case of H_2O_2 as an oxidant and 48% for APS as an oxidant for 1 h of irradiation under the influence of hydroxyl radical scavenger (Fig. 4). The sulfate radical anions produced in the case of APS shows higher efficiency due to the following reasons: (i) abstraction of hydrogen atom from the saturated carbon; (ii) by adding to the unsaturated compounds. (iii) By removing an electron from anions and the neutral molecules. Though hydroxyl radicals are quenched, sulfate/sulfate radicals can mediate the degradation process in the absence of hydroxyl radicals and hence higher efficiency for APS as an oxidant is observed compared to H_2O_2 . Nevertheless it also confirms another important factor that more number of hydroxyl radicals is generated in the case of H_2O_2 compared to APS.

3.1.4. Effect of initial dye concentration:

The degradation efficiency also depends on the initial concentration of the substrate. To study the influence of initial dye concentration on the rate of degradation, the experiments were performed at different initial concentration of the dye by maintaining the other parameters constant. As the initial dye concentration increases, the rate of the degradation decreases. This is due to the non-availability of sufficient number of hydroxyl radicals and also due to the poor penetration of UV light into the intense colored solution [28]. The extent of decrease in the degradation rate varies

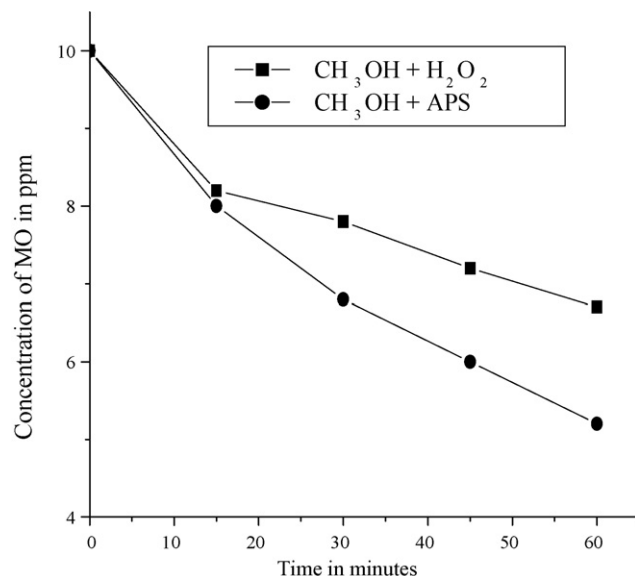


Fig. 4. Effect of hydroxyl radical scavenger on the degradation using H_2O_2 /APS (iron dosage = 10 mg, pH 3, dye concentration = 10 ppm, H_2O_2 = 10 ppm, APS = 40 ppm and CH_3OH = 1 ml).

with the oxidants. When H_2O_2 is used as an oxidant, discoloration of the MO dye completes in 15 min for 10 ppm, 60 min for 15 ppm and only 51% of the dye degraded for 20 ppm in 1 h irradiation period. In the case of APS the discoloration of the dye completes in 45 min for 10 ppm. Where as it is only 73% for 15 ppm and 34% for 20 ppm in 45 min of irradiation (Fig. 5). The calculated rates showed that with increase in the initial dye concentration from 10 ppm to 20 ppm, the rate decreases from $48.0 \times 10^{-3} \text{ min}^{-1}$ to $6.3 \times 10^{-3} \text{ min}^{-1}$ in the case of H_2O_2 . In the case of APS the rate decreases from $17.5 \times 10^{-3} \text{ min}^{-1}$ to $6.2 \times 10^{-3} \text{ min}^{-1}$ for similar concentrations of MO. These results showed that as the initial dye concentration increases the rate decreases drastically for H_2O_2 as an oxidant than for APS. In the case of APS the rate value remains

