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HETEROGENEOUS FENTON PROCESS USING THE MINERAL HEMATITE FOR THE DISCOLOURATION OF A REACTIVE DYE SOLUTION

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Abstract - This work reports a study on the heterogeneous Fenton reaction using hematite powder (Fe_2O_3) in suspension for the discolouration of the reactive dye Drimarene Red X-6BN in aqueous solutions. The efficiency of the process was studied as a function of the experimental conditions: initial pH; H_2O_2 dose; and hematite powder concentration; all of which showed a strong effect on the reaction kinetics. Under the best experimental conditions: pH = 2.5; H_2O_2 dose = 800 mg/L; and [Hematite] = 20 g/L, it was possible to remove about 99% of the initial colour in 120 minutes in a batch reaction at 25^oC. The analysis of the kinetic results suggests that the reaction is initiated by heterogeneous generation of free radicals on the hematite surface, but as soluble iron (III) and iron (II) species are released into the solution during the course of the reaction, a simultaneous homogeneous Fenton reaction step propagates and contributes to the overall reaction.

Keywords: Heterogeneous Fenton reaction; Hematite; Reactive dye.

INTRODUCTION

Reactive dyes are a major class of coloured organic compounds commonly used as dyestuffs in textiles. Most of these dyes contain the azo group (-N=N-) in their structure, which is responsible for the colour applied on the fibre. Until recently, no really effective physical-chemical or biological methods existed for removing the colour produced by residual dyes in wastewaters (Arslan *et al*., 2000). Alternative routes to the conventional treatments have been reported, including Advanced Oxidative Processes such as H_2O_2/UV, O_3/UV and Fenton reagent (Georgiou *et al*., 2002; Neamtu *et al*., 2002; Swaminathan *et al*., 2003). The Fenton process has so far been the preferred process used in the treatment of this kind of industrial effluent because it is a cost effective source of hydroxyl radicals ($^{\bullet}OH$) and easy to operate (Lin and Lo, 1997; Kang *et al*., 2002; Kin *et al*., 2004). The degradation of organic pollutants by the Fe^{3+} / H_2O_2 system is much slower than that achieved by the Fe^{2+} / H_2O_2 system, due to the lower reactivity of Fe^{3+} with H_2O_2 (Pignatello, 1992). However, to our knowledge, despite its high efficiency, the adoption of the Fenton process in actual industrial operations is still not considered to be the ultimate treatment process due to the need of conducting the operation at low pH and the amount of sludge generated in the neutralization / coagulation step.

The homogeneous Fenton process is usually conducted at pH 3 to maintain the iron species in

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*To whom correspondence should be addressed solution and requires a down-stream treatment to raise the pH and precipitate and settle the catalyst as ferric hydroxide. This separation is not simple due to the colloidal characteristics of the resulting dispersion (Plata *et al*., 2010).

More recently, research has been oriented toward the immobilization of iron compounds on different supports or the use of insoluble iron oxides (goethite, magnetite and hematite) in order to facilitate iron separation, employing mainly solid supports to avoid more complex post-treatments (Khan and Watts, 1992; Lin and Gurol, 1998; Valentine and Wang, 1998; Herrera *et al*., 2001). This process has been referred to as the heterogeneous Fenton reaction and employs a variety of iron immobilization techniques (Pham *et al.*, 2009) or makes use of a mass of aggregated iron such as different iron oxides, which are separated at the end of the reaction. From the point of view of an industrial application, a heterogeneous Fenton process is conceptually attractive because it should not require the sludge separation step typical of the conventional homogeneous process (Dantas *et al*., 2006).

Kwan and Voelker (2003) concluded that the heterogeneous Fenton reaction occurs at the mineral catalyst surface and reported that the rate of production or formation of hydroxyl radicals depends on the hydrogen peroxide concentration and the surface area of the iron oxide. In another approach, other investigators (Chou and Huang, 1999; Teel *et al*., 2001; Lu *et al*., 2002) have suggested that the mechanism of the heterogeneous Fenton reaction only starts on the surface and then continues mainly in the bulk of the aqueous solution with participation of dissolved iron species, just like in the conventional homogeneous Fenton reaction.

The objective of the present work was to investigate the efficiency of naturally-occurring hematite (Fe_2O_3) as an iron-containing solid catalyst for use in Fenton processes directed to the discolouration of effluents of textile industries. This chosen catalyst is particularly attractive because: (1) it is an abundant low-cost mineral; and (2) when it loses its surface activity and the time comes for replacement, it can be discarded in blast furnaces as feed material for pig-iron production without causing environmental impact. Drimarene Red, which is one of the various azo dyes used in the textile industry, was chosen as the target dye for the present study due to its high resistance to degradation and its relevance as a type of compound typical of those found in difficult-to-treat effluents of textile industries.

MATERIALS AND METHODS

Materials

A sample of the reactive dye Drimarene Red X-6BN (C.I. Reactive Red 243) was supplied by Clariant. Distilled water was used to prepare the 100 mg/L dye solution. Hydrogen peroxide (50% w/w) was provided by Peróxidos do Brasil (Solvay Group). The hematite mineral used in this work was a ground sample obtained from Vale (mining company); it was used without any purification. It had a BET surface area of 0.85 m^2/g and a mean particle size of 0.064 mm; its characterization is presented in Tables 1 and 2. Other reagent grade chemicals used in this study were supplied by Vetec ($FeSO_4.7H_2O$, H_2SO_4 and NaOH).

