

## INFLUENCE OF CERTAIN INORGANIC IONS AND LIGANDS ON DEGRADATION OF METHYL RED BY FENTON'S REAGENT

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### ABSTRACT

Fenton's process is one of the most advanced methods for wastewater treatment. The speculations are that the performance of this process is greatly affected by the presence of certain ions. In this work the effect of some ions and ligands on the degradation of methyl red by Fenton's process have been investigated. The results showed that in general the matrix composition has a negative effect on the performance of Fenton's process. The inhibition effect varied with the nature and the concentration of the inhibitor ion. KBr was most influential inhibitor among the halides. Sulfate and nitrate ions have negligible inhibition effect on the degradation of methyl red compared to the other ions added. The inhibition effect of oxalate and EDTA ligands is much greater than that of the halides. The inhibition effect increases in the following order:  $\text{NO}_3^- \sim \text{SO}_4^{2-}$ , Cl, I, F, phosphate, Br, carbonate, oxalate, EDTA~ orthophenantroline. The most important possible reasons for this inhibition is the direct interaction between OH radicals produced during the process and negative ions or ligands present in solution and/or inhibition of OH radical production, through complex formation, in either the Fe(II)/H<sub>2</sub>O<sub>2</sub> stage or the Fe(III)/H<sub>2</sub>O<sub>2</sub> stage.

Keywords: Fenton's reagent, inhibition, azodye, matrix effect.

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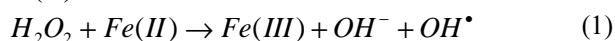
### INTRODUCTION

The Fenton's process is an advanced, promising oxidation method that is used for treatment of wastewaters obtained from several industries, such as textile and paper manufacturing industries. Such industries produce large quantities of effluents that contain significant concentrations of toxic compounds. These wastewaters are usually directly disposed off in rivers and other water courses. However, the discharge of this type of compounds has a negative impact on the environment, especially the aquatic life [1]. Therefore, the removal or the degradation of these dyes from wastewaters is a great challenge for the related industries as well as environmentally.

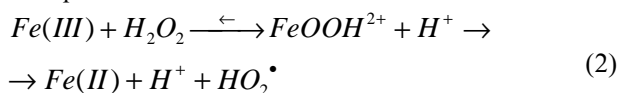
Several methods with different efficiency are being used for the removal of such dyes [2], as biological degradation, physicochemical treatment (coagulation-flocculation), classical filtration or adsorption [3-5] and

photodegradation [6]. However, these processes are either costly or inefficient and often produce high amounts of undesirable by-products.

Recent progress on the subject has led to the development of an advanced oxidation process (AOP) using Fenton's reagent. AOP is an oxidation process that produces hydroxyl radicals in sufficient amounts for treatment of wastewaters [7]. Hydroxyl radical (OH<sup>•</sup>) has high oxidizing power, next only to fluorine, and therefore has the ability to degrade the organic hazardous dyes to harmless substances, such as CO<sub>2</sub> and H<sub>2</sub>O [8, 9]. OH<sup>•</sup> is generated by the reaction between H<sub>2</sub>O<sub>2</sub> and Fe(II) ion:



The regeneration of Fe (II) from Fe(III) is a very slow process:



The rate of dye degradation is fast at the beginning of the reaction due to initial high concentration of Fe (II), and then it drastically decreases due to the poor rate of its regeneration [10].

Fenton's process is a promising wastewater treatment method due to its high oxidation power, cheap cost and its ease of operation [11]. The mechanism can not be considered as well-known, because of the numerous radical intermediate products [12].

The performance of the oxidation process may be affected by the background impurities present in wastewaters. Certain anions are common ions in wastewaters for instance, industrial dye manufacturing wastewater, may exhibit high concentration of chloride ions [13]. It may also contain phosphate, carbonate and nitrate ions [14, 15]. These ions are usually introduced during the various steps involved in textile processing [13].

It has been reported that the oxidation of aniline and the insecticide Dichlorovos by Fenton's reagent is inhibited by chloride ion [16,17]. Also the photocatalytic mineralization of  $\beta$ -naphthol in presence of  $\text{TiO}_2$  is also inhibited by chloride and Cr(III) ions, but increased in the presence of Cu(II) and Fe(III) [15]. Ashraf et al. observed a little increase in the percentage of methyl red degradation in presence of a chloride salt, a noticeable increase in presence of phosphate, but a large decrease in presence of Cu(II) [14]. As seen above there are a lot of contradictions in some previous results about the effect of some ions.

Therefore due to the great importance of this method, the effect of matrix composition on the efficiency of the process is explored in greater detail. The effect of various ions on the degradation of Methyl Red (MR) has been investigated. The ions added are  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , nitrate, phosphate, sulfate, and carbonate. The effect of some ligands such as oxalate, EDTA, and orthophentroline (ophen) has also been investigated. Some of them are not necessarily present in wastewater but they are chosen to understand better the matrix effect. Methyl Red was chosen as model for this study, since azodyes are an important dye group used in textile industry.

Most articles dealing with the degradation of organic compounds with Fenton's reagent suggested that the optimal conditions are obtained when the concentration of Fe(II) is less than that of  $\text{H}_2\text{O}_2$ , but there is

controversy about the best  $[\text{Fe(II)}]/[\text{H}_2\text{O}_2]$  ratio [18, 19]. These contradictions may be due to the fact that several parameters affect the oxidation efficiency such as initial concentrations of Fenton's reagent, dye concentration and its chemical structure, and temperature. For this reason, in this study and before studying the matrix effect on the degradation of MR some preliminary studies were performed to determine the optimal degradation conditions.

