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Comparative removal of Magenta MB from aqueous solution by homogeneous and heterogeneous photo-Fenton processes

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ABSTRACT

Wastewaters originating from dyes production and application industries pose a major threat to surrounding ecosystems because of their toxicity and potentially carcinogenic nature. In this study, the removal of a reactive azo dye called Magenta MB (MMB) was done by photo-Fenton process using heterogeneous Fe_3O_4 catalyst and homogeneous $FeSO_4$ catalyst. The effect of different system variables namely catalyst concentration, H_2O_2 dosage, pH, and initial concentration of the dye were studied. The influence of inorganic salts and ligands in the photo-Fenton system were examined. The stability of Fe_3O_4 catalyst has also been determined. The homogeneous photo-Fenton system exhibited the highest removal efficiency of 96.7% under the operating conditions of catalyst concentration of 300 mg L^{-1}, H_2O_2 dosage of 9 g L^{-1}, initial pH of 2.5, and concentration of MMB of 50 mg L^{-1}. The optimum operating condition as per the experimental results for the heterogeneous photo-Fenton system, while using Fe_3O_4 catalyst is 500 mg L^{-1} of catalyst dosage and 6 g L^{-1} of H_2O_2 dosage for 50 mg L^{-1} of initial dye concentration at an initial pH of 2.5 in 90 min with a dye removal efficiency of 94.9%. The addition of salts and ligands were found to be having an inhibiting effect on the Fenton system. Results showed that magnetite was found to be an efficient photo-Fenton catalyst for dye removal.

Keywords: Fenton process; Dye removal; Magnetite; Photo-Fenton; Magenta MB

1. Introduction

Dyes stuff are produced over 700,000 tons annually estimated from more than 100,000 commercially available dyes [1] and applied in many different industries, including the textiles, paper, cosmetic, leather, food, and pharmaceutical industries. The azo dyes, characterized by an azo group (–N=N–), are the largest class of dyes used in textile industry for dyeing several natural and synthetic materials [2]. There are numerous types of dyes, which can be classified as acetate rayon dyes, acid dyes, azoic dyes, basic dyes, direct dyes, mordant or chrome dyes, lake or pigment dyes, sulfur or sulfide dyes, and vat dyes. Due to their strong interaction with many surfaces of synthetic and natural fabrics, reactive dyes are used for dyeing wool, cotton, nylon, silk, and modified acrylics [3]. These dyes are the most important class of synthetic

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organic dyes used in the textile industries and are therefore common industrial pollutants [4].

About 1–2% dyes are lost during production and 1–10% is lost during the use. Due to the large-scale production and extensive application, synthetic dyes can cause considerable environmental pollution and serious health hazards [5,6]. The effluents from the textile dyeing industry contain many organic pollutants and are a serious environmental hazard because of their lasting color, high chemical oxygen demand, and non biodegradability [7]. The conventional treatment techniques applied in textile wastewaters, such as chemical coagulation/flocculation, membrane separation (ultrafiltration, reverse osmosis), or elimination by activated carbon adsorption, are not only costly, but also result in phase transfer of pollutants [8]. The process of biodegradation has the advantage that it is an environmental friendly and cost competitive alternative, but under anaerobic conditions toxic aromatic amines are produced as intermediates which makes the process ineffective [9]. Advanced oxidation processes have shown a great potential to decolorize and reduce recalcitrant organic compounds such as dyes, surfactants, other auxiliaries from dyeing process and finishing textile process [9,10].

The rate of destruction of organic pollutants and the extent of mineralization can be considerably increased using Fe^{2+} or Fe^{3+}/H_2O_2 reagent irradiated with near-UV and/or visible light, in a reaction that is called the “photo-Fenton reaction” [11]. The addition of UV radiation to Fenton’s reagent process could be an interesting allied in dye decolorization due to its capacity in influencing direct formation of $HO^{\cdot}$ radicals. The reason for the positive effect of irradiation on the degradation rate include the photoreduction of Fe^{3+} to Fe^{2+} ions, which produce new $HO^{\cdot}$ radicals with H_2O_2 according to the following mechanism [11]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{1-} + HO^{\cdot} \tag{1}$$

$$Fe^{3+} + H_2O \xrightarrow{hv} Fe^{2+} + HO^{\cdot} + H^{1+} \tag{2}$$

$$H_2O_2 \xrightarrow{hv} 2HO^{\cdot} (\lambda < 400 \text{ nm}) \tag{3}$$

It is also known that the photo-excitation of Fe^{3+}–carboxylate complexes results in the formation of Fe^{2+} carboxylate radicals through a ligand-to-metal charge transfer path [12]. This allows additional catalyst regeneration and produces additional radicals.

The homogeneous Fenton’s process has significant disadvantages such as (i) tight pH range in which the reaction proceeds and (ii) need for recovery of the precipitated catalyst after treatment [13]. To overcome the disadvantages of homogeneous Fenton process, much attention had been focused on development of heterogeneous catalyst.

Some attempts had been made recently to develop heterogeneous photo-Fenton catalyst such as iron corrosion products [12], Fe-alginate beads [14], magnetite [15,16], copper–iron bimetal modified PAN fiber complexes [17], iron-containing mesostructured silica [18] for the removal and degradation of various organic pollutants from aqueous solution.