Table 1: Chemical Composition of the hematite sample

Component	(%)
Fe	63
SiO_2	8.55
P	0.01
Al_2O_3	0.42
TiO_2	0.02
CaO	0.01
Mn	0.28
MgO	0.03

Table 2: Physical properties of the hematite sample

BET Area (m^2/g)	0.85
Particle Size (mm)	0.075-0.064
Volume of micropores (cm^3/g)	0.0028
Area of micropores (m^2/g)	0.22
Average pore diameter (A)	97.5

Kinetic Experiments

The effects of the relevant variables, pH, H_2O_2 dose, and Fe_2O_3 suspension concentration, were investigated over ranges compatible with a potential industrial application. The influence of a possible simultaneous conventional homogeneous Fenton reaction occurring in the solution phase was also evaluated, especially the possible influence of the chain reaction initiated by the soluble Fe^{3+} in the degradation of the chosen dye. The oxidation experiments were carried out as batch runs in a stirred 600 mL open cylindrical Pyrex reactor, with 500 mL of dye solution with a concentration 100 mg/L and a predetermined amount of suspended hematite powder at room temperature (25 ± 1°C). The reactions were initiated by adding a calculated shot of 50%H_2O_2 solution to the pH-adjusted dye - hematite aqueous suspension. Samples were withdrawn at predetermined time intervals, filtered through a 0.45 μm cellulose ester membrane, and analyzed for absorbance, residual hydrogen peroxide and dissolved iron concentrations. The rate of discolouration of the dye solution was studied at different pH values and dosages of hematite and hydrogen peroxide. Additional sets of experiments were carried out to check for the possibility of a contribution from a homogeneous Fenton reaction, caused by the dissolution of iron from the hematite catalyst. In these trials, the same dye solution used in the discolouration experiments was kept in contact with the same hematite catalyst powder for 2 hours. The solution was then filtered through a 0.45 μm membrane and a calculated dose of H_2O_2 was added to the dye solution and left to react for 120 minutes. At the end of the reaction time, the pH was adjusted to pH = 8 and the solution was analyzed for residual H_2O_2, and its absorbance was measured.

Analytical Methods

Colour removal was measured using a Shimadzu UV-mini 1240 spectrophotometer. UV–VIS spectra were recorded at 516 nm where the maximum absorbance was obtained. Residual hydrogen peroxide was determined by a colorimetric method based on the generation of peroxovanadium formed by the reaction of hydrogen peroxide with ammonium metavanadate (Oliveira *et al*., 2001), with maximum absorption at 446 nm. The COD determination was corrected for residual H_2O_2 accordingly. The presence of dissolved Fe was determined by colorimetry, by means of the reaction with ortho-phenanthroline (APHA, 2005) and confirmed by atomic absorption spectrometry (Shimadzu, model AA-7000).

RESULTS AND DISCUSSION

Effects of Dosage of H_2O_2; Fe_2O_3 Suspension Concentration; pH; and Temperature

Figure 1 shows the effect of adding different H_2O_2 doses on the discolouration of dye solutions at pH = 3.5 and [hematite powder] = 20 g/L.

No significant colour removal was observed without H_2O_2, indicating that dye adsorption on the solid does not contribute to significant colour removal, but this does not mean that dye molecules do not adsorb on the catalyst surface. As the H_2O_2 dose was increased up to 800 mg/L, a corresponding gain in the discolouration rate was observed; this confirms the effect of free radical oxidation of the dye molecule, since H_2O_2 on its own is not sufficiently reactive for the oxidation of azo dyes.

The other significant parameter is the hematite suspension concentration; its effect on the discolouration rate at pH = 3.5 and dosage of H_2O_2 = 800 mg/L, is shown in Figure 2.

The increase of the hematite dosage increased the discolouration rate as a result of the correspondingly higher mineral surface area available for the reaction. This was also seen by Kwan and Voelker (2003), who observed that the organic matter decomposition rate is favoured by increasing the iron oxide concentration in a heterogeneous Fenton-like reaction. The increase in the concentration of the mineral suspension promoted the decomposition of the compounds, probably by increasing the available area and / or the amount of available iron (surface or aqueous) for the Fenton reaction, thus promoting the generation of hydroxyl radicals (Kong *et al*., 1998).

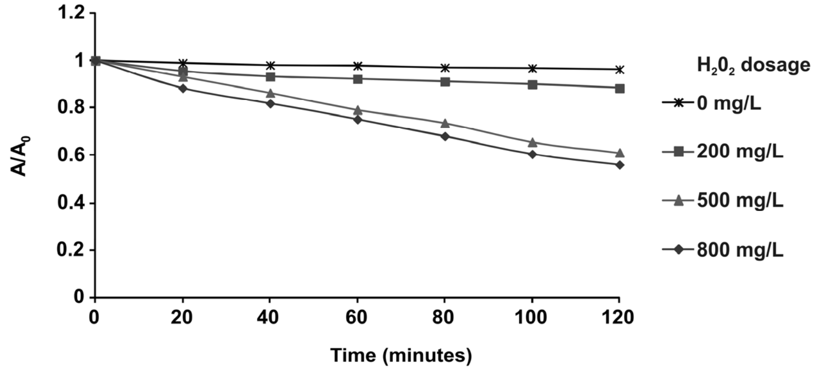

Figure 1: Effect of hydrogen peroxide dosage on the colour removal of the dye solution by heterogeneous Fenton oxidation. A = final absorbance, A_0 = initial absorbance. Initial conditions: [hematite] = 20 g/L; [dye] = 100 mg/L; T = 25ºC; pH = 3.5.