## EXPERIMENTAL

Methyl Red ( $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_2$ , molecular mass 269.31) was purchased from Fluka. The salts, ligands, and  $\text{H}_2\text{O}_2$  (35 % W/W) were obtained either from BDH or Merck industries. Mohr salt ( $(\text{NH}_4)_2\text{SO}_4\text{FeSO}_4\cdot 6\text{H}_2\text{O}$ ), which is used as a source for Fe(II), was obtained from BDH. MR solutions were prepared in distilled water without any further addition of ethanol since it usually stops Fenton's process [15]. 1 M solution of  $\text{H}_2\text{O}_2$  was prepared and stored in a refrigerator to maintain stability. Fe(II) was prepared as a 0.1 M solution in 0.01 M  $\text{H}_2\text{SO}_4$ . These initial solutions were used to prepare other solutions with variable concentrations which were prepared freshly on a weekly basis. UV-VIS studies were carried out using Specord 200, analytical Jena spectrophotometer, using a 1 cm quartz cell. pH adjustment was done with Crison pH-meter, GLP 22. FTIR spectra of the precipitate were recorded using Thermo, Nicolet IR 200 spectrophotometer in a wave range from 4000 to 400  $\text{cm}^{-1}$ .

Solutions of Fe(II) and  $\text{H}_2\text{O}_2$  with different concentrations:  $10^{-4}$  M,  $5 \times 10^{-4}$  M,  $10^{-3}$  M and  $5 \times 10^{-2}$  M were prepared from the initial solutions of Fe(II) and  $\text{H}_2\text{O}_2$  and were used for the preliminary study. Different or same concentrations were used for both Fe(II) and  $\text{H}_2\text{O}_2$  in order to prepare reaction mixtures of variable  $[\text{Fe(II)}]/[\text{H}_2\text{O}_2]$  ratios ranging between 0.005 and 5. Reaction mixtures (preliminary study) were obtained by mixing (in 100 ml beakers) the following solutions added in order: 5 ml of  $3 \times 10^{-4}$  M MR, 25 ml of distilled water, X ml of Fe(II) (by an increment of 2 ml up to 20 ml). The pH of the mixture was then adjusted to about 3.2 by adding several drops of 0.04 M  $\text{H}_2\text{SO}_4$  [18-20]. The obtained solutions were stirred using a magnetic stirrer. Fenton's process was then initiated by the addition of  $\text{H}_2\text{O}_2$  ((20-X) ml) and the absorbance at 515 nm

( $\lambda_{\max}$  of the acidic form of MR) was recorded immediately. The total volume of the reaction mixture was equal to 50 ml every time. Since in the Fenton's process, the degradation occurs via two stages, fast (Fe(II)/H<sub>2</sub>O<sub>2</sub> stage) then slow (Fe(III)/H<sub>2</sub>O<sub>2</sub> stage) [19], the data was recorded every 2 s in the first stage and every 20 s in the second stage. All experiments were conducted at room temperature and monitored for 16 min.

For the purpose of our study, examining the matrix effect on MR degradation, the experiments were carried out based on the results obtained in the preliminary studies as: 4 ml of 3x10<sup>-4</sup> M MR solution were mixed with 10 ml of 5x10<sup>-4</sup> M Fe (II), Y ml of 1M solution of halide or 10<sup>-3</sup> M solution of ligands (by an increment of 2 ml up to 10 ml) and (25 - Y) ml of distilled water were then added. The pH<sub>0</sub> was adjusted to ~ 3.2 by the addition of few drops of 0.04 M H<sub>2</sub>SO<sub>4</sub>. Finally, 10 ml of 10<sup>-3</sup> M H<sub>2</sub>O<sub>2</sub> were added and the absorbance at 515 nm was recorded immediately. The [Fe(II)]/[H<sub>2</sub>O<sub>2</sub>] ratio remained constant and equal to 0.5 in this part. The total volume of the reaction mixture was equal to 50 ml and the reaction was monitored for 16 min (as in the preliminary study).

## RESULTS AND DISCUSSION

### Determination of the best [Fe(II)]/[H<sub>2</sub>O<sub>2</sub>] ratio for optimum MR degradation

The principle aim of this work is to study the influence of certain ions and ligands on the degradation of MR by Fenton's process. However preliminary experiments were performed for the purpose of finding the optimal conditions for the degradation reaction of MR using Fenton's reagent. The results of these preliminary experiments indicated that a better performance occurred when all the amount of H<sub>2</sub>O<sub>2</sub> is added at once, rather than successively, at the beginning of the reaction.

As seen in Fig. 1 the UV-VIS spectra of one of the preliminary experiments, showed that the absorbance at 515 nm ( $A_{515}$ ), which corresponds to the chromophore -N=N- present in MR, decreased quickly at first then it slowed down with time. It decreased linearly at least in the first 50 s as seen in Fig. 2. It was also observed that in certain mixtures, the absorbance decreased at the beginning of the reaction but after ~ 300 s, it increased again. This phenomenon is related to the formation of ferric salt precipitate (Fig. 2).