Our previous studies [19,20] show that magnetite is an efficient Fenton and electro Fenton catalyst. But the catalytic activity of this magnetite in the presence of UV light is not tested. Therefore, the present study compares the performance of laboratory prepared magnetite with photo-Fenton processes using $FeSO_4$ for the removal of reactive dye Magenta MB (MMB) from aqueous solution. During the study the effect of various parameters was evaluated namely pH, dosage of catalyst, dosage of H_2O_2, and initial concentration of the dye. The influence of inorganic ions and ligands at the optimum conditions were also investigated.

2. Materials and methods

2.1. Chemicals

The $FeSO_4{\cdot}7H_2O$, $FeCl_3$, H_2O_2 (30%, w/w), NaOH, NaF, NaCl, Na_2SO_4, EDTA, oxalic acid, and H_2SO_4 were purchased from Merck. Ethanol (99.9%) was purchased from Jiangsu Huaxi International.

2.2. Dye

In this study, MMB which is a reactive dye has been selected as a model dyeing pollutant. It has widespread application and recalcitrant nature. Most of the fiber reactive dyes are anionic, since they have negative molecular charges. Therefore, MMB is also an anionic dye. The maximum absorption wavelength of MMB was 532.5 nm. A concentration of 1,000 mg L^{-1} of MMB stock solution was prepared by diluting 1 g of dye salt in 1 L distilled water and this was later diluted to the required concentrations. For the batch studies these solutions were used.

2.3. Preparation of catalyst

$FeSO_4{\cdot}7H_2O$ and Fe_3O_4 were used as catalyst for the homogeneous and heterogeneous photo-Fenton processes, respectively. $FeSO_4{\cdot}7H_2O$ and $FeCl_3$ were taken in the ideal molar ratio of Fe^{2+}/Fe^{3+} of 0.5 and mixed in 100 mL deionized water to prepare Fe_3O_4. This was done because Nidheesh et al. [19] had reported that magnetite with iron species ratio two is the efficient Fenton catalyst for the abatement of dyes from aqueous solution. Into this solution 8 M NaOH solution was added drop wise while stirring vigorously for half an hour, a formation of black precipitate was observed. This precipitate was later filtered, washed with deionized water and ethanol. These products were finally dried in room temperature. Eq. (4) indicates the formation of magnetites [21].

$$\begin{aligned}&Fe^{2+} + 2Fe^{3+} + 8OH^{1-}\\ &\quad \rightarrow Fe_3O_4(\text{Black colloidal particles}) + 4H_2O\end{aligned} \tag{4}$$

2.4. Dye removal study

The study was carried out in a 500 mL glass beaker filled with 250 mL of dye solution. Predetermined amounts of H_2O_2 solution were added into the cylinder. The pH was adjusted to the desired value using 0.5 N H_2SO_4. The catalyst was added into this solution and this was magnetically stirred and subjected to UV radiation. A Philips UV lamp (11 W and 253.7 nm) was used as the source of UV radiation and the lamp was positioned at the top of the glass beaker. Samples were withdrawn at regular intervals of time for analysis. The UV–vis spectra of MMB were recorded using a UV–vis spectrophotometer (Lambda 25, Perkin Elmer, USA) with a silica cell of path length 1 cm. The pH was measured using Orion EA 940 Ion analyzer (Thermo, USA).

The same procedure was followed in order to study the effect of catalyst dosage, initial H_2O_2 concentration, pH, and initial dye concentration in the photo-Fenton systems. The influence of inorganic salts and ligands at the optimal conditions in the photo-Fenton processes was evaluated. The stability of the Fe_3O_4 catalyst was examined at the optimal conditions in the heterogeneous photo-Fenton process. Also the mineralization study was conducted in the photo-Fenton systems by analyzing the total organic carbon (TOC) removal.

The maximum absorbance wavelength (λ_{max}) of MMB was found at 532 nm using the UV–vis spectrophotometer. The decolorization efficiency (%) of MMB was defined as follows:

$$\text{Decolorization efficiency } (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{5}$$

where C_0 (mg L^{-1}) is the initial concentration of MMB and C_t (mg L^{-1}) is the concentration of MMB at reaction time, t (min).

To quantitatively characterize the mineralization of dye in the solution, the TOC removal efficiency is used in the study, which is defined as follows:

$$\text{TOC Removal Efficiency} = \frac{(TOC_0 - TOC_t)}{TOC_0} \times 100 \tag{6}$$

where, TOC_t and TOC_0 are the TOC values at reaction time t and 0, respectively.

The TOC measurements were carried out with a multi N/C 3100 Analyzer (Analytik Jena, Germany).

