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Comparison of homogeneous and heterogeneous Fenton processes for the removal of reactive dye Magenta MB from aqueous solution

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ABSTRACT

The contamination of water due to dyes coming from different industries is the current problem all over the world and is a demanding environmental issue that needs to be addressed. In this study, the removal of a reactive azo dye called Magenta MB was done by Fenton process using heterogeneous Fe_3O_4 catalyst and homogeneous $FeSO_4$ catalyst. The homogeneous Fenton system had a removal efficiency of 90.9% under operating conditions of catalyst concentration of 400 mg/L, H_2O_2 dosage of 0.38 M, initial pH of 3 and concentration of Magenta MB of 50 mg/L. The optimum operating condition as per the experimental results for the heterogeneous Fenton system while using Fe_3O_4 catalyst was 600 mg/L of catalyst dosage and 0.26 M of H_2O_2 for 50 mg/L of initial dye concentration at an initial pH of 2 in 60 min. The dye removal efficiency under this condition was 86.8%. An inhibiting effect of salts and ligands on Fenton system was observed and this inhibition effect increases in the following order: $Cl^- < SO_4^{2-} \sim EDTA < F^- <$ oxalate. The dye removal efficiency of the recycled magnetite was found to be 76%, which is less than that of newly prepared catalyst. Magenta MB was successfully removed by Fenton processes. Results showed that magnetite was found to be an efficient Fenton catalyst for dye removal.

Keywords: Fenton; Magenta MB; Magnetite; Dye removal; Advanced oxidation process

1. Introduction

Dye-containing wastewater from the textile industry is a principal source of environmental contamination because over 15% of the dyes are lost in wastewater without treatment during their synthesis and dyeing processes [1]. These dye stuffs are reported to cause formation of toxic aromatic amines under anaerobic conditions in receiving media, and are carcinogenic and contaminate the soil and groundwater [2]. For the removal of such recalcitrant pollutant, traditional physical techniques (coagulation, adsorption on activated carbon, reverse osmosis and ultrafiltration, etc.) can generally be used [3]. Nevertheless, these methods are usually non-destructive, and the post-treatment of the adsorbent materials or solid wastes is necessary and expensive [3]. Furthermore, high cost of equipments involved in these processes limits their practical large-scale implementation [4]. Biodegradation is an environmentally friendly and cost-competitive alternative, but the conventional aerobic treatments have been proved ineffective while highly

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toxic aromatic amines can be formed by reductive fission under anaerobic conditions [5].

The efficiency and simplicity of advanced oxidation processes (AOP) make them a suitable choice for the removal of toxic chemicals from wastewaters in the recent years [6]. Among the various AOPs, Fenton process based on the use of H_2O_2 with Fe^{2+} ions is well known as a powerful source of reactive radicals $OH^{\cdot}$, which are able to degrade various refractory compounds [7]. The Fenton oxidation has a wide variety of applications due to its higher generation rate of hydroxyl radicals, rate of mineralisation, cheap availability and easy handling [8]. The Fenton reaction can be outlined as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{-} + HO^{\cdot} \qquad (1)$$

In Eq. (1), the ferrous ions (Fe^{2+}) are oxidised to ferric ions (Fe^{3+}/Fe(III)) ions in acidic aqueous solution giving rise to hydroxyl radicals ($OH^{\cdot}$). The generated hydroxyl radicals oxidise the target organic compounds (RH) as shown in Eq. (2).

$$OH^{\cdot} + RH \rightarrow R^{\cdot} + H_2 \qquad (2)$$

During the reaction, ferric ions can be reacted to produce ferrous ions according to Eq. (3).