The best degradation conditions (cleavage of the azo bond) were estimated by studying the percentage of degradation and the rate of degradation (M.s<sup>-1</sup>) during the first 50 second (slope of the curve [MR] vs. time). The percentage of degradation is defined as

$$\frac{(A_o \times f - A_e)}{A_o \times f} \times 100$$

where  $A_o$ , and  $A_e$  correspond to  $A_{515}$  before adding H<sub>2</sub>O<sub>2</sub>, and at the end of the experiment (16 min), respectively. The term  $f$  corresponds to the dilution factor (for example in the preliminary study

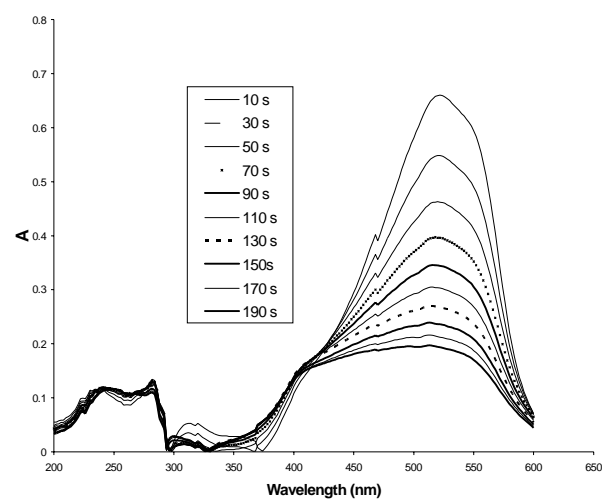


Fig. 1. UV-visible spectra of MR during egradation by Fenton's process. 3x10<sup>-5</sup> M MR, [Fe(II)]=[H<sub>2</sub>O<sub>2</sub>]= 2x10<sup>-4</sup> M, pH<sub>0</sub>:3.2, 293 K.

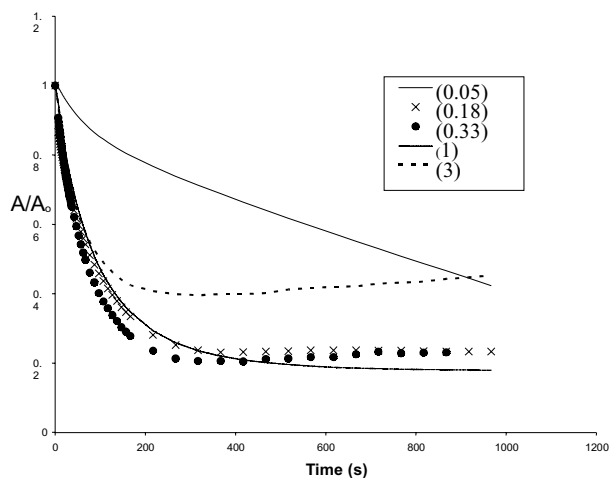


Fig. 2. Effect of [Fe(II)]/[H<sub>2</sub>O<sub>2</sub>] ratio on Fenton's process: Variation of  $A/A_0$  at 515 nm vs. time. 3x10<sup>-5</sup> M MR, pH<sub>0</sub>~ 3.2.

$$f = \frac{30 + X}{50} ml).$$

The relative error of percentage of degradation is  $\pm 3\%$ .

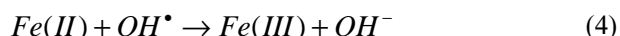
The results showed that no degradation of MR is obtained in the absence of either  $H_2O_2$  or Fe(II), both has to be present. Also degradation does not occur when the concentration of Fe(II) and  $H_2O_2$  is low ( $10^{-4}$  M). However, at a higher initial concentration of the Fenton's reagent ( $5 \times 10^{-2}$  M) the decolouration is very fast and presumably complete but is accompanied by the appearance of a brown–yellow precipitate. The FTIR spectrum of the dried precipitate (at 383 K) showed a large band between 3100 and 3500  $cm^{-1}$  which is due to the O-H bond. This could be related to the formation of  $Fe(OH)_3$  or other hydrated ferric salts [21], (Fig. 3). The narrow band at 1120  $cm^{-1}$  is attributed to S=O already present in the solution.

The best percentage of degradation and the best degradation rates were obtained when  $[Fe(II)]/[H_2O_2]$  ratio was between 0.5 and 1, (Fig. 4). Further experiments, carried out with fixed initial concentration of Fe (II) ( $5 \times 10^{-4}$  M) and variable initial concentration of  $H_2O_2$  gave similar results.

When  $H_2O_2$  is present in high concentration with respect to that of Fe(II) a decrease in the final color leaching occurs. This is possibly due to the competition between the dye and  $H_2O_2$  (Eq. 3) for  $OH^\bullet$ , since  $OH^\bullet$  is quite non-selective [19]:



Also an increase in the  $[Fe(II)]/[H_2O_2]$  ratio implies higher Fe(II) loads, excess Fe(II) may however lead to a loss of  $OH^\bullet$  species according to the following scavenging reaction [19]:



Therefore, for the matrix effect study, performed afterwards, and based on our results, intermediate concentrations of the Fenton's reagent were chosen. The amounts selected for the study are:  $2.4 \times 10^{-5}$  M MR,  $10^{-4}$  M Fe(II) and  $2 \times 10^{-4}$  M  $H_2O_2$ . The  $[Fe(II)]/[H_2O_2]$  ratio is 0.5.

#### Effect of initial pH

The performance of the Fenton's process depends mainly on the concentration of hydroxyl radicals produced in the reaction mixture. The pH of the reaction