3. Results and discussion

3.1. Effect of catalyst dosage

In the photo-Fenton system the effect of catalyst dosage was studied by varying the catalyst concentration from 0 to 500 mg L^{-1} in the homogeneous photo-Fenton system and from 300 to 700 mg L^{-1} in the case of heterogeneous photo-Fenton system (Fig. 1). The optimum dosage of $FeSO_4$ in the homogeneous photo-Fenton system was 300 mg L^{-1} and a removal efficiency of 93.99% was obtained in 15 min. The optimum Fe_3O_4 dosage was 500 mg L^{-1} and an efficiency of 78.92% was obtained in 90 min in the heterogeneous photo-Fenton system. At the beginning of the reaction the dye removal rate is fast due to the high initial concentration of catalyst, and then it drastically decreases due to the poor rate of regeneration [22]. The removal efficiency increased with the catalyst dosage and then decreased upon further addition of the catalyst. With increased dosage of catalyst, more active iron sites would be available on the catalyst surface for accelerating the decomposition of H_2O_2. This would result in more iron leaching in the solution, leading to an increase in the number of OH radical [23]. Increasing Fe content caused more active sites, which could decompose H_2O_2 into high concentration of $\cdot OH$ radicals in solution by the heterogeneous photo-Fenton reaction, thus promoting the dye degradation [14]. However, in the case of photo-Fenton systems, the reaction suspension becomes more turbid in the presence of excessive catalyst, which may inhibit the penetration of light and decreases the production of $\cdot OH$ [24]. High dosage of iron powder increases the concentration of Fe^{2+} ions in the solution which can also act as hydroxyl radical scavenger [25]. Thus, the catalyst dosage was found to be least for the homogeneous photo-Fenton system.

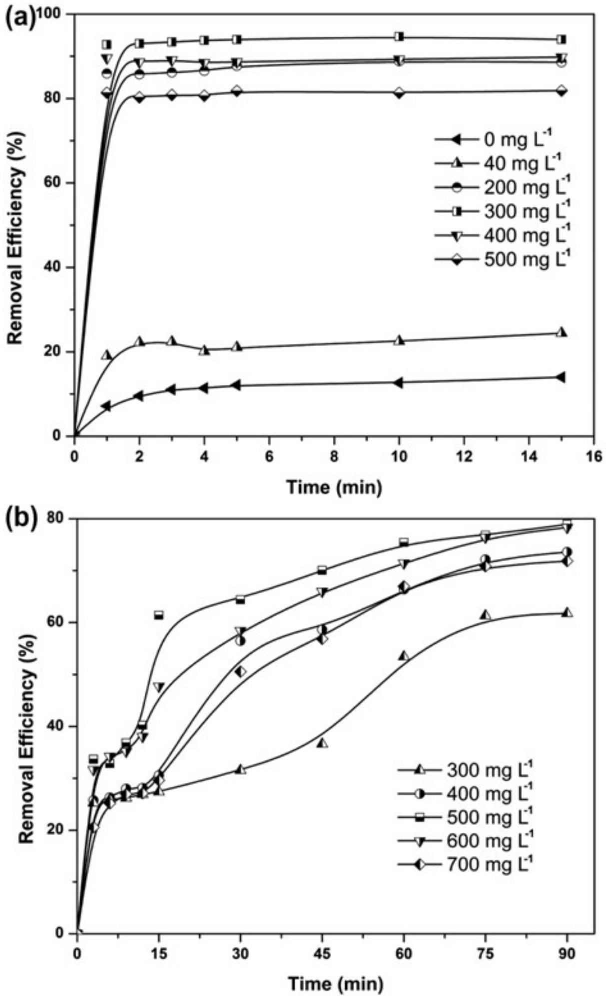

Fig. 1. Effect of catalyst dosage on the decolorization by (a) homogeneous and (b) heterogeneous photo-Fenton systems. Reaction conditions: MMB = 50 mg L^{-1}, [H_2O_2] = 7.5 g L^{-1}, pH 3.

3.2. Effect of the initial H_2O_2 concentration

It is known that addition of H_2O_2 influences the decomposition of complex organic compounds by Fenton's reaction. From a practical point of view the selection of an optimum H_2O_2 concentration is important for the degradation of the dyes by photo-Fenton's reagent due to the cost of H_2O_2 [26]. The optimum H_2O_2 concentration was found to be 9 g L^{-1} and it showed a removal efficiency of 95.4% for the homogeneous photo-Fenton system. For the heterogeneous photo-Fenton system, the optimum H_2O_2 dosage was 6 g L^{-1} and a removal efficiency of 82.54% was obtained (Fig. 2). Without H_2O_2 the removal efficiency was only 24.59% in the heterogeneous photo-Fenton system. This was mainly due to adsorption. At low H_2O_2 concentration, H_2O_2 cannot generate enough hydroxyl radicals and the oxidation rate is logically slow [27]. Further, most of the free radicals are directly consumed by the dye [27]. Initially the removal efficiency increases with increasing H_2O_2 dosage mainly due to the effect of $HO^\cdot$ radicals produced additionally. As the H_2O_2 dosage exceeded additionally, scavenging of hydroxyl radicals occurred at a higher H_2O_2 concentration, leading to decrease in the number of hydroxyl radicals in solution through the formation of perhydroxyl radicals (Eq. (7)) [24]. These perhydroxyl radicals have lower oxidation potential than $HO^\cdot$ radicals.