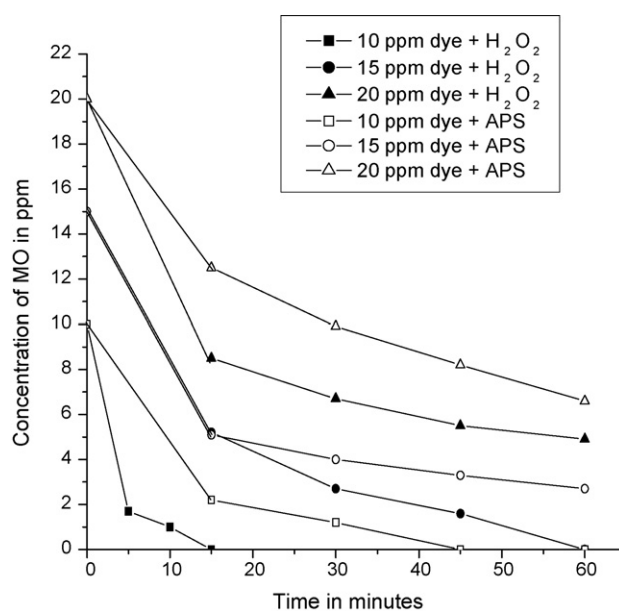


Fig. 5. Effect of different initial concentration of the MO dye in the presence of H_2O_2 /APS (iron dosage = 10 mg, pH 3, dye concentration = 10 ppm, H_2O_2 = 10 ppm and APS = 40 ppm).

constant beyond 10 ppm concentration of MO. From the above results, it can be summarized that for higher dye concentration (>20 ppm), the rate reaches a constant value for both the oxidants. Therefore it is desirable to have lower initial dye concentrations for the effective degradation by AFP.

4. Kinetic studies

The kinetics of de colorization for all the above oxidation processes was summarized and presented in Fig. 6. The dye solution was de colorized up to 23%, 47% and 75% for the Fe⁰/dark, Fe⁰/APS/dark and Fe⁰/H₂O₂/dark process respectively in 15 min. The de colorization in the presence of Fe⁰/dark may be attributed to the formation of iron complexes between iron ions and dye molecules preferably with the chromophore of the MO. The lower efficiency of the dark process can be accounted to the formation of stable iron complexes. In the presence of oxidants the de colorization efficiency is slightly increased even in the dark condition. This can be due to the oxidation of iron powder in acidic condition leading to the formation of Fe²⁺ ions which further reacts with H₂O₂/APS to generate hydroxyl radicals as shown in Eqs. (4), (6), (10) and (14). The higher efficiency of 75% de colorization in 16 min for Fe⁰/H₂O₂/dark can be accounted for its higher reactivity at the iron surface. In the presence of oxidants alone in the dark, dye de colorization is almost negligible. On UV irradiation the de colorization efficiency for the above-mentioned process increased up to 61%, 71% and 100%, respectively. The increase in the efficiency of UV/Fe⁰ process is due to the fact that the iron complex so formed in the dark is destroyed under UV irradiation and the iron ions can be returned to the iron regeneration cycle, which participates actively in the formation of hydroxyl free radicals through photo Fenton process [29]. The generation of hydroxyl radicals via photolysis of H₂O₂ and the degradation of dye molecules through the direct photolysis, additionally contributes to the overall enhancement in the mineralization process. The calculation of apparent first order constant 'k' for the MO degradation by the above mentioned processes is studied for the time period of 16 min (Fig. 7). The calculated rate constant values for UV/H₂O₂ process is 2.8 times higher than UV/APS process. This difference can be attributed to the fact that two hydroxyl radicals can be generated by the cleavage of one molecule of H₂O₂. While in the case of APS hydroxyl radical is