$$R^{\cdot} + Fe^{3+} \rightarrow R^{+} + Fe^{2+} \qquad (3)$$

However, the usage of homogeneous Fenton has a number of disadvantages such as the formation of different Fe(III) complexes as solution pH changes, requirement of narrow range of pH value for reaction and the problem of separation and regeneration at the end of the reaction [1,9]. The homogenous catalyst, usually added in the Fenton reaction as metal salt, is not easy to be retained in the degradation process; therefore, continuous addition of the catalyst is necessary to sustain the reaction [10]. However, this will increase the metal ions in the process which will lead to difficulties in post-treatment and sludge production [10]. To overcome the disadvantages of homogeneous Fenton process, much attention had been focused on the development of heterogeneous catalyst. The heterogeneous method lays out that the iron catalyst will be present but not dissolved, being thus impregnated at the surface of a solid [11]. Therefore, leaching of iron ions from heterogeneous Fenton catalyst is limited and the catalyst can easily be recovered after the reaction [12]. Recently, some attempts had been made to develop heterogeneous Fenton catalysts such as, iron-containing mesostructured silica [7], nanomagnetite [13], acid-activated fly ash [14], Fe–zeolite [15], Fe/clinoptilolite [16], $Fe_2(MoO_4)_3$ [17], mesoporous activated carbon [8], ceria-based catalysts [11], iron-containing ZSM-5 zeolites [12], chromium-substituted magnetite [18], copper–iron bimetal modified PAN fibre complexes [1], mesoporous Fe_2O_3–SiO_2 composite [4], ball clay [9], Fe_3O_4/MWCNTs [19], etc. for the removal and degradation of various organic pollutants from aqueous solution. Iron-containing mesostructured silica was found as an efficient heterogeneous Fenton catalyst for the removal of C.I. Acid Orange 7 from aqueous solution [7]. Magnetite has the ability to degrade more than 90% of p-nitrophenol after 10 h of reaction time under the optimum conditions of 1.5 g/L Fe_3O_4, 620 mM H_2O_2 and pH 7 [13]. Similarly, 98% of p-Nitrophenol degradation was observed in the case of nitric acid-treated fly ash at optimal conditions [14]. Iron-loaded clay was also found as an efficient heterogeneous Fenton catalyst for the degradation of phenol [16] and dyes [12,15]. Ceria-based iron catalysts had proved their good performance enhancing the removal of organic compounds, reducing toxicity and improving biodegradability of phenolic wastewaters [11]. Cu–Fe bimetal amidoximated PAN fibre complexes have higher dye degradation efficiency in water than Fe-amidoximated PAN fibre complex [1]. At the same time, 94% of 100 mg/L Acid Orange II at neutral pH was effectively degraded by the catalytic action of $Fe_2(MoO_4)_3$ [17]. These studies indicate that by combining the efficiency of the homogeneous Fenton process with the advantages of heterogeneous catalysts show great promise for the treatment of dyes [12].

Magnetite has been proved as an efficient heterogeneous Fenton catalyst for the removal of dyes [18], 17α-methyltestosterone [19], p-nitrophenol [13], etc. Liang et al. [18] used chromium-substituted magnetite for the degradation of aqueous methylene blue and acid orange II. Laboratory-prepared inverse-spinel ferroferric oxide nanoparticles-decorated multiwalled carbon nanotubes have been used effectively for the degradation of 17α-methyltestosterone [19]. But less attention has been made for comparative studies in most of the cases. Therefore, the present study compares the performance of laboratory-prepared magnetite with conventional Fenton process using $FeSO_4$ for the removal of reactive dye Magenta MB (MMB) from aqueous solution. The effect of operational parameters, namely, pH, dosage of catalyst, dosage of H_2O_2 and initial concentration of the dye were evaluated. The influence of inorganic ions and ligands in the Fenton process were also examined.

2. Materials and methods

2.1. Chemicals and reagents

The $FeSO_4.7H_2O$, $FeCl_3$, 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.

In this study, MMB which is a reactive dye has been selected as a model dyeing pollutant because of its widespread application and recalcitrant nature. All fibre-reactive dyes are anionic, since they have negative molecular charges. Therefore, MMB is also an anionic dye. Fig. 1 shows the structure of MMB and the properties of MMB are given in Table 1. The MMB stock solution was made up to a concentration 1,000 mg/L by diluting one gram of dye salt in 1 L distilled water and was subsequently diluted to the required concentration. These solutions were used for batch study.

In this study, $FeSO_4{\cdot}7H_2O$ and Fe_3O_4 were used as catalyst for the homogeneous and heterogeneous Fenton processes, respectively. A recent study revealed that the reaction of Fe_3O_4 and H_2O_2 generated hydroxyl and perhydroxyl radicals [20]. Fe_3O_4 was prepared by taking $FeSO_4.7H_2O$ and $FeCl_3$ in the ideal molar ratio of Fe^{2+}/Fe^{3+} of 0.5 and mixed in 100 mL deionised water. 8 M NaOH solution was added drop wise to this solution under vigorous stirring. This solution was mixed for a half an hour. The black precipitate that was formed was filtered and washed with deionised water and ethanol. Finally, the products were dried in room temperature. Eq. (4) indicates the formation of magnetites [20,21]. All the experiments were carried out twice and the error in the experimental was very less and insignificant.

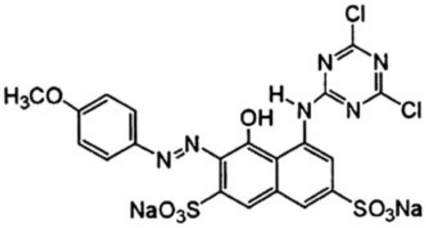

Fig. 1. MMB structure.

Table 1
Properties of MMB

Type	Reactive dye
Molecular formula	$C_{20}H_{12}Cl_2N_5Na_2O_8S_2$
Molecular weight	631.36
Molecular structure	Azo class
λ_{max}	532.5 nm

$$2Fe^{3+} + Fe^{2+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O \tag{4}$$

The properties of magnetite (Fe_3O_4) are given in Table 2. Scanning electron microscopy (SEM) investigations of the magnetite samples were conducted in a JEOL JMT-300 operated at 15 kV. The SEM analysis was done at $1{,}000 \times g$ magnification (Fig. 2). From their SEM images, most of the particles were found to be of less than 10 μm in size. A test with the magnet showed that all the prepared samples are magnetic and completely attracted to the magnet, which is helpful for their practical application in wastewater decontamination with facile recycle.