$$H_2O_2 + OH^\cdot \rightarrow H_2O + HO_2^\cdot \tag{7}$$

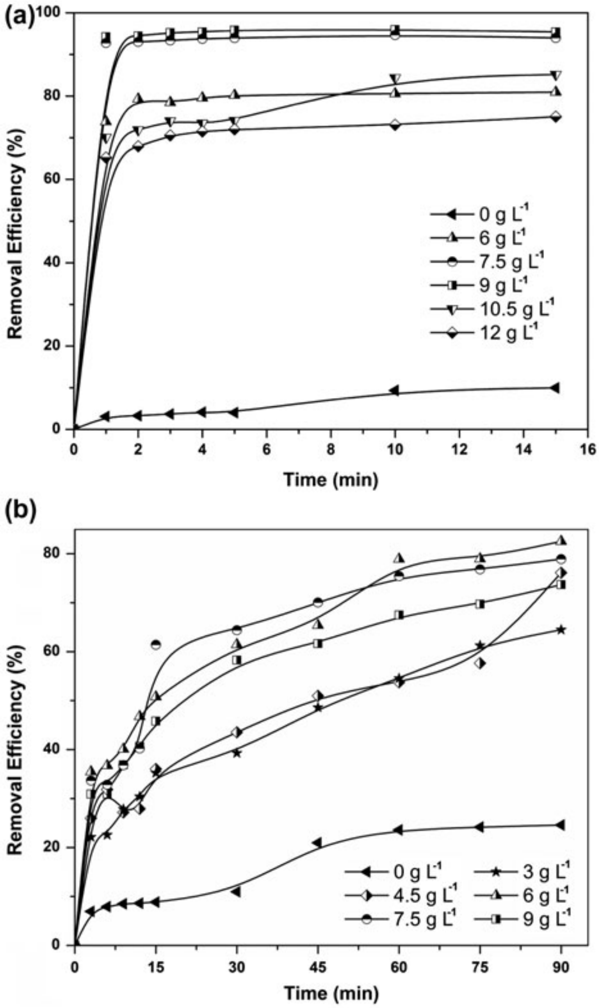

Fig. 2. Effect of H_2O_2 dosage on the decolorization (a) homogeneous photo-Fenton system: MMB = 50 mg L^{-1}, [$FeSO_4$] = 300 mg L^{-1}, pH 3 and (b) heterogeneous photo-Fenton system: MMB = 50 mg L^{-1}, [Fe_3O_4] = 500 mg L^{-1}, pH 2.

The H_2O_2 concentration was found to be least for the heterogeneous photo-Fenton system.

3.3. Effect of pH

The pH was varied from 2 to 3.5 in both the photo-Fenton systems (Fig. 3). The optimum pH was found to be 2.5 in both the systems. The removal efficiency of homogeneous photo-Fenton system under this condition was 96.7%, whereas for the heterogeneous photo-Fenton system was 94.9%. The low decolorization at pH 2 is probably due to the hydroxyl radical scavenging by the H^+ ions [8].

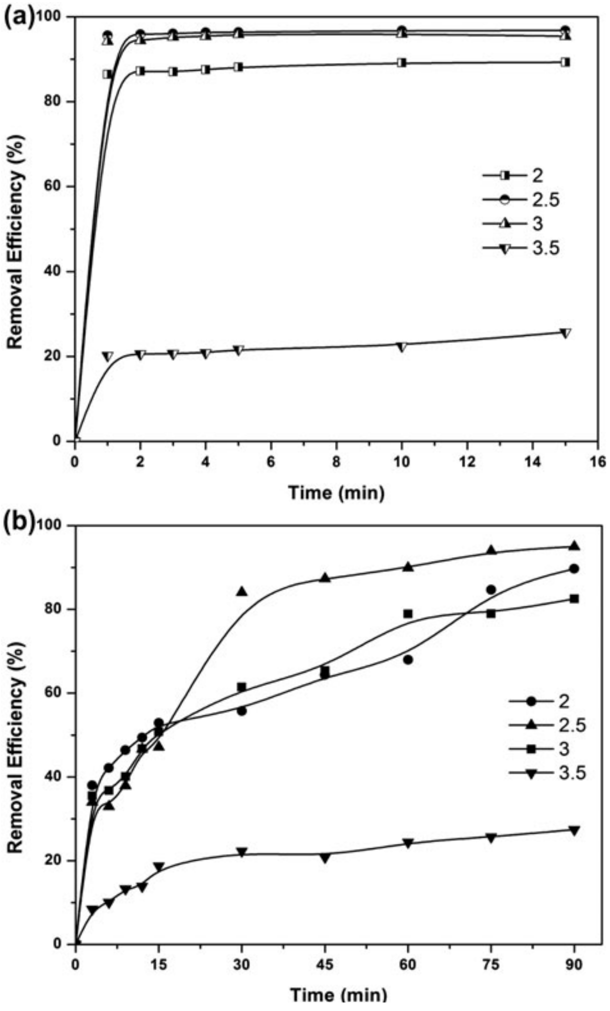

Fig. 3. Effect of pH on the decolourization (a) homogeneous photo-Fenton system: MMB = 50 mg L^{-1}, $[FeSO_4]$ = 300 mg L^{-1}, $[H_2O_2]$ = 9 g L^{-1} and (b) heterogeneous photo-Fenton system: MMB = 50 mg L^{-1}, $[Fe_3O_4]$ = 500 mg L^{-1}, $[H_2O_2]$ = 6 g L^{-1}.

$$HO^{\bullet} + H^{1+} + e^- \rightarrow H_2O \tag{8}$$

The lowering of removal rate in this pH range can also be attributed to the reduction of hydroxyl radical concentration.