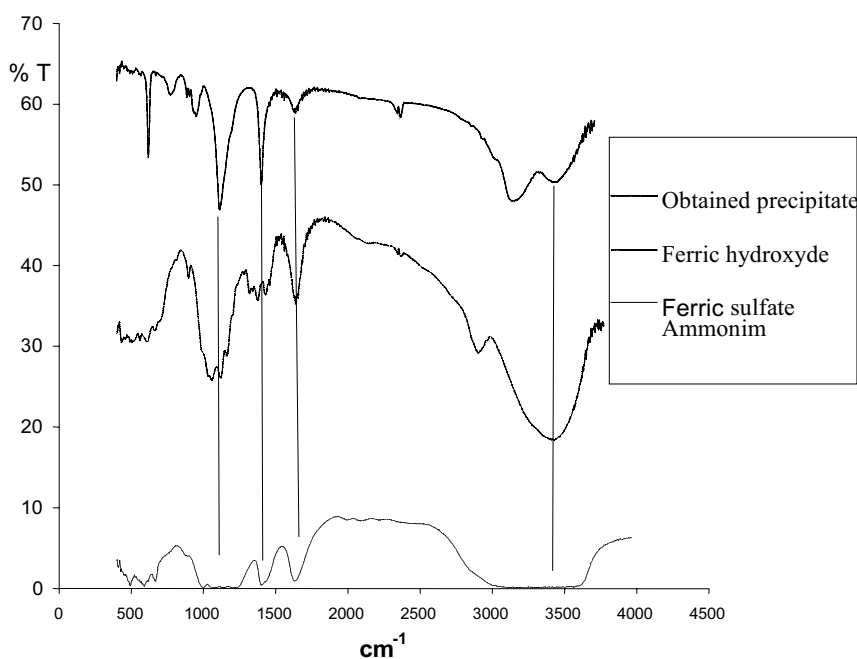


Fig. 3. FTIR spectrum of the precipitate obtained during Fenton's reagent.

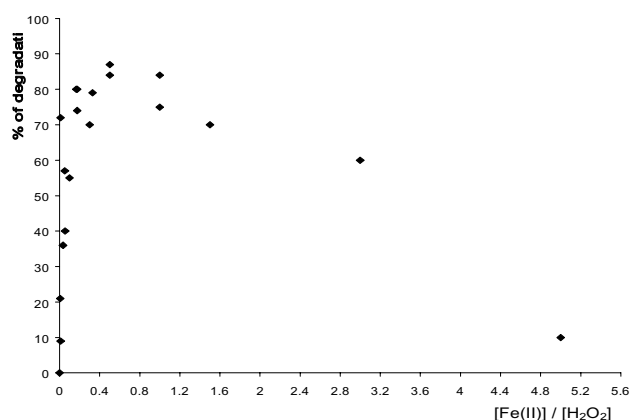


Fig. 4. Variation of the degradation percentage as a function of  $[\text{Fe(II)}]/[\text{H}_2\text{O}_2]$  ratio.  $\text{pH}_0 \sim 3.2$ ,  $3 \times 10^{-5}$  M MR, T: 293 K.

mixture affects the amount of OH radicals produced. Therefore, controlling the pH between 2 and 4 is a very important factor for an efficient treatment of wastewaters [22, 23].

The experimental results showed that at pH less than 3.0 and higher than 4.0 the degradation of MR was negligible. The degradation of MR at pH 4 is 50 % and at pH 3.2 is 88 %. At pH lower than 3, the Fenton's reactions (Eqs. (1) and (2)) slow down probably because  $\text{H}_2\text{O}_2$  becomes non-reactive due to the formation of the stable  $\text{H}_3\text{O}_2^+$  ions [24]. At pH higher than 4, the oxidation efficiency rapidly decreases, due to the decomposition of  $\text{H}_2\text{O}_2$  [24]. So it is preferable to work in a pH range between 3 and 4. This range of pH yield high amount of OH radicals and is in accordance with the published results. The pH of the solution remained constant through out the reaction. The use of  $\text{KH}_2\text{PO}_4$  buffer to adjust the pH is to be avoided since it accelerates the precipitation of Fe(III) and so affects the absorbance accuracy.

#### Effect of MR concentration

The extent of degradation of a certain dye depends largely on its concentration. Contradicting results about the effect of dyes concentrations on the degradation percentage have been reported. For example Banerjee et al. observed that the degradation of Eosine increases with the increase of its concentration [25]. Whereas other publications reported a decrease in the degradation of Amido black 10B and Malachite Green with the increase of their concentrations in the reaction

mixture [24, 26]. For this reason, several experiments have been conducted in this work to confirm the relation between the concentration of MR and the extent of degradation. In these experiments, various concentration of MR were used, while other conditions were held constant ( $10^{-4}$  M Fe(II),  $2 \times 10^{-4}$  M  $\text{H}_2\text{O}_2$ ,  $\text{pH}_0 \sim 3.2$ ). The results showed that as the concentration of MR increased (Table 1) the percentage of degradation decreased, but an increase in the initial rate occurred. This behaviour is reasonable and can be explained as follows: since the amount of  $\text{OH}^{\bullet}$  produced is constant, the percentage of MR degradation is more complete for lower MR concentrations.

#### Matrix effect

The chemical analyses of industrial wastewaters revealed the presence of several ions such as: chloride, sulfate, nitrate and carbonate [14]. The matrix composition is related to the chemical reagents used in industrial factories.

To evaluate the matrix effect on the performance of Fenton's process, variable concentrations of some ions and ligands are introduced into the reaction mixture. The optimal conditions obtained for Fenton's reagent were used ( $10^{-4}$  M Fe(II),  $2 \times 10^{-4}$  M  $\text{H}_2\text{O}_2$  ( $[\text{Fe(II)}]/[\text{H}_2\text{O}_2] = 0.5$ ),  $2.4 \times 10^{-5}$  M MR, and  $\text{pH} \sim 3.2$ ).