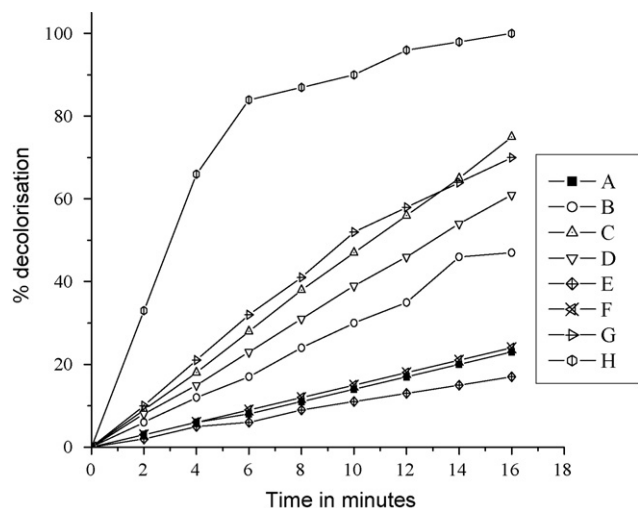


Fig. 6. %Decolorization of MO dye for different oxidation processes. (A) Fe⁰/dark; (B) Fe⁰/APS; (C) Fe⁰/H₂O₂; (D) Fe⁰/UV; (E) UV/APS; (F) UV/H₂O₂; (G) UV/Fe⁰/APS; (H) UV/Fe⁰/H₂O₂ (iron dosage = 10 mg, pH 3, dye concentration = 10 ppm, H₂O₂ = 10 ppm and APS = 40 ppm).

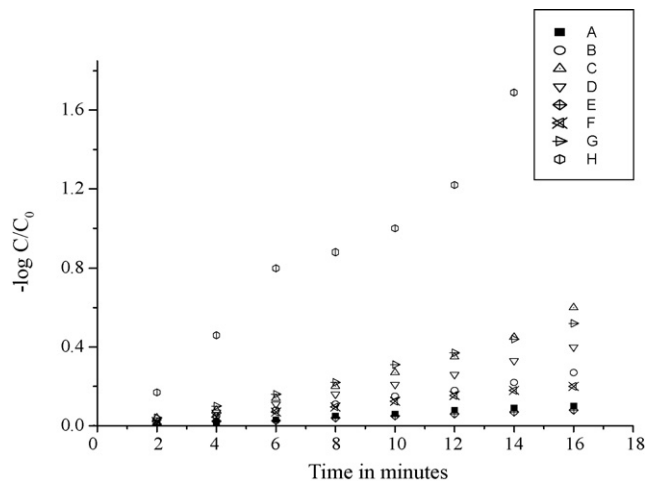


Fig. 7. Plot of negative log C/C₀ versus time for the degradation of MO using various oxidation processes. (A) Fe⁰/dark; (B) Fe⁰/APS; (C) Fe⁰/H₂O₂; (D) Fe⁰/UV; (E) UV/APS; (F) UV/H₂O₂; (G) UV/Fe⁰/APS; (H) UV/Fe⁰/H₂O₂ (iron dosage = 10 mg, pH 3, dye concentration = 10 ppm, H₂O₂ = 10 ppm and APS = 40 ppm).

generated along with a proton as shown in Eq. (14). Since the degradation process is carried out under acidic condition, excess protons so generated slightly lowers the pH. The excess protons produced acts as hydroxyl radical scavenger. Rate constant calculated for Fe⁰/H₂O₂/UV is four times higher than that of Fe⁰/H₂O₂/dark. While rate constant for Fe⁰/APS/UV is twice than that of Fe⁰/APS/dark. The higher efficiency of UV irradiation is mainly due to the photo reduction of Fe³⁺ ions formed by the dissolution of iron powder as shown in Eqs. (7), (8), (10) and (13). Under experimental conditions, iron powder in the acidic medium undergoes oxidation to form Fe²⁺ ions as shown in Eq. (2). These Fe²⁺ ions so formed reacts with oxidants generating hydroxyl radicals and gets oxidized to Fe³⁺. The kinetics of reduction of Fe³⁺ to Fe²⁺ is higher in the presence of UV light. The Fe²⁺ so formed further acts as the source for generation of hydroxyl radicals thereby increasing the efficiency of the process. The higher efficiency of de colorization for Fe⁰/H₂O₂/dark in comparison with Fe⁰/APS/UV is due to the fact that Fe⁰ under acidic conditions oxidizes to Fe²⁺ and reacts with H₂O₂ to generate hydroxyl radicals as shown in Eqs. (4) and (6). Further reducing property of metallic iron surface and the presence of hydroxyl radicals enhances the de colorization process even in the dark. The kinetics of reaction between Fe⁰ and H₂O₂ is faster which results in the generation of more number of hydroxyl radicals. Hence decolorization for this process is 75% and remained almost same (79%) even after 5 h of stirring in dark. In the case of Fe⁰/APS/UV, Fe⁰ oxidizes to Fe²⁺ and reacts with APS to generate sulfate radicals as shown in Eq. (12). This sulfate radical react with water to generate one hydroxyl radical. Further reaction between iron surface and APS is slow. In addition APS produces protons in the solution as shown in Eq. (14). The excess protons in the solution further lower the pH and acts as hydroxyl radical scavenger. The generation of hydroxyl radicals is a two-step process for APS as an oxidant, while it is single step process for H₂O₂ as an oxidant. The similarity in the rate of de colorization for the process UV/H₂O₂ and Fe⁰/dark can be accounted in the following way: H₂O₂ on photolysis under UV light generates two hydroxyl radicals as shown in Eq. (22)