At high pH the reduction of $HO^{\bullet}$ will occur due to the formation of ferric hydroxide precipitates [7]. Under this condition H_2O_2 undergoes photodecomposition to water and oxygen rather than hydroxyl radical (Eq. (9)) [4].

$$2H_2O_2 \xrightarrow{hv} 2H_2O + O_2 \tag{9}$$

Ferric ions form different complex species in solution at different pH values, and that the quantum yield of light absorption by Fe^{3+} is directly dependent on the specific species responsible for the absorption. The main compounds absorbing light in the Fenton system are ferric ion complexes, e.g. $[Fe^{3+}\cdot(OH)^-]^{2+}$ and $[Fe^{3+}\cdot(RCO_2)^-]^{2+}$, which produce additional Fe^{+2} by photo-induced, ligand-to metal charge-transfer reactions [28]. According to Benfield et al. [29] the concentration of iron complexes such as $Fe(OH)_4^{2-}, Fe_2(OH)_2^{4+}, Fe(OH)_2^{1+}$ and $FeOH^{2+}$ are high at pH < 3. The increased light absorption will lead to increased $HO^{\bullet}$ and Fe^{2+} production, thereby increasing the efficiency of the reaction.

The advantage of heterogeneous catalyst over homogeneous catalyst is its efficiency at wide range of pH values. In the present study, photo-Fenton activity of magnetite is optimum at acidic pH. Our previous studies also proved that acidic pH is the optimal condition for the Fenton and electro Fenton degradation of dyes in the presence of magnetite [19,20]. Some other heterogeneous catalysts also showed optimal activity at acidic pH. For example, iron-based nanoparticles [30], magnetic Fe_2MO_4 [31], mesoporous alumina supported nanosized Fe_2O_3 [32], iron-loaded mangosteen [33] etc. showed optimal activity at acidic pH values.

3.4. Effect of initial dye concentration

The influence of initial dye concentration was evaluated by varying the initial dye concentration from 10 to 150 mg L^{-1} as shown in Fig. 4. Maximum removal efficiency in both the systems was observed around 50 mg L^{-1}. When the dye initial dye concentration was below 50 mg L^{-1} the efficiency was found to be decreasing. When the concentration of one or more reactants is decreased, the frequency of collisions between the reactant molecules also decreases. As a result the reaction rate is reduced [23]. There will be scavenging effect due to surplus Fe^{2+} and

H_2O_2 concentrations. The removal efficiency was found to be decreasing for dosages greater than 50 mg L^{-1}. The experiment parameters being similar, the number of active radical species generated by the process is assumed constant, resulting in the decrease in the decolorization efficiency with the increase in molecules to be oxidized [18]. Along with the dye molecules the intermediate products formed during dye oxidation may probably compete for the available Fe^{3+} active sites [13]. Hydroxyl radical is mainly responsible for dye decolorisation and its concentration remains constant for all dye concentrations. The increase in dye concentration increases the number of dye molecules and not the OH radical concentration and so the removal rate decreases [34].

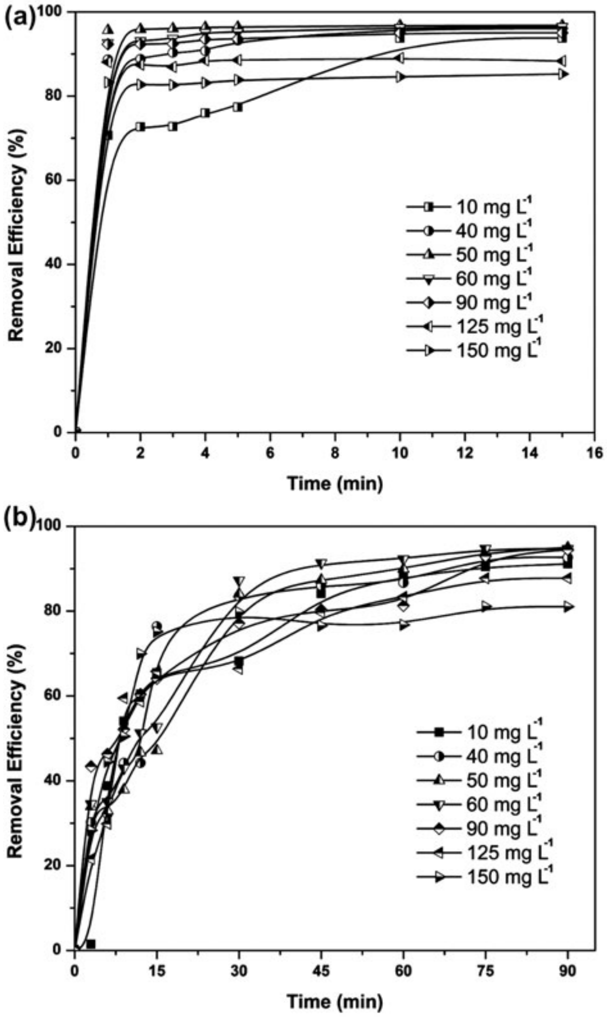

Fig. 4. Effect of initial dye concentration on the decolorization (a) homogeneous photo-Fenton system: [$FeSO_4$] = 300 mg L^{-1}, [H_2O_2] = 9 g L^{-1}, pH 2.5 and (b) heterogeneous photo-Fenton system: [Fe_3O_4] = 600 mg L^{-1}, [H_2O_2] = 6 g L^{-1}, pH 2.5.