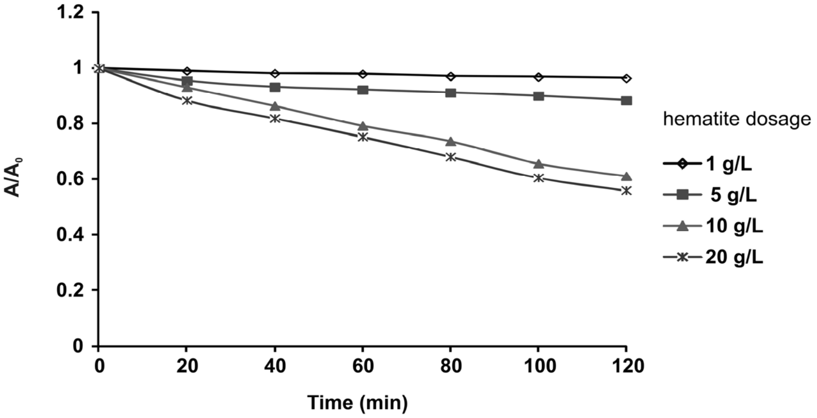

Figure 2: Effect of hematite dosage on the colour removal of the dye solution by heterogeneous Fenton oxidation. A= final absorbance, A_0= initial absorbance. Initial conditions: $[H_2O_2]$ = 800 mg/L; [dye] = 100 mg/L; T = 25ºC, pH = 3.5.

The effect of pH on the decomposition of the dye by hydrogen peroxide and hematite was examined in runs with [hematite] = 20 g/L and H_2O_2 dose = 800 mg/L, as reported in Figure 3. No significant discolouration was obtained in experiments conducted at pH = 5.5, the natural pH of the dye solution.

Lowering the initial pH to pH = 3.5 led to a moderate improvement in the colour removal rate; after 120 minutes of reaction, about 50% discolouration was achieved. An even further significant improvement in the reaction rate was observed in the run conducted at pH = 2.5. This was also reported by Lu *et al*. (2002), who observed that the Fenton system with iron oxide is more effective at pH lower than 3.0.

Additional kinetic runs were performed in order to investigate the effect of temperature and to determine the apparent activation energy of the reaction (Figure 4).

Figure 4 shows the change in absorbance of the solution with temperature. Increasing temperature causes faster reduction in the absorbance with reaction time. When the temperature was varied from 25 to 55°C, there was a significant reduction in the absorbance of the solution within the first hour of reaction.

From the kinetic data at different temperatures it was possible to determine the initial rates of reaction and then calculate the apparent activation energy by applying the Arrhenius equation. These results are described in Table 3. The calculated apparent activation energy of the reaction at pH = 2.5 was found to be 10.6 kcal/mol. This, according to Levenspiel (1962), indicates that the non-elementary reaction studied is controlled by a chemical reaction step.

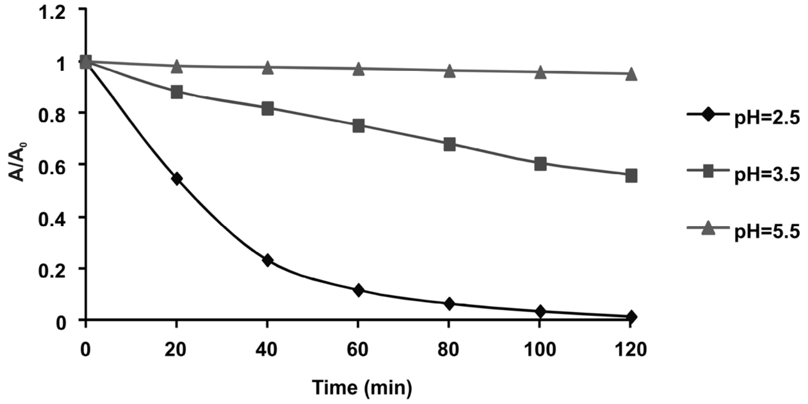

Figure 3: Effect of pH on the colour removal of the dye solution by heterogeneous Fenton oxidation. A= final absorbance, A_0= initial absorbance. Initial conditions: [hematite] = 20 g/L; $[H_2O_2]$ = 800 mg/L, [dye] = 100 mg/L; T = 25ºC.

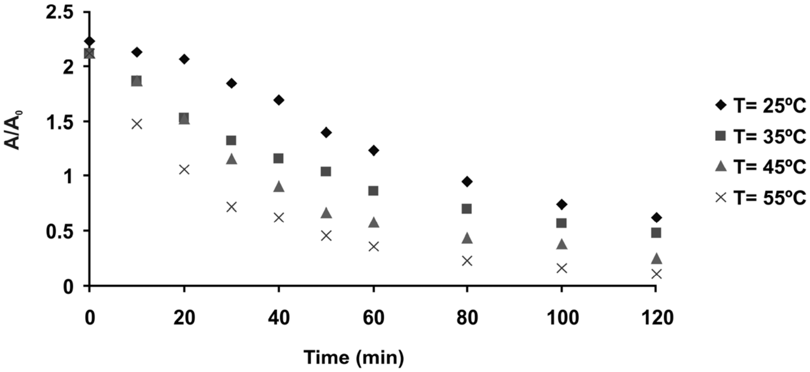

Figure 4: Effect of temperature on the colour removal of the dye solution by heterogeneous Fenton oxidation. A= final absorbance, A_0= initial absorbance. Initial conditions: $[H_2O_2]$ = 200 mg/L; [dye] = 100 mg/L, [hematite] = 10g/L, pH = 2.5.