The point of zero charge (PZC) was determined using the solid addition method [22] viz: a series of 100 mL conical flasks, 45 mL of 0.1 M KNO_3 solution was transferred. The pH_0 values of the solution were roughly adjusted from 2 to 10 by adding either 0.1 N HNO_3 or NaOH. The total volume of the solution in each flask was made exactly to 50 mL by adding the KNO_3 solution. The pH_0 of the solutions were then accurately noted. Magnetite (1 g) was added to each flask and securely capped, immediately. The suspension was then manually agitated. The pH values of the supernatant liquid were noted. The difference between the initial and final pH (pH_f) values ($\Delta pH = pH_0 - pH_f$) was plotted against the pH_0. The point of intersection of the resulting curve is the one at which pH_0 gave the PZC. Several experimental data

Table 2
Properties of magnetite

Formula	Fe_3O_4
System	Isometric
Colour	Greyish black
Molecular weight	231.5
Specific gravity	4.9–5.2

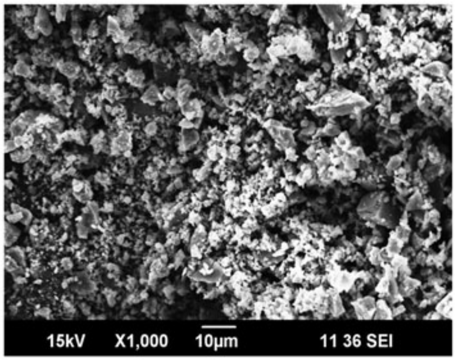

Fig. 2. SEM image of magnetite samples.

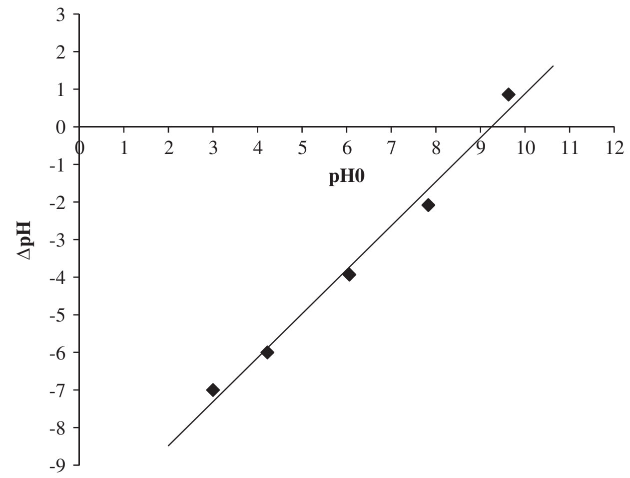

Fig. 3. Point of zero charge of magnetite.

of PZC for iron oxides are available in the literature, the values fall between 3.8 and 9.9 for magnetite [23]. It can be inferred from Fig. 3 that the PZC for the magnetite samples used in this work was around nine. Therefore, below nine the surface of the magnetite samples is positively charged.

2.2. Dye removal study and its analysis

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 was 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. Samples were withdrawn at regular intervals of time for analysis. The same procedure was adopted for studying the effects of other parameters and stability of Fe_3O_4 catalyst.

The pH of the solution was measured using Orion EA 940 Ion analyser (Thermo, USA). The UV–vis spectra of MMB was recorded using a UV–vis spectrophotometer (Lambda 25, Perkin Elmer, USA) with a silica cell of path length 1 cm. The maximum absorbance wavelength ($\lambda_{\max}$) of Magenta MB was found at 532 nm using the UV–vis spectrophotometer. The decolourisation efficiency (%) of Magenta MB was defined as follows:

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

where C_0 (mg/L) is the initial concentration of Magenta MB and C_t (mg/L) is the concentration of MMB at reaction time, t (min).