#### Effect of KI

Iodide ion does not form complexes with Fe(III)/Fe(II) system. According to gamma rule, iodide ion ( $E^\circ 0.62$ ) can be oxidized by  $\text{H}_2\text{O}_2$  ( $E^\circ 1.78$  V) to produce  $\text{I}_2$  and  $\text{H}_2\text{O}$  [27]. Therefore, it is expected that the presence of iodide ions with Fenton's reagent affects the Fe(II)/ $\text{H}_2\text{O}_2$  stage and consequently affects strongly the percentage of degradation and the degradation rate of MR. Some of the  $\text{H}_2\text{O}_2$  will react with the iodide ions present and consequently the  $[\text{Fe(II)}]/[\text{H}_2\text{O}_2]$  ratio will increase. Experimentally, we observed an inhibition effect which

Table 1. Variation of degradation percentage, and degradation rate as a function of MR concentration.

[MR](M)	% of Degradation after 16 min	Initial rate $\times 10^{-9}$ ( $\text{M.s}^{-1}$ )
$1.2 \times 10^{-5}$	94	6.7
$1.5 \times 10^{-5}$	88	7.4
$2.4 \times 10^{-5}$	85	8.0
$3.6 \times 10^{-5}$	75	9.5

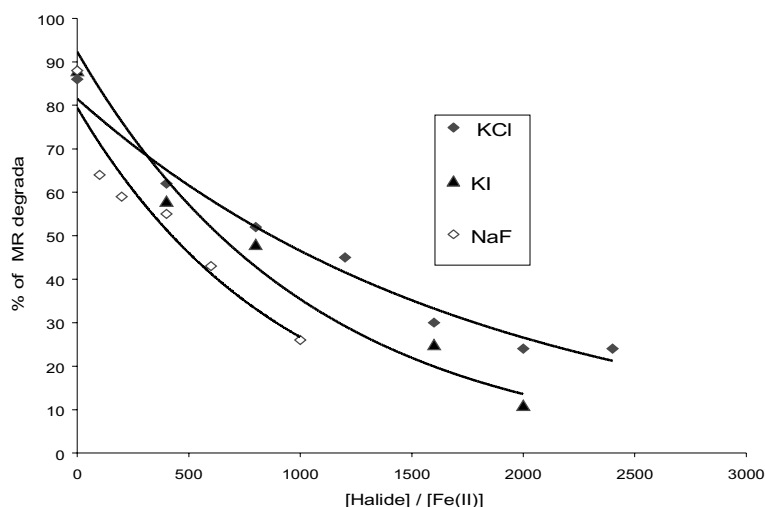


Fig. 5. Variation of degradation percentage of MR as a function of  $[\text{Halide}] / [\text{Fe(II)}]$  ratio,  $2.4 \times 10^{-5}$  MMR,  $2 \times 10^{-4}$  M  $\text{H}_2\text{O}_2$ ,  $10^{-4}$  M Fe(II),  $\text{pH}_0 \sim 3.2$ .

increased with the increase of halide concentration (Fig. 5). With KI, the inhibition follows an exponential decay with  $R^2$  0.95. The formation of iodine was observed by the increase of the absorbance at 360 nm. The presence of large concentration of KI does not completely stop MR degradation, most probably because the reactions  $\text{H}_2\text{O}_2/\text{Fe(II)}$  and  $\text{H}_2\text{O}_2/\text{I}^-$  occur simultaneously.

#### Effect of KCl

It has been reported previously that the chloride ion inhibits the action of Fenton's reagent [12, 13]. But the reason of this inhibition has been interpreted differently. Some researchers attributed the chloride inhibition to the formation of  $\text{ClOH}^{\bullet}$ , which is less oxidant than  $\text{OH}^{\bullet}$  [14, 15], while others explained it as due to the formation of ferric complexes with  $\text{Cl}^-$  which slows down the regeneration of Fe(II) [17]. The inhibition via the formation of  $\text{ClOH}^{\bullet}$  is more probable since it is possible that the sulfate ions that are already present in the solution form more complexes with Fe(II) and Fe(III) [28]. The percentage of degradation of MR in presence of variable concentration of KCl follows an exponential decay ( $R^2$  0.99) as in the case of NaF and KI, (Fig. 5). The inhibition effect of halides increases in the following order:  $\text{KCl} < \text{KI} < \text{NaF}$ . It seems that there is no correlation between the strength of inhibition and polarizability or electronegativity of the halide. NaF has the largest inhibition effect, since it inhibits  $\text{Fe(II)}/\text{H}_2\text{O}_2$

and  $\text{Fe(III)}/\text{H}_2\text{O}_2$  stages. All the halides must be present in considerable concentrations with respect to Fenton's reagent to have a noticeable inhibition effect.

The variation of degradation percentage vs. time for several chloride concentrations are shown in Fig. 6. Although the percentage of degradation depends on the chloride ion concentration, it follows a common pattern. This behaviour can be explained as due to the decrease of OH radicals available to attack MR as follows:



Whatever the chloride concentration or ( $[\text{Cl}^-]/[\text{Fe(II)}]$  ratio) the inhibition effect remain the same during the course of the reaction (60 min). These results are in contradiction with those obtained by Lu who suggested that the inhibition effect of chloride at a ratio  $[\text{Cl}^-]/[\text{Fe(II)}] < 200$  can be overcome with time [17].

The possibility of partial elimination of chloride inhibition effect was also studied. The  $[\text{Cl}^-]/[\text{Fe(II)}]$  ratio was held constant (800). The experiment was first conducted with  $[\text{Fe(II)}]/[\text{H}_2\text{O}_2]$  ratio equal to 0.5, then the concentration of one of the two reagents was increased while the concentration of the other one was kept constant as illustrated in (Table 2). The results showed that the chloride inhibition effect can be overcome slightly by increasing either the concentration of  $\text{H}_2\text{O}_2$  or Fe(II).