These hydroxyl radicals can attack the chromophore (–N=N–) of the molecule. The cleavage of the chromophore yielding hydroxylated products responsible for de colorization is shown in Scheme 2. But this rate of de colorization is comparable to the reducing nature

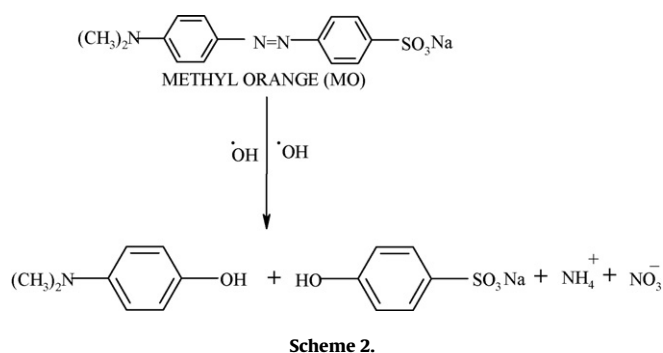


Table 1
Rate constant and process efficiency calculated for various oxidation processes on the degradation of MO

Oxidation processes	Rate constant from $-\log C/C_0$ versus time plot (min^{-1})	Process efficiency (Φ) $\times 10^{-9}$ ($\text{ppm min}^{-1} \text{W}^{-1} \text{cm}^{-2}$)
Fe^0 (dark)	0.005	2.36
Fe^0 -APS (dark)	0.0136	5.07
Fe^0 - H_2O_2 (dark)	0.025	7.94
Fe^0 -UV	0.0177	6.59
UV-APS	0.00439	1.85
UV- H_2O_2	0.0125	2.53
Fe^0 -UV-APS	0.0297	8.78
Fe^0 -UV- H_2O_2	0.1025	15.21

of iron powder which is quite efficient to decolorize the dye yielding amine substituted products as shown in Scheme 1. This reaction can proceed in dark under aerated solution. These results suggest that iron powder is an efficient catalyst and can be used in heterogeneous photo catalysis.

The process efficiency for all the above mentioned processes is defined as the change in the concentration by the amount of energy in terms of intensity and exposure surface area per time.

$$\Phi = \frac{C_0 - C}{t \cdot I \cdot S} \quad (23)$$

C_0 is the initial concentration of the substrate and C is the concentration at time ' t '. $(C_0 - C)$ denotes the residual dye concentration in mg/l or ppm. ' I ' is the irradiation intensity 125 W, ' S ' denotes the solution irradiated plane surface area in cm^2 and ' t ' represents the irradiation time in minutes. The process efficiency (Φ) calculated for the various processes are given in Table 1. It can be seen that process efficiency is lower for the systems Fe^0/dark , UV/ H_2O_2 and UV/APS while for all the other Photo Fenton process it is higher. The system with $\text{Fe}^0/\text{H}_2\text{O}_2/\text{UV}$ showed highest efficiency. From the kinetics data the extent of de colorization for the various processes is of the order: $\text{Fe}^0/\text{H}_2\text{O}_2/\text{UV} > \text{Fe}^0/\text{H}_2\text{O}_2/\text{dark} > \text{Fe}^0/\text{APS}/\text{UV} > \text{Fe}^0/\text{UV} > \text{Fe}^0/\text{APS}/\text{dark} > \text{UV}/\text{H}_2\text{O}_2 \approx \text{Fe}^0/\text{dark} > \text{UV}/\text{APS}$.