Table 3: Reaction rates and apparent activation energy for the hematite/H_2O_2 system

Experimental Condition	T (°C)	R_0 (min^{-1})	R^2 Coefficients	Activation Energy (kcal/mol)
$[H_2O_2]_0$=200 mg/L	25	0.0104	0.9814	10.6
$[Hematite]_0$ 10 g/L	35	0.0245	0.9054	
pH=25	45	0.0248	0.8461	
	55	0.0642	0.7509	

Mechanistic Considerations

The following thermodynamic evaluations and further experiments were made in an attempt to further elucidate the reaction mechanism. Such considerations are made initially in the next sections, for simplified conditions, taking into consideration the interactions between Fe_2O_3, aqueous Fe species, and H_2O_2 in water only, without the dye; subsequently, the presence of the dye is considered.

Calculations of Fe(II) and Fe(III) Speciation in Aqueous Solutions in Contact with Fe_2O_3 (in the Absence of the Dye)

The e_H - pH diagram for Fe species (for [Fe] total = $1x10^{-6}$ mol/L) in water shown in Figure 5 was calculated in the present work using Outotek´s HSC 7.0 programme. It shows the known aqueous and most stable solid iron species that may be present under the considered reaction conditions in the range pH 2.5 to 5.5. It can be seen that the solid Fe_2O_3 species is predominant over the aqueous Fe(III) species (Fe^{3+}; $FeOH^{2+}$; and $HFeO_2$) in the range of pH > 2.0 and that this same solid species can be converted to aqueous Fe^{2+} by a reduction in the operating pH range of the present study. The diagram also shows that, although Fe_2O_3 has a very low aqueous solubility across the considered range of pH 2.5 to 5.5, aqueous iron species can exist in equilibrium with the mineral suspension, these being: Fe^{3+} (pH < 2.1); $FeOH^{2+}$ (2.1 < pH < 3.2); $HFeO_2$ (pH > 3.2); and Fe^{2+} (over the whole pH range considered).

Calculation of the Possibility of the Fe_2O_3 Surface Redox Reaction with H_2O_2 Leading to Mineral Dissolution and Decomposition of H_2O_2 to O_2

Lin and Gurol (1998) and Kwan and Voelker (2003) have considered that the mechanism of the heterogeneous Fenton process involves a complex series of reactions on the surface of the catalyst producing $HO^\bullet$ and $HO_2^\bullet$ radicals (reactions 1 - 4).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+\cdot} \quad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{-}OH + HO^{\bullet} \quad (2)$$

$$HO_2^{\bullet} \leftrightarrow H^{+} + O_2^{\bullet -} \quad (3)$$

$$Fe^{3+} + HO_2 \rightarrow Fe^{2+} + H^{+} + O_2 \quad (4)$$

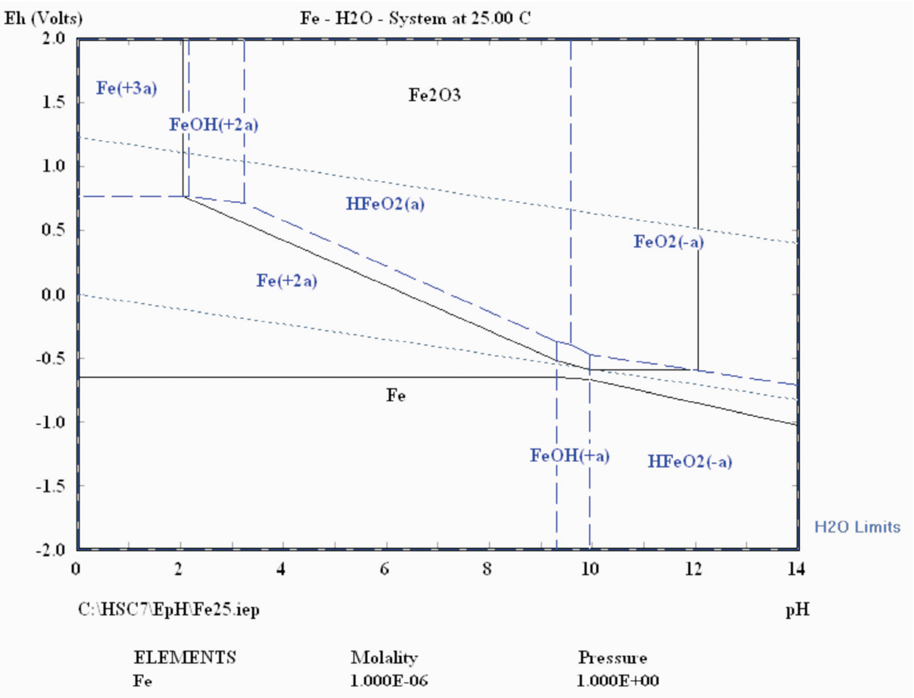

Figure 5: E_H – pH diagram of Fe species in water with total [Fe] = $1.0x10^{-6}$ mol/L – dotted lines show the boundaries of aqueous species only.

Pham *et al.* (2009) have also suggested other rather similar mechanisms – including adaptations to heterogeneous Fenton reaction condition steps based on the original Haber-Weiss mechanism. In those studies, the bottom line is: aqueous H_2O_2 on the surface of hematite decomposes to $H_2O + O_2$. This may either initiate via a true surface catalytic path of generation of intermediate $HO^•$ or $HO_2^•$free radicals or, as we will discuss below, a non-catalytic, non-radical redox route by which solid Fe_2O_3 may actually release Fe ions to the solution via a reductive step that leads to aqueous Fe^{2+} (+ O_2). The released aqueous Fe^{2+}, together with remaining H_2O_2 in the solution, could then fuel a continuing conventional homogeneous Fenton reaction step.