Even though the dye removal efficiency of both photo-Fenton systems decreased with increase in initial dye concentration, the absolute dye removed had increased with increase in initial dye concentration. For example, the amount of dye removed via homogeneous photo-Fenton process for the system having initial MMB concentrations of 10 and 150 mg L^{-1} were 9.3 and 125 mg L^{-1}, respectively. This is mainly due to the increased effective collision between the hydroxyl radicals and dye molecules at higher dye concentrations [35]. Similar results have been observed by Nidheesh and Gandhimathi [36] for the removal of dyes using peroxi-coagulation process.

3.5. Influence of inorganic ions and ligands

The chemical analysis of industrial waste waters revealed the presence of several ions such as: chloride, sulfate, nitrate, and carbonate. The performance of the oxidation process may be affected by the background impurities present in wastewaters [22]. The effect of addition of salts such as NaF, NaCl, Na_2SO_4, and ligands such as EDTA and oxalate were studied (Fig. 5). Variable concentrations of these salts were introduced into the system in order to evaluate this influence. The removal efficiency decreased with increasing salt/ligand concentration in each case. The inhibition effect was in the order: EDTA < SO_4^{2-} < F^{1-} < oxalate < Cl^{1-}.

Multiple factors could cause these unexpected matrix effect and it cannot be attributed to only one factor. The predominance of the factors causing these inhibition effects may vary from time to time [22]. The reduction in the removal efficiency is due to the

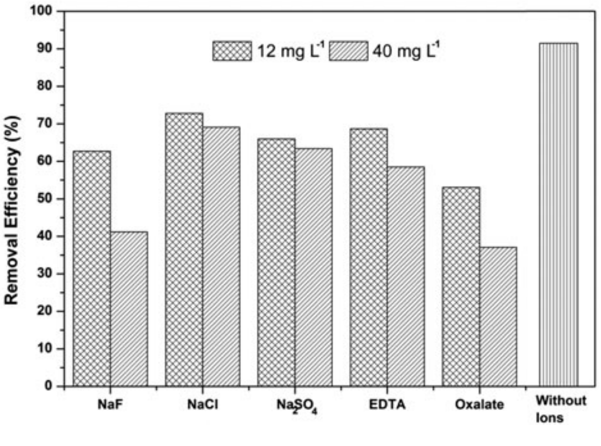

Fig. 5. Influence of inorganic ions and ligands on homogeneous photo-Fenton system: [$FeSO_4$] = 300 mg L^{-1}, [H_2O_2] = 9 g L^{-1}, MMB = 50 mg L^{-1}, pH 2.5.

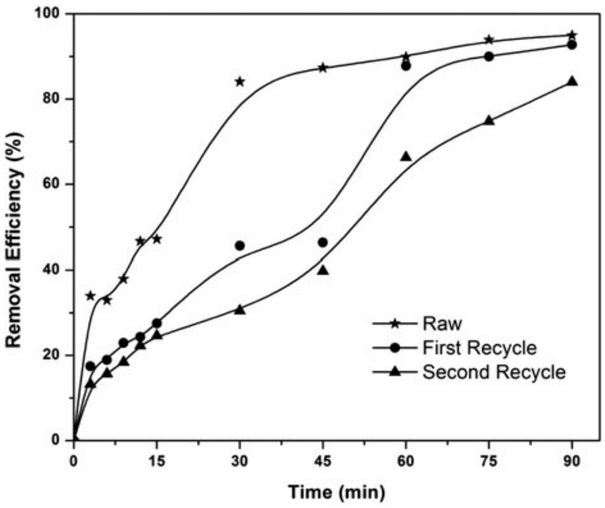

Fig. 6. Stability of Fe_3O_4 catalyst, experimental conditions: $[Fe_3O_4] = 500$ mg L^{-1}, $[H_2O_2] = 6$ g L^{-1}, MMB = 50 mg L^{-1}, pH 2.

hydroxyl radical scavenging effect of chloride ion [28]. SO_4^{2-} may consume the generated hydroxyl radicals [37]. The inhibition of EDTA was mainly due to Fe^{2+}–EDTA complex formation. It is possible that the reaction EDTA with $OH^{\cdot}$ is also present. The inhibition by F^{1-} may be due to the decrease in $OH^{\cdot}$ production via the formation of $OH^{-\cdot}$ [22]. F^{1-} may form complexes with Fe^{3+} that prevents the regeneration of Fe^{2+}. The formation of Fe^{3+}-oxalate ions would prevent the regeneration of Fe^{2+} ions [22].