### Effect of NaF

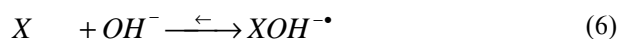
The fluoride ion does not react with  $H_2O_2$  and does not form complexes with Fe(II); but it forms successive complexes with Fe(III) ranging from  $[FeF]^{2+}$  to  $[FeF_3]$  [27]. It was chosen in order to investigate the mechanism of inhibition. However, theoretically if  $F^-$  does not capture  $OH^\bullet$ , the degradation of MR in the first stage must remain constant. Experimentally it was found that the degradation rate in the first stage decreased with the increase of the fluoride ion concentration in the reaction mixture. For example the initial rate of degradation decreased by 50 % for  $[NaF]/[Fe(II)]$  ratio equal to  $10^3$ . The percentage of degradation follows an exponential decay with  $R^2$  0.95, (Fig. 5). So most probably the inhibition by  $F^-$  is not only due to complex formation with Fe(III) which prevents the regeneration of Fe(II), but also due to a decrease in  $OH^\bullet$  production in the first stage via the formation of  $FOH^\bullet$ . According to our results, fluoride ions have a negative influence in both stages.

### Effect of KBr

Bromide ion does not form complexes with Fe(II)/Fe(III) system, so its inhibition via complex formation is to be eliminated. For high initial concentrations of KBr ( $10^{-1}$  and 1 M), the addition of small volume of KBr to the reaction mixture inhibited the oxidation process by Fenton's reagent completely. So for bet-

ter understanding, the effect of KBr was monitored by using lower initial concentration ( $10^{-2}$  M). The percentage of degradation decreased exponentially ( $R^2$  0.95) with the increase in KBr concentration, (Fig. 7). It seems that the inhibition effect of  $Br^-$  is due to its reaction with  $OH^\bullet$  to form  $BrOH^{\bullet-}$  and/or  $Br_2$  (as tested by fluorescein). These two species of bromine are less oxidant than  $OH^\bullet$ .

The inhibition effect of KBr is much greater than that observed for the other halides. This can be explained as due to the fact that the reaction between  $OH^\bullet$  with  $Br^-$  (Eq. (6)) is more shifted to the right than that with  $Cl^-$  and  $F^-$ :



It seems that each halide inhibits Fenton's process differently, some has an effect on the Fe(II)/ $H_2O_2$  stage such as KI and KBr, others such as NaF has an effect on both stages.

### Effect of phosphate, sulfate, nitrate, and carbonate

It is well known that phosphate ion forms complexes with Fe (II) and Fe (III), where Fe(III)-phosphate complexes are more stable than those of Fe(II)-phosphate. The stability of Fe(III) complexes increases in the following order: chloride, sulfate, phosphate. For initial high concentrations of  $KH_2PO_4$ , between 0.1 M and 1 M, the inhibition effect is complete. But with lower initial concentration ( $10^{-2}$  M) the MR degrada-

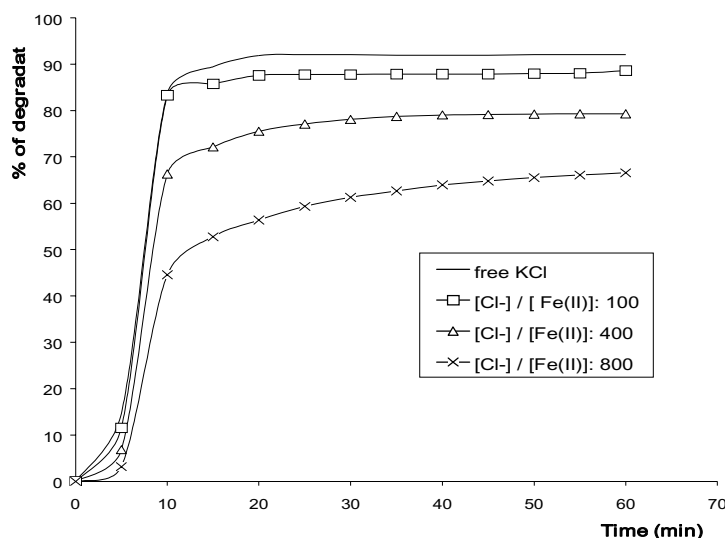


Fig. 6. Effect of  $[chloride] / [Fe(II)]$  ratio on MR degradation by Fenton's reagent.  $2.4 \times 10^{-5}$  M MR,  $2 \times 10^{-4}$  M  $H_2O_2$ ,  $10^{-4}$  M Fe(II) ( $[Fe(II)]/[H_2O_2]:0.5$ ),  $pH_0 \sim 3.2$

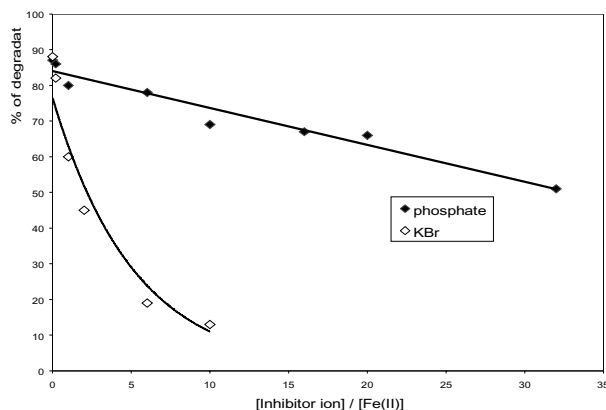


Fig. 7. Inhibition effect of bromide and phosphate  $2.4 \times 10^{-5}$  M MR,  $2 \times 10^{-4}$  M  $\text{H}_2\text{O}_2$ ,  $10^{-4}$  M Fe(II) ([Fe(II)]/[ $\text{H}_2\text{O}_2$ ]:0.5),  $\text{pH}_0 \sim 3.2$ .