3. Results and discussion

3.1. Effect of catalyst dosage

The effect of catalyst dosage was investigated by varying the dosage of $FeSO_4$ from 40 to 500 mg/L in the homogeneous Fenton system and from 400 to 800 mg/L in the case of heterogeneous Fenton system. For both homogeneous and heterogeneous Fenton systems, the experiments were conducted under the following conditions: MMB concentration of 50 mg/L, H_2O_2 concentration of 0.22 M and solution pH of 3. Fig. 4 illustrates the MMB removal efficiency of Fenton process as a function of time at varying catalyst dosages. In both the cases, the rate of dye removal is fast at the beginning of the reaction due to the high initial concentration of catalyst and then it drastically decreases due to the poor rate of regeneration [24]. An increase in MMB removal efficiency from 47 to 69% after 1 min of experiments was observed for homogeneous Fenton process when the catalyst concentration increased from 40 to 200 mg/L. The same trend was observed in the case of heterogeneous Fenton process when the catalyst dosage increases from 400 to 600 mg/L. The removal efficiency increased with the catalyst dosage due to more active iron sites on the catalyst surface for accelerating the decomposition of H_2O_2, and more iron leaching in the solution, leading to an increase in the number of OH radical [9]. Further increase in the catalyst concentration leads to decrease in MMB removal efficiency in both systems. This is due to the scavenging of $OH^\bullet$ by Fe^{2+} ions and inducing the formation of hydroxyl ion at higher concentration of catalyst as shown in Eq. (6) which favours the formation of $Fe(OH)_3$ [24]. Since, Fe^{2+} is the active catalyst for the Fenton reactions, the formation of its hydroxide complexes reduces the efficiency of the system. Thus, the optimum catalyst concentrations for homogeneous and heterogeneous Fenton processes were obtained as 400 mg/L and 600 mg/L, respectively. When the $FeSO_4$ dosage was 400 mg/L, an efficiency of 84.17% was obtained within 15 min for the homogeneous Fenton system; whereas for the heterogeneous Fenton system, the optimum catalyst dosage of Fe_3O_4 was observed to be 600 mg/L with a removal efficiency of 64.2% in 60 min.

$$OH^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \quad (6)$$

From Fig. 4, it can be also observed that the rate of dye removal is very high for homogeneous Fenton process than that of heterogeneous Fenton process. After first minute itself, $FeSO_4$ attained maximum dye removal efficiency, while magnetite obtained the optimal removal after 30 min of reaction. In conventional Fenton process, all the reagents and catalysts are in homogeneous form. This results in increased rate of reaction between hydrogen peroxide and iron species and forms abundant hydroxyl radicals. Thus, the rate of effective collision between hydroxyl radical and contaminants increased in the initial stages of reactions and results in high removal efficiency. But in heterogeneous Fenton process, the time for leaching of iron species reduces the dye removal rate. Lots of degradation by-products forms from these reactions. Therefore, more collision takes place between hydroxyl radical and by-products than that of dye molecules in later stages. This results in reduced rate of dye removal of Fenton process.

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. The selection of an optimum H_2O_2 concentration for the degradation of the dyes by Fenton's reagent is important from a practical point of view (due to the cost of H_2O_2) [25]. This effect was studied by varying the initial H_2O_2 concentration

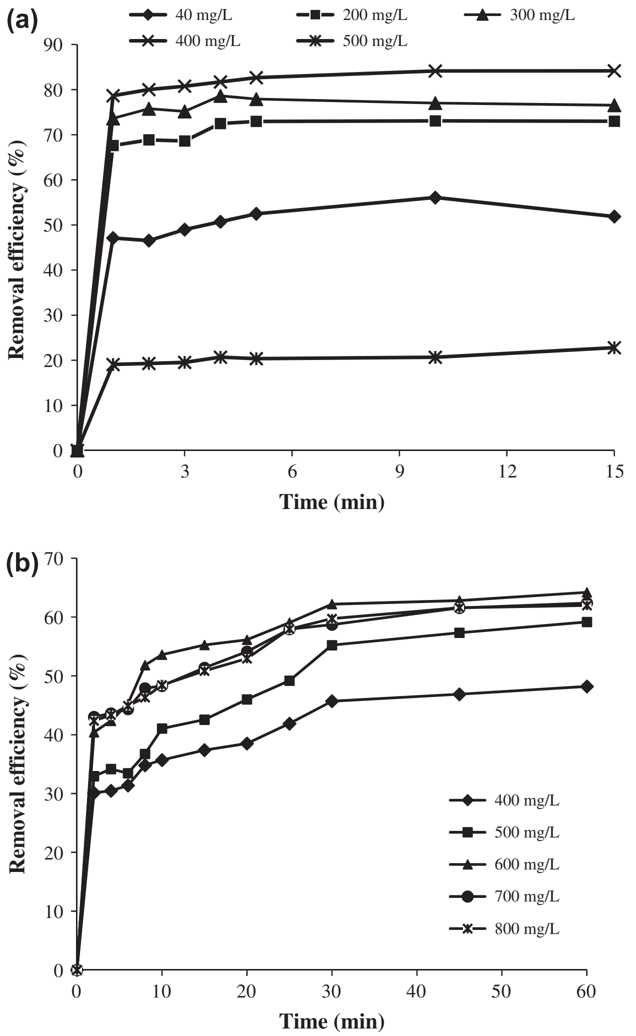

Fig. 4. Effect of catalyst dosage on the decolourisation (a) $FeSO_4$ (b) Fe_3O_4 reaction conditions: [MMB] = 50 mg/L, $[H_2O_2]$ = 0.22 M, pH = 3.