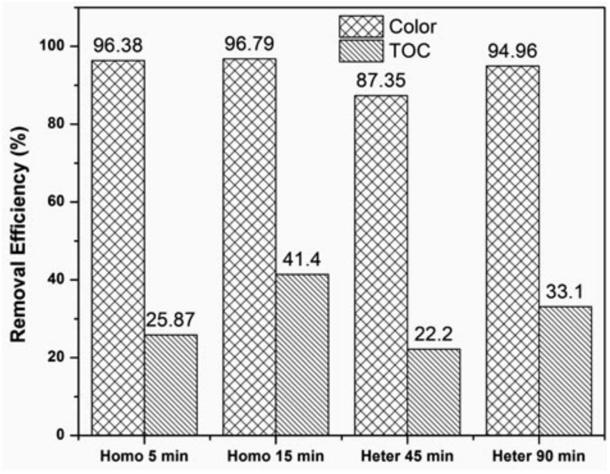

Fig. 7. Comparison of color removal and TOC removal. Homogeneous photo-Fenton system: $[FeSO_4] = 300$ mg L^{-1}, $[H_2O_2] = 9$ g L^{-1}, MMB = 50 mg L^{-1}, pH 2.5. Heterogeneous photo-Fenton system: $[Fe_3O_4] = 500$ mg L^{-1}, $[H_2O_2] = 6$ g L^{-1}, MMB = 50 mg L^{-1}, pH 2.5.

3.6. Stability of Fe_3O_4 catalyst

For studying the stability of Fe_3O_4 catalyst, the residue catalyst after many experiments were collected, filtered, and washed with distilled water and dried in room temperature. Again experiments were conducted utilizing this recycled catalyst. It can be seen from Fig. 6 that the removal efficiency of the dye had decreased to 84.03% for the photo-Fenton system after the second run. The activity reduction observed may be due to the active phase leaching. The leaching of Fe could attribute to the coordination effect of organic and/or inorganic acids generated during the degradation of azo dyes, as observed for other heterogeneous Fenton-like catalysts [7].

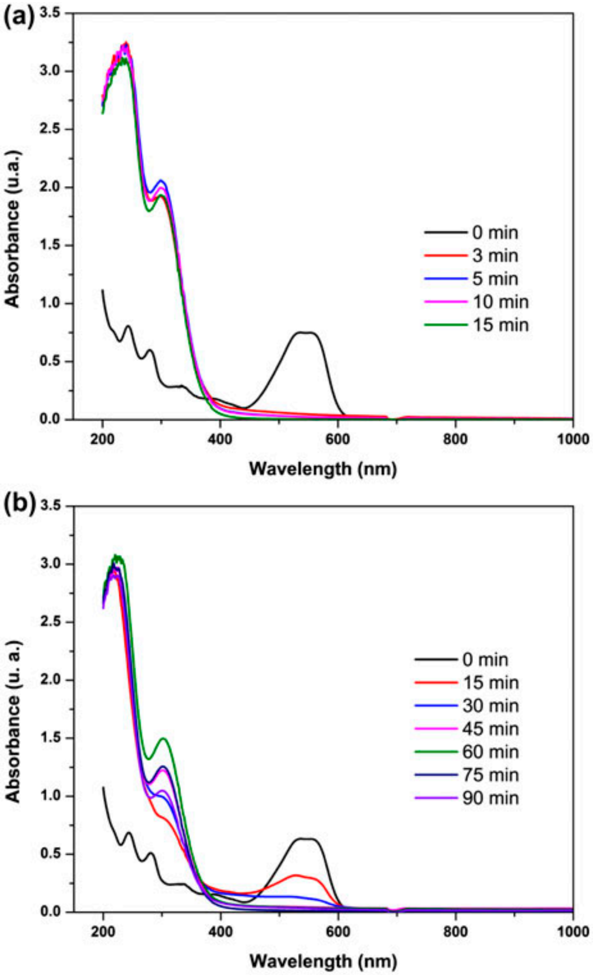

Fig. 8. UV–vis absorption spectra of MMB. (a) homogeneous photo-Fenton system: $[FeSO_4] = 300$ mg L^{-1}, $[H_2O_2] = 9$ g L^{-1}, MMB = 50 mg L^{-1}, pH 2.5 and (b) heterogeneous photo-Fenton system: $[Fe_3O_4] = 500$ mg L^{-1}, $[H_2O_2] = 6$ g L^{-1}, MMB = 50 mg L^{-1}, pH 2.5.

Table 1
Catalytic activity comparison of magnetite with other heterogeneous Fenton catalysts

Catalyst name	Process	Optimal operating conditions	Removal efficiency	Stability
Iron-containing mesostructured silica [18]	Sono–photo-Fenton process	Hydrogen peroxide concentration of 8 mmol L^{-1}, catalyst concentration of 0.3 g L^{-1}, an ultrasonic power of 80 W and pH 2	More than 85% of dye removal from the initial dye concentration of 100 mg L^{-1}	Highly stable even after 3rd recycling
$LiFe(WO_4)_2$ [7]	Fenton process	Initial H_2O_2 concentration 6.8 g L^{-1}, catalyst load 10 g L^{-1} and pH of 3	Almost complete decolorization of 500 mg L^{-1} of dye solution after 60 min	Highly stable even after 3rd recycling
Sludge produced from peroxicoagulation process [40]	Electro Fenton process	pH 3, applied voltage of 7 V and catalyst concentration of 10 mg L^{-1}	97% of color, 47% of COD and 33.2% of TOC removal from real textile wastewater	Not tested
Magnetite [20]	Fenton process	Catalyst concentration of 600 mg L^{-1}, 8.8 g L^{-1} of H_2O_2 and initial pH of 2.	More than 86% of dye removal after 60 min	Rate of dye removal reduced with recycling
Magnetite [19]	Electro Fenton Process	pH 3, catalyst concentration of 10 mg L^{-1}, an applied voltage of 8 V	97% of dye removal after 180 min of electrolysis from the initial dye concentration of 10 mg L^{-1}	Highly stable even after 5th recycling
Magnetite	Photo Fenton	500 mg L^{-1} of catalyst dosage, 6 g L^{-1} of H_2O_2, pH of 2.5	Almost 95% of dye removal after 90 min of UV irradiation	Rate of dye removal reduced with recycling

3.7. Mineralization study

It is known that reaction intermediates can be formed during the oxidation of azo dyes and some of them could be long-lived and even more toxic than the parent compounds. Therefore, it is necessary to understand the mineralization degree of the MMB dye to evaluate the degradation level applied by homogeneous photo-Fenton and heterogeneous photo-Fenton processes.