5. Recycling efficiency of iron powder

The efficiency of the iron powder was tested by recycling the iron catalyst for de colorizing the MO dye with respect to the optimized conditions as reported. When H_2O_2 is used as oxidant, experiments were carried out for 15 min and for APS as oxidant, experiments were carried out for 45 min as these were the optimum standardized conditions for de colorization of MO dye. After each run, fresh dye solution along with the oxidant is replaced in the reactor using the same iron powder. When H_2O_2 is used as oxidant, for the first two runs of the experiment, dye de colorization takes place at 15 min. For the third and fourth runs the efficiency of the iron pow-

der decreased to 73% and 70%. From fifth to eighth run the efficiency remained almost constant and only 35% of the dye was decolorized. Beyond this cycle, the catalyst surface showed resistance for the degradation of MO. In the case of APS, the efficiency of iron powder retained only for the first two runs, 100% de colorization took place in 45 min. For the third run only 73% of the dye de colorized in 45 min. Beyond fifth run de colorization remained almost constant and it is only 35% at 45 min.

The higher efficiency of iron powder in the presence of H_2O_2 is due to the fact that, the reaction between H_2O_2 at the iron surface is higher compared to reaction of iron surface with APS. Secondly the excess acidity provided by the APS leads to oxidation of iron. With subsequent runs, generation of hydroxyl radicals will be lower, and excess Fe^{2+} ions either acts as hydroxyl radicals quencher or precipitates as iron hydroxides which leads to deactivation of iron surface.

6. UV-vis spectroscopic analysis

The color of the dye solution changes from yellow to red as the pH of the dye solution is lowered. In alkaline pH, MO exists as an anion and it shows orange yellow color. The molecule in the pH range 4.1–9.5 is characterized by a band in the range 485–465 nm in the visible region attributed to azo form (λ_{max}) and the bands at 276 nm and 197 nm is due to the presence of benzene rings in MO. Under progressive protonation, color of the solution changes from orange yellow to red due to the formation of mono protonated form of MO, which exists as resonance hybrid between its quinone diimine and azonium structures. For an acidic solution, more intense absorption band shifts to a longer wavelength (appears at 506 nm). The visible region band can be attributed to azonium ions [30]. Two new bands at 317 nm and 226 nm in UV region appear due to modification of the π system delocalization. On irradiation along with iron powder and H_2O_2 as oxidant, band at 505 nm completely disappears at 15 min of irradiation as shown in the spectra (Fig. 8). Only the band at 200 nm retains its intensity up to 1 h of irradiation. This band can be attributed to benzene. At 1.5 h of irradiation this band completely diminishes indicating complete degradation of the dye. Similarly for APS as an oxidant, the de colorization of the dye takes place at 45 min while the complete mineralization was achieved at 3.5 h of UV irradiation. From the spectroscopic analysis it can be concluded that H_2O_2 is better oxidant than APS.

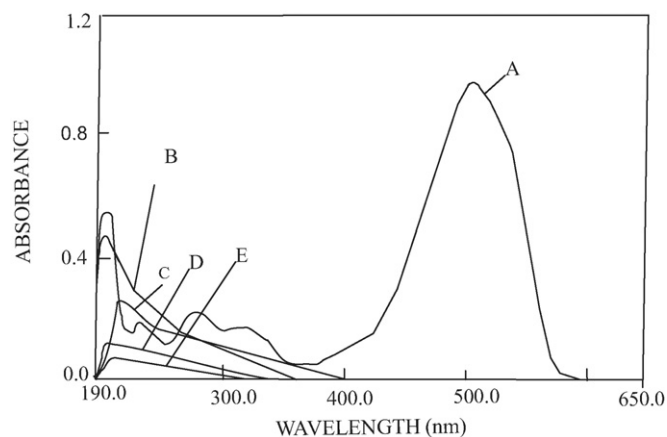
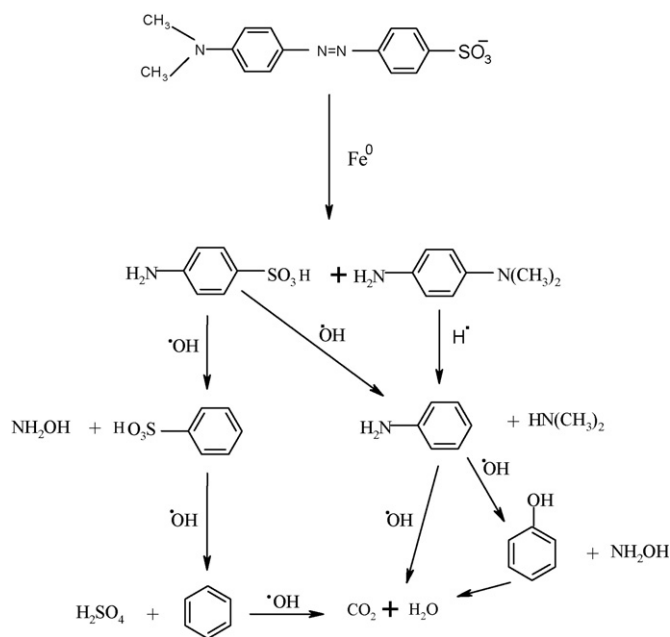