The Fe_2O_3 dissolution reactions below will occur to a certain extent limited by pH and reach equilibrium with the specific predominant dissolved Fe species indicated for each pH range (equilibrium solubility constants calculated using Outotek´s HSC 7.0):

$$\left(\text{at pH} > 3.2\right)$$

$$Fe_2O_{3(s)} + H_2O \rightarrow 2\ HFeO_{2(aq)} \qquad (5)$$

$$K = 1.1x10^{-17}$$

$$\left(\text{at } 2.1 < \text{pH} < 3.2\right)$$

$$Fe_2O_{3(s)} + 4\ H^+_{(aq)} \rightarrow 2\ FeOH^{2+}_{(aq)} + H_2O \qquad (6)$$

$$K = 8.7x10^{-5}$$

$$\left(\text{at pH} < 2.1\right)$$

$$Fe_2O_{3(s)} + 6\ H^+_{(aq)} \rightarrow 2\ Fe^{3+}_{(aq)} + 3\ H_2O \qquad (7)$$

$$K = 1.9$$

The magnitudes of the constants indicate that the more acidic dissolution of Fe_2O_3 to Fe^{3+} is more favourable than less acidic dissolution to $FeOH^{2+}$ or to neutral $HFeO_2$, but in each of the above considered pH ranges, at least one of the three species will be dissolved, even if only to a limited extent, as is the case of $HFeO_2$ and $FeOH^{2+}$.

Once the aqueous Fe species are released into solution, these can induce the redox decomposition of H_2O_2 through the following Equations (8-10):

$$HFeO_{2(aq)} + 3/2\ H_2O_2 + 2\ H^+ \rightarrow$$

$$Fe^{2+}_{(aq)} + 3\ H_2O + O_2 \qquad (8)$$

$$K = 1.3x10^{25}$$

$$FeOH^{2+}{}_{(aq)} + 3/2\ H_2O_{2(aq)} \rightarrow$$

$$Fe^{2+}{}_{(aq)} + 2\ H_2O + O_2 \qquad (9)$$

$$K = 4.6x10^{18}$$

$$Fe^{3+}{}_{(aq)} + ½\ H_2O_{2(aq)} + OH^{-}{}_{(aq)} \rightarrow$$

$$Fe^{2+}{}_{(aq)} + ½\ O_{2(aq)} + H_2O \qquad (10)$$

$$K = 4.9x10^{27}$$

The combination of the above reactions in pairs (5 with 8; 6 with 9; and 7 with 10) for each pH range results in the same overall reaction:

$$Fe_2O_{3(s)} + H_2O_{2(aq)} + 4\ H^{+}{}_{(aq)} \rightarrow$$

$$2\ Fe^{2+}{}_{(aq)} + 3\ H_2O + O_2 \qquad (11)$$

$$K = 7.1x10^{2}$$

This analysis shows that it is thermodynamically feasible that Fe_2O_3 in contact with H_2O_2 in acidic solutions will lead to Fe^{2+} ions in solution, which in turn will initiate the homogeneous Fenton reaction step with the remaining H_2O_2. This is depicted by the equilibrium constant expression for reaction (11) rearranged below:

$$\left[Fe^{2+}\right] = 710\left[H^{+}\right]^{4}\left[H_2O_2\right]/\left[O_2\right] \qquad (12)$$

This expression shows how strongly dependent on pH the critical step of $Fe^{2+}{}_{(aq)}$ generation and propagation of the homogeneous Fenton reaction is in the overall dye degradation reaction. This is supported by our results presented here and by those of previous investigators.

Thus, at this point of the discussion, it may be considered that the heterogeneous Fenton process is likely to start on the hematite surface by either: (a) catalytic decomposition of adsorbed H_2O_2 leading to adsorbed $HO^{\bullet}$ and $HO_2^{\bullet}$, which, either still on the surface or just after desorption, will attack nearby (adsorbed or not) dye molecules, as proposed by Lin and Gurol (1998) – reactions (1) to (4); or (b) as proposed in the present work: with reduction and release of surface Fe^{3+} as Fe^{2+} into the solution, in which H_2O_2 plays the role of reductant. Once in solution, Fe^{2+} will react with the remaining H_2O_2, as in a conventional homogeneous Fenton reaction, inducing degradation of the dye molecules. Although not specifically demonstrated in previous works, this hypothesis supports the findings of previous authors (Chou and Huang, 1999; Teel *et al*., 2001; Lu *et al*., 2002) who suggested that the mechanism of the heterogeneous Fenton reaction merely starts on the surface and continues mainly in the bulk of the aqueous solution as a homogeneous Fenton reaction.

Decomposition of H_2O_2 Induced by the Hematite Surface

Figure 6 shows the decomposition of 0.5 g/L H_2O_2 (solution without added dye), induced by 10 g/L of hematite powder in the absence of the dye. It can be seen that the decomposition is appreciably faster at pH 2.5 as compared to that at pH 5.5. Whatever the decomposition mechanism may be, i.e., either true surface Fenton-like or reductive, the experiment shows a slow rate of H_2O_2 disappearance at pH 5.5, which is in agreement with the observed effect of pH seen in the dye degradation runs.