As could be seen from Fig. 7, dye decolorization is much higher than TOC removal even in homogeneous photo-Fenton and also in heterogeneous photo-Fenton processes. The final TOC removal by the homogeneous photo-Fenton and heterogeneous photo-Fenton processes were 41.4 and 33.1%, respectively.

As MMB has a maximum absorbance at 532.5 nm, this wavelength was used to monitor the discoloration of the solution during the reactions. Fig. 8 indicates the nearly complete discoloration of solution after 15 min in the case of homogeneous photo-Fenton process and after 90 min in the case of heterogeneous photo-Fenton process. After degradation, the absorbance of the remaining solution at visible light region decreased quickly, while simultaneously the absorbance at UV region increased, indicating that azo band was destroyed and many degradation intermediates containing benzene ring and acids generated (300 and 224 nm) [13,37].

Studies have shown that during Fenton oxidation, color removal of dye was faster than COD removal [38]. The reason could be due to the formation of stable intermediate products, which require longer time for further oxidation. Moreover, the absorbance region near UV region started decreasing after some time, which indicates that when the intermediates of degradation in the solution accumulated to a certain concentration, the intermediates also began to degrade along with the degradation of the residual MMB [39]. So, from this analysis it is evident that neither homogeneous photo-Fenton process and heterogeneous photo-Fenton process has the capacity to eliminate the MMB dye completely.

3.8. Comparison of different systems

It can be understood from the results that the time taken for the heterogeneous photo-Fenton system was higher when compared to the homogeneous photo-Fenton system. While the heterogeneous catalyst being in solid form does not get mixed thoroughly, the homogeneous catalyst gets uniformly mixed in the dye solution. In addition to this, the catalyst dosage for heterogeneous photo-Fenton system was also found to be higher than the homogeneous photo-Fenton system. The dye removal efficiency of Fe_3O_4 catalyst used in heterogeneous catalyzed reaction system may in fact be augmented by improved mixing techniques. The performance of both the catalyst was good in the acidic range and at various concentration of the dye they had displayed similar removal efficiencies. As the dosage of H_2O_2 was found to be lesser for the heterogeneous catalyst, it was better. In addition to this, Fe_3O_4 catalyst can be reutilized to give sufficient removal efficiency and also the separation of this catalyst from the effluent is also easier. Thus, it can be inferred that although $FeSO_4$ had shown marginally better dye removal efficiency than Fe_3O_4, Fe_3O_4 was found to be satisfactory for the removal of MMB.

The efficiency of magnetite as a heterogeneous Fenton catalyst is compared with the efficiencies of other heterogeneous catalysts used for the removal of dyes from aqueous solution and the results are given in Table 1. Most of the catalyst used were highly stable. But the present study shows that the activity of the catalyst reduces with recycling. Similar results have been observed by Laiju et al. [33] for the degradation of organic pollutants from stabilized landfill leachate using iron-loaded mangosteen shell powder as a heterogeneous Fenton catalyst. But the presence of electric potential the same material showed higher stability [19]. The removal efficiency of the prepared catalyst is comparable with other catalysts. But in most of cases, the concentrations of catalyst and hydrogen peroxide are not in the same range. For example, the optimal concentration of $LiFe(WO_4)_2$ is in the range of $g\,L^{-1}$ [7], while that of magnetite in electro Fenton process is in the range of $mg\,L^{-1}$ [19]. This indicates that the catalytic activity of heterogeneous catalyst also depends on the process.

4. Conclusions

For the degradation of the dye MMB Fe_3O_4 catalyst was found to effective. For the heterogeneous photo-Fenton system, the optimal operating conditions when Fe_3O_4 catalyst was used were $500\,mg\,L^{-1}$ of catalyst dosage for $6\,g\,L^{-1}$ of H_2O_2 dosage and $50\,mg\,L^{-1}$ of initial dye concentration at an initial pH of 2.5 achieved in 90 min. Under these conditions dye removal efficiency of 94.9% was observed. When $FeSO_4$ catalyst was used for the homogeneous photo-Fenton system, the optimal operating conditions achieved were $300\,mg\,L^{-1}$ of catalyst dosage, and $9\,g\,L^{-1}$ of H_2O_2 for $50\,mg\,L^{-1}$ of initial dye concentration at an initial pH of 2.5 in 15 min. Dye removal efficiency of 96.7% was observed under these conditions. An inhibiting effect was observed in the addition of salts and ligands. After two runs the dye removal efficiency has reduced to 84.03% in 90 min in the heterogeneous photo-Fenton system. During photo-Fenton's oxidation it was observed that, decolorization was occurring faster than mineralization.

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