Fig. 8. Degradation of MO dye by photo Fenton process. (A) Initial solution of the dye; (b) degradation after 15 min of irradiation (H_2O_2 as oxidant); (C) degradation after 45 min of irradiation (APS as oxidant); (D) degradation after 3.5 h of irradiation (APS as oxidant); (E) degradation after 1.5 h of irradiation (H_2O_2 as oxidant) (iron dosage = 10 mg, pH 3, dye concentration = 10 ppm, H_2O_2 = 10 ppm and APS = 40 ppm).



Scheme 3.

7. GC–MS analysis

The GC–MS analysis has been performed for the experiment ($\text{Fe}^0/\text{H}_2\text{O}_2/\text{UV}$) which showed highest rate constant and process efficiency. The formation of intermediates during the degradation process was identified by this technique. The sample before UV irradiation shows two m/z peaks at 327 of high intensity corresponding to parent dye molecule and m/z peak of medium intensity at 304 attributed to ionization of the dye molecule. The sample after 10 min of irradiation showed two m/z peaks of high intensity at 137 and 173 and a lower intensity m/z peak at 176. These peaks can be attributed to the substituted aromatic amines. This shows that degradation proceeds through the cleavage of azo group connecting two aromatic rings. The azo group $-\text{N}=\text{N}-$ may convert to amines when they are adsorbed on iron surface as shown in Scheme 1. The sample after 30 min of irradiation showed two m/z peaks at 158 and 93 of medium intensity. This may correspond to benzene sulfonic acid and aniline. The sample after 1 h of irradiation shows m/z peaks at 78 and 94 of high intensity may be due to the formation of benzene and phenol. The sample after 75 min of irradiation shows one m/z peak at 78 of high intensity corresponding to benzene. This shows that benzene may be a stable intermediate during the course of reaction. The sample after 90 min of irradiation shows m/z peak at 44 corresponding to CO_2 confirming the complete degradation of the dye. The other m/z peaks at 57, 49, 62, 113 of medium intensity is left unaccounted. Based on the intermediates analyzed by GC–MS technique, a probable degradation mechanism is proposed (Scheme 3).

8. Conclusion

The degradation of MO was investigated by AFP using iron powder as a source of Fe^{2+} . The rate constant and process efficiency calculated for the different process in dark and in the presence of UV light showed that the efficiency of the process was enhanced in the presence of UV light and Fe^0 powder. The decrease in the reaction rate for APS as an oxidant is accounted to its lower reactivity with iron surface compared to H_2O_2 . The higher dosage of iron decreases the degradation rate either by inhibition effect of Fe^{2+} or by precip-

itation of hydroxides as the reaction tends towards basic condition. At lower pH, formation of amine substituted benzene sulfonic acid retards the degradation rate while at higher pH, formation of aniline decreases the mineralization of the dye. Iron powder retains its recycling efficiency better in the presence of H_2O_2 compared to APS. Though H_2O_2 seems to be a better oxidant than APS in all the aspects, but its efficiency decreases drastically in the presence of hydroxyl radical scavenger. Based on the intermediates analyzed by UV–vis spectroscopy and GC–MS technique, a probable degradation pathway has been proposed. The concentration of Fe^{2+} ions leached at the end of the optimized degradation experiment is found to be 2.78×10^{-3} M. The present research approaches a simple, cost effective and novel technology for the heterogeneous photo degradation of azo dye using eco friendly iron powder as the catalyst.

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