tion decreased linearly ( $R^2 = 0.94$ ) with the increase of the  $\text{KH}_2\text{PO}_4$  concentration in the reaction mixture from  $2 \times 10^{-5}$  M to  $3 \times 10^{-3}$  M, (Fig. 7). Our results are in contradiction with those obtained by Ashraf et al., who found a remarkable increase in the percentage of degradation of MR in presence of calcium phosphate [14]. This increase in percentage of MR degradation is hard to understand since most studied salts have inhibited Fenton's process. Phosphate ions interact with  $\text{OH}^\bullet$ , so it is expected that  $\text{H}_2\text{PO}_4^-$  ions compete with organic compounds present in MR for  $\text{OH}^\bullet$ . This competition slows down the oxidation rate. The inhibition effect with phosphate is lower than that with bromide ion, (Fig.7). Therefore, and based on our results, it can be concluded that complex formation with the iron system is not the only important factor affecting the Fenton's process inhibition.

The presence of sulfate ( $\text{Na}_2\text{SO}_4$ ) or nitrate ( $\text{NaNO}_3$ ) in large concentration (0.1M) has a negligible effect on the performance of Fenton's reagent. Their inhibition effect is minimal compared to that of the other ions used in this study. Perhaps there is no interaction between them and  $\text{OH}^\bullet$ , due to electronic resonance of sulfate and nitrate. Carbonate ion usually form a precipitate with Fe(II) ( $\text{pK}_{\text{sp}}$  of  $\text{FeCO}_3$  10.58). According to the  $\text{pK}_a$  values of  $\text{H}_2\text{CO}_3$ , at  $\text{pH} \sim 3.2$ , carbonate is mainly present as  $\text{H}_2\text{CO}_3$ . The presence of carbonate ions in the reaction mixture is expected to decrease the amount of Fe(II) available to react with  $\text{H}_2\text{O}_2$ . The curve percentage of degradation vs. [carbon-

ate]/[Fe(II)] ratio showed a sigmoidal shape, (Fig. 8). For [carbonate]/[Fe(II)] ratio less than 2, there is a little decrease of  $\text{OH}^\bullet$ . But for higher ratios, a significant drop in the amount of  $\text{OH}$  radicals occur due to the decrease in the amount Fe(II) resulting from the formation of  $\text{FeCO}_3$ . At low pH, this ratio does not correspond to stoichiometric ratio, since the apparent  $\text{pK}_{\text{sp}}$  value of  $\text{FeCO}_3$  is lower than 10.58.

### Effect of oxalate

Oxalate ligand forms many complexes with both Fe(III) and Fe(II). Fe(III) ion forms three stable complexes:  $\beta_1:10^{9.5}$ ,  $\beta_2:10^{16}$ ,  $\beta_3:10^{20}$  whereas Fe(II) ion forms less stable complexes  $\beta_1:10^{4.5}$ ,  $\beta_2:10^{5.2}$  [27]. The acid dissociation constants of oxalic acid are  $10^{1.2}$  and  $10^{3.9}$  [27]. At  $\text{pH} \sim 3.2$  and in presence of high concentration of oxalate with respect to that of Fe(II),  $E^\circ$  of the system  $[\text{Fe}(\text{III})(\text{oxalate})_3]^{3-} / [\text{Fe}(\text{II})(\text{oxalate})_3]^{4-}$  is  $\sim 0.14$  V, [29].

When the [oxalate]/[Fe(II)] ratio is  $\leq 3$ , the percentage of degradation is linear with the increase in the oxalate concentration ( $R^2 = 0.98$ ), but for [oxalate]/[Fe(II)] ratio  $> 3$  the percentage of degradation remained constant (Fig. 9). For this reason it is presumed that this inhibition of the Fenton's process by the oxalate ions is due to formation of Fe(III)-oxalate complexes that would prevent the regeneration of Fe (II) ions [30].

### Effect of EDTA

Fe(III) forms a very stable complex with EDTA which is more stable than that with Fe(II), [28]. However, both the Fe(II)-EDTA and Fe(III)-EDTA com-

Table 2. Partial elimination of KCl inhibition on Fenton's process ( $[\text{Cl}^-] / [\text{Fe(II)}] = 800$ )  $2.4 \times 10^{-5}$  M MR,  $\text{pH}_0 \sim 3.2$  (\* KCl free).

[Fe(II)] (M)	[ $\text{H}_2\text{O}_2$ ] (M)	% of degradation after 16 min.
$1.0 \times 10^{-4}$	$2.0 \times 10^{-4}$	59
$1.2 \times 10^{-4}$	$2.0 \times 10^{-4}$	65
$1.5 \times 10^{-4}$		70
$1.8 \times 10^{-4}$		70
$1.0 \times 10^{-4}$	$2.4 \times 10^{-4}$	63
	$3.0 \times 10^{-4}$	69
	$3.6 \times 10^{-4}$	68
$1.0 \times 10^{-4}$ *	$2.0 \times 10^{-4}$ *	90*

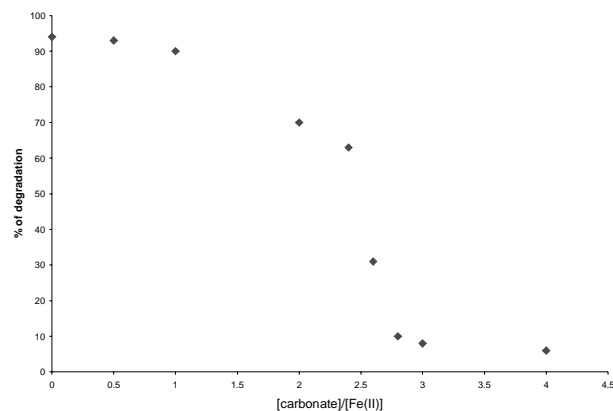


Fig. 8. Variation of the % of MR degradation as a function of [carbonate]/[Fe(II)] ratio,  $2.4 \times 10^{-5}$  M MR,  $2 \times 10^{-4}$  M  $H_2O_2$ ,  $10^{-4}$  M Fe(II) ([Fe(II)]/[ $H_2O_2$ ]:0.5),  $pH_0 \sim 3.2$ .