At pH 5.5, the H_2O_2 decomposition reaction is fairly slow and the pH remains basically stable during the reaction. This may be due to the occurrence of sequential redox reactions that end up converting Fe_2O_3 to the sparingly soluble neutral complex $HFeO_2$ (aq) without overall variation in acidity:

$$2\ Fe^{2+} + H_2O_2 + 2\ H_2O \rightarrow 2\ HFeO_{2(aq)} + 4\ H^{+} \qquad (13)$$

$$K = 2.1x10^{16}$$

which combines with Eq. (11) to give:

$$Fe_2O_{3(s)} + 2\ H_2O_{2(aq)} \rightarrow 2\ HFeO_{2(aq)} + H_2O + O_2 \qquad (14)$$

$$K = 1.6x10^{19}$$

However, at pH 2.5, the analogous reaction path can lead to the conversion of Fe_2O_3 into the more soluble $FeOH^{2+}{}_{(aq)}$, according to the following reaction:

$$2\ Fe^{2+} + H_2O_2 \rightarrow 2\ FeOH^{2+}{}_{(aq)} \qquad (15)$$

$$K = 1.8x10^{29}$$

which combines with Eq. (11) to give:

$$Fe_2O_{3(s)} + 2\ H_2O_{2(aq)} + 4\ H^{+} \rightarrow$$

$$2\ FeOH^{2+}{}_{(aq)} + 3\ H_2O + O_2 \qquad (16)$$

$$K = 1.8x10^{29}$$

Under this condition of initial pH = 2.5, as the reaction proceeds, the pH should increase; this is also supported by the results of the decomposition runs in Figure 6.

Thus, it can be concluded that the hypothesis of a non-radical path for the decomposition of H_2O_2 by Fe_2O_3, proceeding via reductive Fe^{2+} dissolution leading to O_2 generation, followed by oxidation to Fe(III) (as $HFeO_2$ at pH 5.5 or $FeOH^{2+}$ at pH 2.5) by peroxide, may be a possible inducer of a conventional homogeneous Fenton degradation step of the dye.

In addition to this conclusion, one should also bear in mind that, at pH 2.5, as will be seen below, some dissolution of iron from the hematite surface occurs – and, because the aqueous couple Fe^{2+} / Fe^{3+} is a known catalyst for H_2O_2 degradation, like other aqueous transition metal species, this will also contribute to H_2O_2 decomposition in the dye degradation process.

The solubilisation rates of iron as Fe^{2+} and Fe^{3+} were also measured. In runs conducted at pH = 5.5, after 120 minutes, only a very limited extent of iron dissolution was detected - a maximum of 0.21mg/L. At pH = 2.5, though, a higher extent of iron dissolution (up to 0.68 mg/L) was observed in the same period of time. The evolution of iron dissolution with time is shown in Figure 7. It is seen that the presence of H_2O_2 causes faster iron dissolution from the hematite surface.

The acidic medium condition (pH = 2.5) resulted in some dissolution of the mineral catalyst, leading to total dissolved iron levels reaching 0.68 mg/L and 0.63 mg/L for runs with and without hydrogen peroxide, respectively. Because the concentration levels of leached iron were very low, there will be no need for control of the amount of iron in solution.

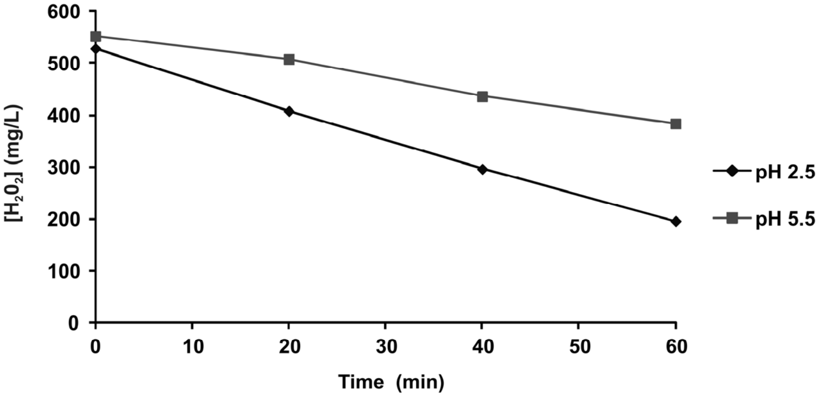

Figure 6: Disappearance of initial 0.5 mg/L H_2O_2 in contact with suspended hematite powder at [hematite] = 20 g/L, pH 2.5 and pH 5.5, at 25 °C.

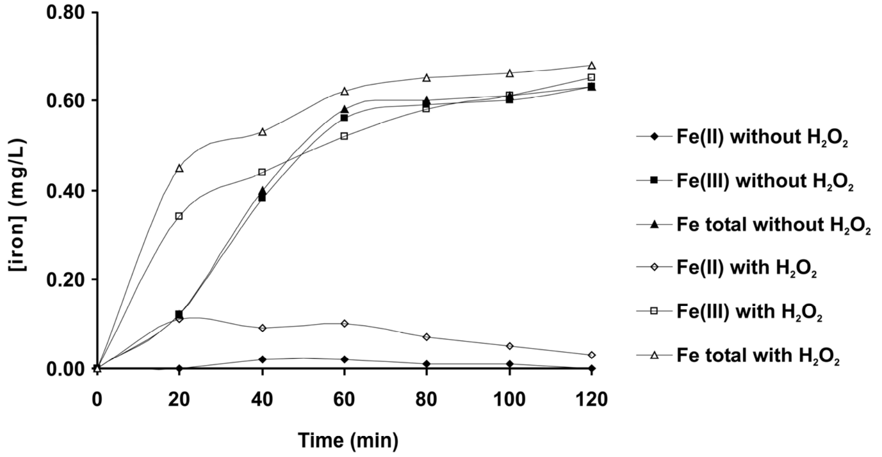

Figure 7: Effect of hydrogen peroxide on the dissolution of hematite. Initial conditions: [hematite] = 20 g/L, pH = 2.5, T = 25ºC.