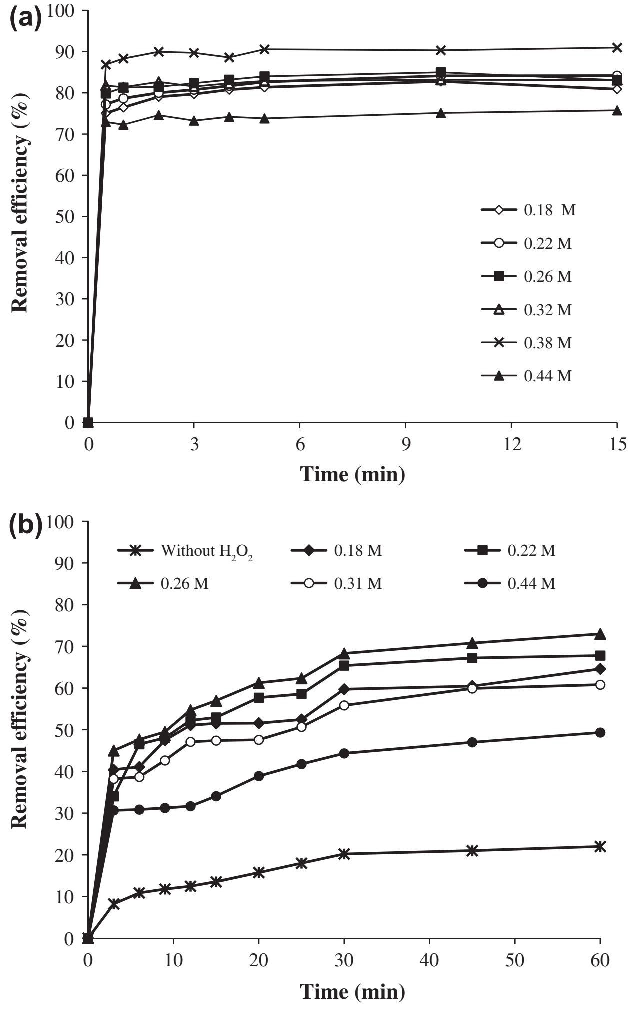

Fig. 5. Effect of H_2O_2 dosage on the decolourisation (a) homogeneous Fenton system: [MMB] = 50 mg/L, $[FeSO_4]$ = 400 mg/L, pH = 3, (b) heterogeneous Fenton system: [MMB] = 50 mg/L, $[Fe_3O_4]$ = 600 mg/L, pH = 3.

from 0.18 M to 0.44 M in the homogeneous Fenton system and from 0 to 0.44 M in the case of the heterogeneous Fenton system at optimal catalyst concentrations, while maintaining the other experimental conditions constant. The influence of various initial H_2O_2 concentrations on decolourisation is presented in Fig. 5. Initially, the removal efficiency increased with increasing H_2O_2 dosage mainly due to the effect of $OH^{\cdot}$ radicals produced additionally [24]. However, the increase of H_2O_2 further results in the decrease in dye removal process because surplus H_2O_2 molecules act as scavengers of hydroxyl radical to generate perhydroxyl radical (Eq. (7)), which has lower oxidation potential than the former [4]. When the H_2O_2 concentration was increased to 0.38 M, 90.9% removal could be achieved in 15 min in the homogeneous Fenton system; and for greater H_2O_2 concentration, a decrease in the removal was observed. Similar trend was even observed for the heterogeneous Fenton system. The optimal initial H_2O_2 concentration was obtained at 0.26 M with an efficiency of 71% for the heterogeneous Fenton system. In comparison to the homogeneous Fenton system, the H_2O_2 dosage was found to be lesser for the heterogeneous Fenton system. Without H_2O_2, the removal efficiency in the heterogeneous Fenton system was observed as 22%. This was mainly due to the adsorption of MMB on magnetite surface.

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

3.3. Effect of pH

The effect of solution pH on the decolourisation of MMB is shown in Fig. 6. The pH was varied from 2.5 to 3.5 in the case of homogeneous Fenton system and from 2 to 7 in the case of the heterogeneous Fenton system. The optimum pH for the homogeneous Fenton system was found to be around 3 with a removal efficiency of 90.99%. In this case, at pH values lower than 3, OH radicals production reduced due to the formation of the complex species $[Fe(H_2O)_6]^{2+}$ [26]. The low efficiency at lower pH could be attributed to the stabilisation of H_2O_2 that can form oxonium ion by solvating a proton [9]. An oxonium ion makes hydrogen peroxide electrophilic to enhance its stability and presumably to reduce substantially the reactivity with ferrous ion as follows: [9]

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \tag{8}$$

However, for the heterogeneous Fenton system, the lower pH was quite suitable as the optimum pH was found to be 2 with a removal efficiency of 86.86%. The need for lower pH may be due to the formation of more oxidant, i.e. the hydroxyl radical [4]. Again, also at lower pH the catalyst surface is positively charged which facilitates the adsorption of the negatively charged dye and hence enhancing the decolourisation [4]. The efficiency of both systems reduced on further increase in pH. This is mainly due to the formation of iron complexes and instability of H_2O_2. At higher pH, Fe^{3+} precipitates as $Fe(OH)_3$, causing H_2O_2 to be decomposed into O_2 and H_2O [27]. Under this condition, the removal of pollutant is mainly due to coagulation or sorption process and not by Fenton process [28].