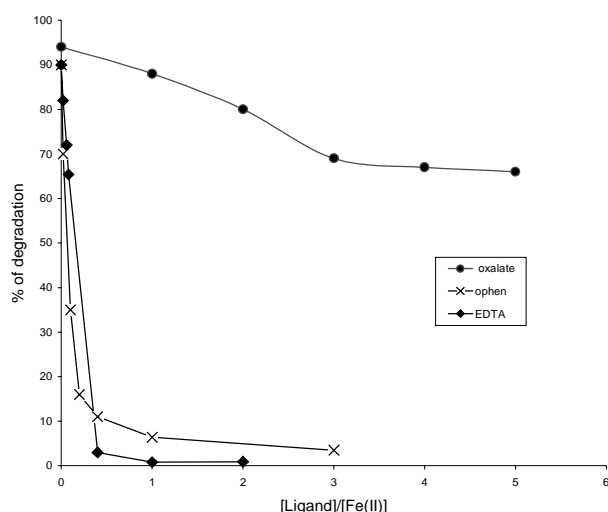


Fig. 9. Variation of the % of MR degradation as a function of [ligand]/[Fe(II)] ratio  $2.4 \times 10^{-5}$  M MR,  $2 \times 10^{-4}$  M  $H_2O_2$ ,  $10^{-4}$  M Fe(II) ([Fe(II)]/[ $H_2O_2$ ]:0.5),  $pH_0 \sim 3.2$ .

plexes are stable in acidic medium, [29]. The percentage of degradation of MR by Fenton's reagent decreases linearly ( $R^2$  0.99) with the increase in EDTA concentration up to a point where [EDTA]/[Fe(II)] is 0.4 (MR degradation 3 %) (Fig. 9). So it is obvious that the inhibition effect of EDTA is mainly due to the formation of Fe(II)-EDTA complex. However, and since the inhibition is almost complete, it is possible that the reaction of EDTA with  $OH^\bullet$  is also present.

### Effect of Ophen

The  $[Fe(II)(ophen)_3]^{2+}$  complex ( $\lambda_{max}$  510 nm) is more stable than  $[Fe(III)(ophen)_3]^{3+}$  complex, [31]. As the concentration of ophen increased the inhibition effect increased, (Fig. 9). For the [ophen]/[Fe(II)] ratio equal to 3, the inhibition is complete. Since A (515 nm) remained constant with time then  $H_2O_2$  was not able to react with  $[Fe(II)(ophen)_3]^{2+}$  to produce  $OH^\bullet$ , and so it was unable to degrade MR.

The inhibition order of the ligands studied in this work is in the following order: ophen  $\sim$  EDTA  $>$  oxalate. According to the standard potential of Fe(III)/Fe(II) system in presence of a complexing agents, the reductive property of Fe(II) increases in the following order  $[Fe(II)(ophen)_3]^{2+} \sim FeCO_3$ , Fe(II)-chloride, Fe(II)-phosphate, Fe(II)-oxalate, Fe(II)-EDTA and according to the simplified theory of redox reactions (available only for fast system) the production of  $OH^\bullet$  in Fenton's process should be in the same order. For example the production of  $OH^\bullet$  and consequently the percentage of degradation in presence of phosphate, oxalate and EDTA must be larger or at least equal to that with free Fe(II) (positive matrix effect), but our experimental results showed the reverse. The production of  $OH^\bullet$  is not always proportional to the decrease in the apparent standard potential of Fe(III)/Fe(II) system or to the stability of ferric complex.

### CONCLUSIONS

The results of this work show the importance of the matrix composition on the performance of Fenton's reagent. Industrial factories that use this process must take into consideration the matrix composition since most of the ions have inhibition effect. The strength of the inhibition is not the same for all halide ions, with KBr being the one with the most inhibition effect. EDTA and ophen ligands have the greatest inhibition effect much greater than that of the halides. The inhibition effect increases in the following order:  $NO_3^- \sim SO_4^{2-}$ ,  $Cl^-$ ,  $I^-$ ,  $F^-$ ,  $Br^-$ , carbonate, oxalate, EDTA  $\sim$  ophen.

Our conclusion is that there is no correlation between the extent of polarizability or electronegativity of the halides. The unexpected matrix effect has several causes and it can not be attributed to only one cause. Sometimes one parameter predominates, but other times

different other parameters contribute to the inhibition effect. The possible matrix inhibition effects are:

- A decrease in the amount of free Fe(II) (in the first and second stages) due to complex formation with the inhibitor, and consequently a decrease in the production of  $\text{OH}^\bullet$ .

- A direct reaction between the inhibitor ion and  $\text{OH}^\bullet$ , such as the formation of  $\text{FOH}^\bullet$  and  $\text{BrOH}^\bullet$ .

- A possible orientation of the redox reaction between  $\text{H}_2\text{O}_2$  and Fe(II)-complex to produce other end products other than  $\text{OH}^\bullet$  or  $\text{HO}_2^\bullet$  may react with the inhibitor ion as in the presence of EDTA and oxalate.

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