A point to be noted is that, in the trials carried out at pH = 2.5 without hydrogen peroxide, most of the iron ions present in solution were ferric ions (Fe^{3+}> 99%) and no significant amounts of ferrous ions were detected. However, in the trials carried out with H_2O_2, ferrous ions were detected in solution, reaching a maximum of 0.11 mg/L at 20 minutes of reaction, and decreasing to 0.03 mg/L after 120 minutes. Since these ions were not added to the solution and the mineral had only Fe^{3+} ions in its structure, the ferrous ions were produced by the reaction between Fe^{3+}ions on the hematite surface and H_2O_2 (reaction 11). This confirms our thermodynamic analysis of the generation of Fe^{2+} ions in solution. This is also in reasonable agreement with the results reported by Lin and Lu (2006), who observed that, after 90 minutes of contact between iron oxides and solutions containing hydrogen peroxide, more than 90% of the ions present in the solution were ferrous ions; after that period, the concentration of Fe^{2+} ions decreased to a negligible value.

Further Experiments in the Presence of the Dye

In an attempt to correlate aqueous iron dissolution (homogeneous Fenton activity) with discolouration during the heterogeneous Fenton reaction at pH 2.5, the experiment shown in Figure 8 was performed (evolution of iron Fe^{2+} and Fe^{3+} in solution and colour removal).

Although it was seen that in the presence of the dye, a non-negligible amount of dissolved iron (which could function as a homogeneous Fenton catalyst) was detected only after 20 minutes of reaction. In this same period of time, about 50% of the colour had already been removed. Although the presence of the dye seems to interfere with the F_2O_3/aqueous interface, the dye molecules, being much larger in size than single iron ions on the hematite surface, are somehow able to inhibit dissolution of Fe from the mineral. Thus, at the beginning of the reaction the colour removal occurs predominantly as result of a heterogeneous reaction between hydrogen peroxide and the hematite surface, which is sufficiently active to initiate a process of generation of free radicals that attack the nearby dye molecules.

Heterogeneous and Homogeneous Generation of Free Radicals

In order to evaluate the contribution of the homogeneous reaction during the overall heterogeneous Fenton process, a further trial was carried out by using as catalyst only the aqueous iron ions produced by hematite dissolution at pH = 2.5 in the absence of Fe_2O_3. The experiment was carried out after 120 min of contact between the suspended hematite powder (20 g/L) and the dye solution (100mg/L) at pH = 2.5, without addition of H_2O_2. The solution was then filtered to separate the solid catalyst. The filtrate was analyzed for iron content and, after adding H_2O_2 (800 mg/L), discolouration was monitored for an additional 120 minutes of reaction time.

Figure 9 shows the comparison between the discolouration of the dye solution by the heterogeneous Fenton system with hematite and the homogeneous Fenton process performed with the filtered solution obtained after contact with the hematite powder suspension for 120 min at pH = 2.5. It noted that, after this contact period, the total concentration of dissolved iron in the solution reached 0.49 mg/L and, according to Figure 7, most of which should be in the form of Fe^{3+}.

This experiment showed that the rate of colour removed was significantly higher in the presence of hematite – especially in the first 30 minutes of reaction, where about 70% of the degradation occurs, reaching approximately 99% after 120 min of reaction. In the comparative homogeneous process done with leached aqueous iron only, the discolouration did not exceed 63% in the same 120 min period.

An analogous comparative experiment reported recently by Liang *et al.* (2010) for degradation of an azo dye by H_2O_2 activated by a magnetite catalyst suspension also led to similar conclusions. When the discoloration reaction was conducted at an initial pH 3, the discoloration of Acid Orange II by the homogeneous Fenton reaction was below 10% after 180 min. Most of the decomposition of the dye catalyzed by magnetite was due to a heterogeneous rather than a homogeneous Fenton reaction.

Thus, the above observations support the conclusion of the present study that the dye discolouration by means of the Fe_2O_3 / H_2O_2 system occurs predominantly as a result of the reaction between hydrogen peroxide and iron present on the hematite surface, which generates radicals in conditions adequate for attacking adsorbed dye molecules. In addition, the homogeneous Fenton-type reaction due to the reductive release of ferric ions from the mineral into the solution (as Fe^{2+}) also plays a continuing role in the overall reaction, which should show an autocatalytic kinetic behaviour.

In fact, the kinetic curves shown in Figure 10 show the autocatalytic behaviour derived from a combination of a slow initial heterogeneous step of $HO^{\bullet}$ or $HO_2^{\bullet}$ formation that begins on the hematite surface (and appears as a typical induction period), followed by a dissolution step that reduces and transforms surface Fe^{3+} to aqueous Fe^{2+} that can react with the remaining H_2O_2 to generate more $HO^{\bullet}$ radicals and accelerate the overall reaction.