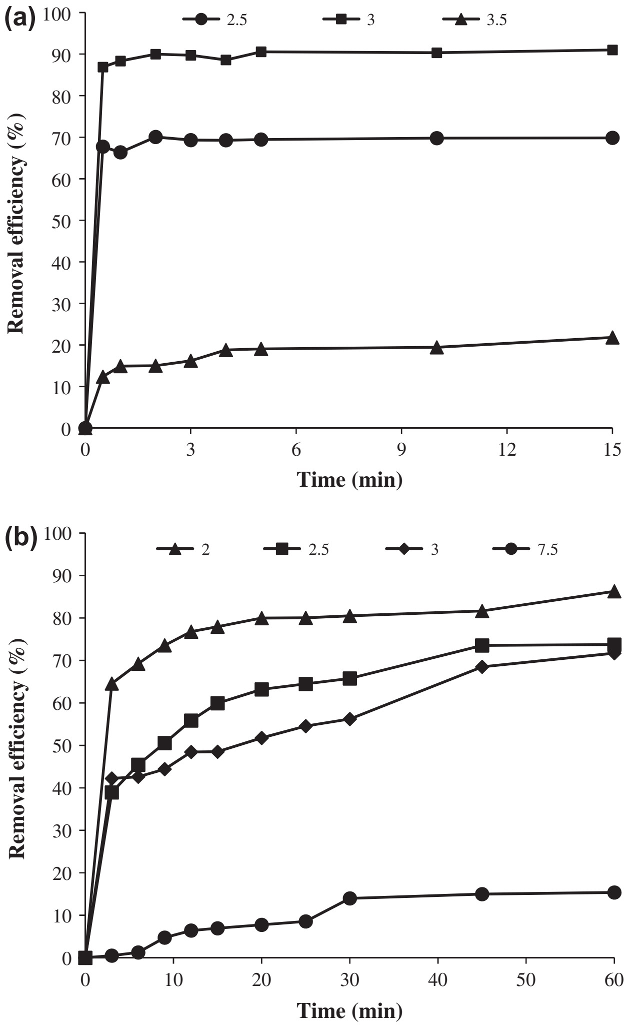

Fig. 6. Effect of pH on the decolourisation (a) homogeneous Fenton system: [MMB] = 50 mg/L, $[FeSO_4]$ = 400 mg/L, $[H_2O_2]$ = 0.38 M, (b) heterogeneous Fenton system: [MMB] = 50 mg/L, $[Fe_3O_4]$ = 600 mg/L, $[H_2O_2]$ = 0.26 M.

3.4. Effect of initial dye concentration

The influence of initial dye concentration was evaluated by varying the MMB concentration from 10 to 80 mg/L in both the systems and the obtained results are shown in Fig. 7. When the initial dye concentration was below and above 50 mg/L, the efficiency was found to be decreasing for both the cases. At initial dye concentration less than 50 mg/L, the collision frequency between Fe^{2+} (both homogeneous and heterogeneous processes) and dye is decreased. This causes the decrease in effective rate of dye removal [9]. Also, the concentrations of both homogeneous and heterogeneous catalysts and hydrogen peroxide required for the lesser dye concentration is also less than that of dye concentration 50 mg/L. This surplus reagent causes scavenging effects as in Eqs. (6) and (7). In the case of heterogeneous Fenton process, with the increase in initial concentration of the dye, more dye molecules were adsorbed onto the surface of magnetite catalyst. Thus, the reaction between the catalyst and the H_2O_2 was inhibited, thereby decreased the dye removal efficiency [29]. In addition to this, the intermediate products formed during dye oxidation probably compete with the dye molecules for the available Fe^{3+} active sites [4].

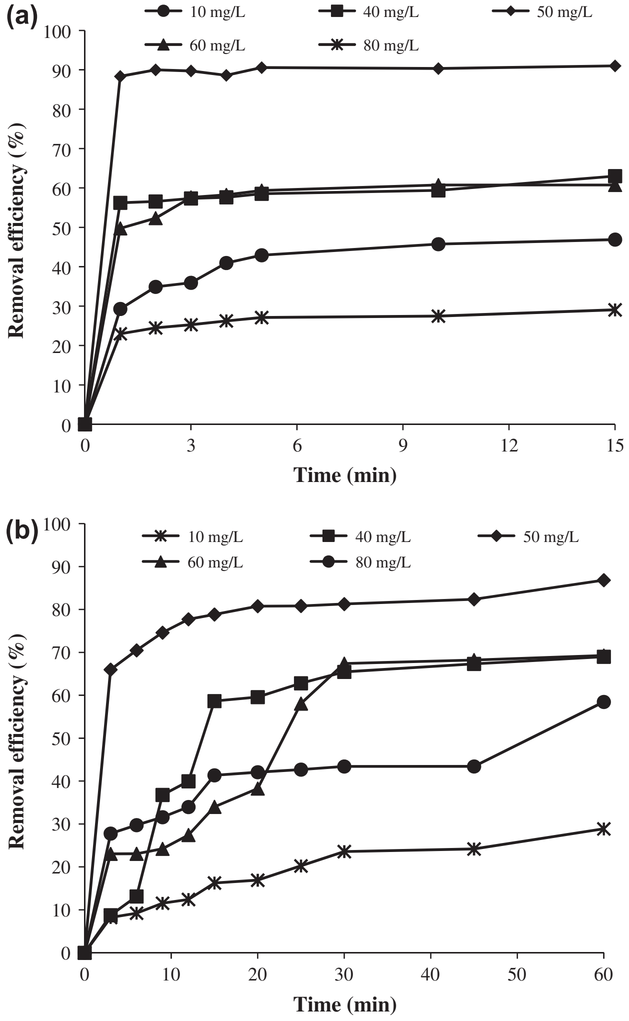

Fig. 7. Effect of initial dye concentration on the decolourisation (a) homogeneous Fenton system: $[FeSO_4] = 400$ mg/L, $[H_2O_2] = 0.38$ M, pH = 3 (b) heterogeneous Fenton system: $[Fe_3O_4] = 600$ mg/L, $[H_2O_2] = 0.26$ M, pH = 2.

3.5. Influence of inorganic ions and ligands on homogeneous Fenton process

The chemical analysis of industrial wastewaters revealed the presence of several ions such as: chloride, sulphate, nitrate, fluorides and carbonate. The performance of the oxidation process may be affected by the background impurities present in wastewaters [24]. To evaluate this influence, variable concentration of these salts and ligands were introduced into the system. The influence of inorganic ions (fluoride, chloride and sulphate ions) and ligands (EDTA and oxalate) in the homogeneous Fenton system is shown in Fig. 8. The removal efficiency was found to be decreasing with increasing salt/ligand concentration in each case. Oxalate ligand was found to have the greatest inhibition effect. The inhibition effect increases in the following order: $Cl^- < SO_4^{2-} \sim EDTA < F^- <$ oxalate. The unexpected matrix effect has several causes and it cannot be attributed to only one cause. Sometimes one parameter predominates, but other times different other parameters contribute to the inhibition effect [24]. With the addition of 12 mg/L NaCl, the removal

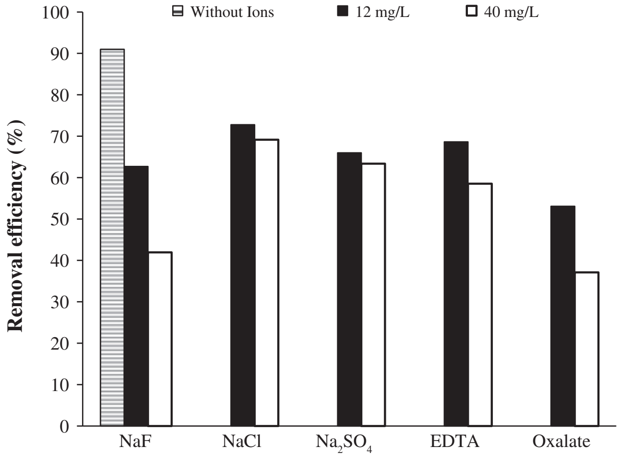

Fig. 8. Influence of inorganic ions and ligands in the Fenton system. Homogeneous Fenton system: reaction conditions: $[FeSO_4] = 400$ mg/L, $[H_2O_2] = 0.38$ M, [MMB] = 50 mg/L, pH = 3.

efficiency of Fenton process was reduced from 90% to 73%. And this removal efficiency was decreased to 69.1% by the addition of 40 mg/L NaCl. This inhibitive effect of chloride ions on the decolourisation of MMB can be explained by the scavenging effect of chloride ion on $^{\cdot}OH$, and chemical reactions are shown in Eqs. (9) and (10) [30]. Sulphate and EDTA addition shows higher scavenging effect on dye removal efficiency of Fenton process than chloride ions. The addition of 12 and 40 mg/L sulphate into the acidic dye solution decreased the efficiency of Fenton process by 31.5 and 37%, respectively. The addition of 12 and 40 mg/L EDTA decreased the dye removal efficiency of system to 68.6 and 58.5%, respectively. The scavenging effect of sulphate ions is mainly due to the formation of sulphate radicals by the reaction between sulphate ions and hydroxyl radicals as in Eq. (11) [31]. Reaction with hydroxyl radicals and complex formation with ferrous ions are the main inhibiting reactions occur in the case of EDTA addition [24]. Addition of fluoride and oxalate results in severe reduction in removal efficiency of Fenton process. The addition of 12 and 40 mg/L NaF reduced the dye removal efficiency of Fenton by 29 and 58%, respectively. At the same time, a reduction of 47 and 53% were noticed for the oxalate addition concentrations of 12 and 40 mg/L, respectively. In the case of fluoride ions, the formation of $FOH^{-\bullet}$ and ferric complexes are the main radical scavenging reactions [24]. The oxidative ability of Fenton process by the addition of oxalate was limited due to the stability of Fe^{3+}-oxalate complexes formed, so it is difficult for the Fe^{2+} to be regenerated from the complexes [32].

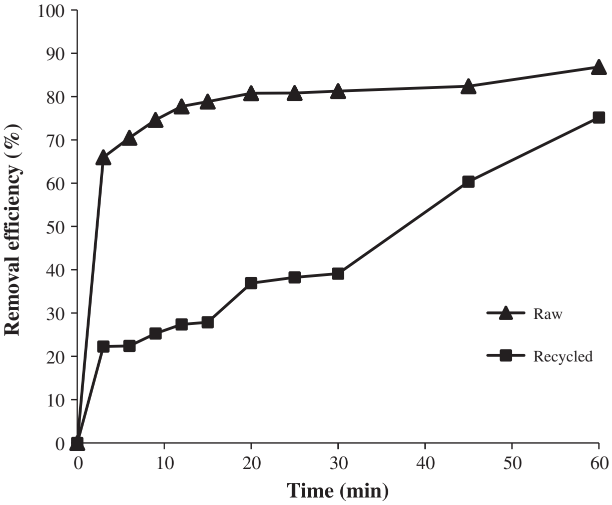

Fig. 9. Stability of Fe_3O_4 catalyst in the heterogeneous Fenton system: reaction conditions: $[Fe_3O_4] = 600$ mg/L, $[H_2O_2] = 0.26$ M, $[MMB] = 50$ mg/L, pH = 2.

$$Cl^- + OH \rightarrow ClOH^{\cdot -} \tag{9}$$

$$ClOH^{-\cdot} + Fe^{2+} \rightarrow Cl^- + OH^- + Fe^{3+} \tag{10}$$

$$OH^{\cdot} + SO_4^- \rightarrow OH^- + SO_4^{\bullet -} \tag{11}$$

3.6. Stability of Fe_3O_4 catalyst

In order to study the stability of Fe_3O_4 catalyst, the residue catalyst after many experiments were collected, filtered, washed with distilled water and dried in room temperature. This recycled catalyst was again utilised for conducting an experiment. It can be seen from Fig. 9 that the removal efficiency of the dye had decreased to 75.16 and 62.58% in 60 min for the recycled catalyst for the first and second runs, respectively. The rate of dye removal was reduced abruptly for the recycled magnetite particles. This is mainly due to the leaching behaviour of the heterogeneous catalyst. During the initial experiment, the iron species from the active sites of magnetite catalyst leached into the solution. This iron species reacts with hydrogen peroxide and forms hydroxyl radicals as in conventional Fenton process. But the leached iron species may not adsorb on the active sites of heterogeneous catalyst. This reduces the activity of recycled magnetite catalyst and shows a drastic reduction in rate of dye removal. Reduction of catalytic activity of recycled magnetite is also due to the poisoning of active catalytic sites by the adsorption of organic species [9].

3.7. Comparison of performance of homogeneous and heterogeneous Fenton systems

The time taken for the homogeneous Fenton system was found to be lesser in comparison to the heterogeneous Fenton system. This may be because the homogeneous catalyst gets uniformly mixed in the dye solution, while the heterogeneous catalyst being in solid form does not get mixed thoroughly. Also, the catalyst dosage for the homogeneous Fenton system was also found to be lesser than the heterogeneous Fenton system. In fact, improved mixing techniques used in heterogeneous catalysed reaction system may improve the dye removal efficiency of Fe_3O_4 catalyst. Both the catalysts performed well in the acidic range and had displayed similar removal efficiencies at various concentrations of the dye. However, it is the H_2O_2 dosage that chiefly decides the cost of the treatment system. In relevance to this, the heterogeneous catalyst was found to be better as it had lesser H_2O_2 dosage. In addition to this, Fe_3O_4

catalyst can be reutilised to give sufficient removal efficiency and also the separation of these catalysts from the effluent are 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.

4. Conclusions

Fe_3O_4 catalyst was found to be effective for the removal of the dye MMB. The optimal operating conditions for the heterogeneous Fenton system when Fe_3O_4 catalyst was used were 600 mg/L of catalyst dosage, and 0.26 M of H_2O_2 for 50 mg/L of initial dye concentration at an initial pH of 2 in 60 min. Dye removal efficiency of 86.8% was observed under these conditions. The optimal operating conditions for the homogeneous Fenton system when $FeSO_4$ catalyst was used were 400 mg/L of catalyst dosage and 0.38 M of H_2O_2 for 50 mg/L of initial dye concentration at an initial pH of 3 in 15 min. Dye removal efficiency of 90.9% was observed under these conditions. The addition of salts and ligands were found to be having an inhibiting effect. The inhibition effect increases in the following order: $Cl^- < SO_4^{2-} \sim EDTA < F^- <$ oxalate. The stability of Fe_3O_4 catalyst was examined by using the recycled catalyst. Dye removal efficiency has reduced to 62.58% in 60 min during this condition after two runs.

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