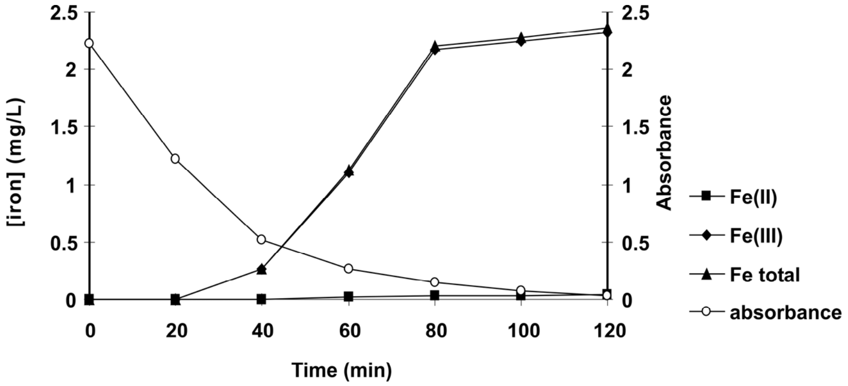

Figure 8: Dissolution of iron and absorbance of reactive dye solution in the heterogeneous Fenton reaction. Initial conditions: [dye] = 100 mg/L; [hematite] = 20 g/L; [H_2O_2] = 800 mg/L; pH = 2.5.

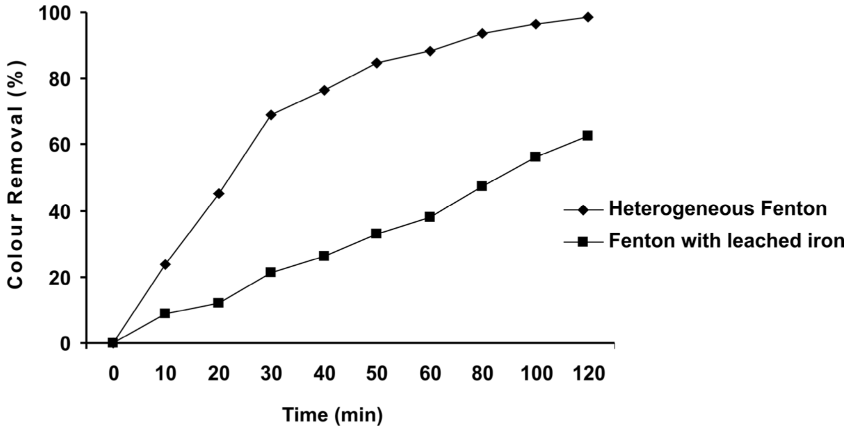

Figure 9: Discolouration of reactive dye solutions by the heterogeneous Fenton process with [hematite] = 20 g/L and the homogeneous Fenton process with leached iron ([Fe] = 0.49 mg/L) obtained from leaching hematite for 2 hours under same conditions. Initial conditions: [dye] = 100 mg/L; [H_2O_2] = 800 mg/L; pH = 2.5.

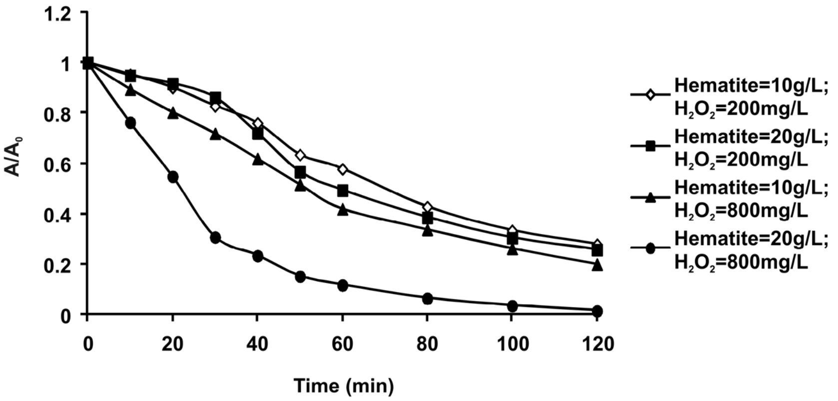

Figure 10: Additional dye degradation runs showing autocatalytic kinetic behavior. Initial conditions: [dye] = 100 mg/L; [H_2O_2] = 200 - 800 mg/L; [hematite] = 10 – 20 g/L; pH = 2.5.

CONCLUSIONS

1. The heterogeneous Fenton process using the mineral hematite in powder form was effective in removing the colour of 100 mg/L Drimarene Red X-6BN azo-dye solutions.

2. The three process variables investigated: H_2O_2 dose (100 – 800 mg/L); hematite powder concentration (1 – 20 g/L), and pH (2.5 – 5.5), showed strong effects on the rate and efficiency. An increased hematite concentration and hydrogen peroxide dose both contributed to an increase in the rate and efficiency of the dye colour removal, due to the greater surface area of the catalyst and supply of free radicals from H_2O_2 decomposition. A strongly acidic medium (pH = 2.5) was found to be much more favourable than a near neutral pH 5.5 for the generation of free radicals that are capable of attacking the dye molecules. The apparent activation energy of the reaction was calculated to be 10.6 kcal/mol, indicating a mechanism controlled by chemical reaction.

3. A thermodynamic evaluation of possible reactions, confirmed by kinetic runs, indicated that the action of hydrogen peroxide on the hematite surface can provide a significant contribution to the reaction kinetics by promoting the formation of ferrous ions in the course of the reaction via a Fenton-like heterogeneous step, according to the following reaction:

$$Fe_2O_{3(s)} + 4\,H^+_{(aq)} + H_2O_{2(aq)} \rightarrow$$

$$2\,Fe^{2+}_{(ads,\,aq)} + 3\,H_2O + O_2$$

4. By analogy to a conventional homogeneous Fenton process, surface Fe^{3+} ions in the presence of adsorbed H^+ may be reduced by adsorbed H_2O_2 in what would be a (heterogeneous) Fenton-like reaction, inducing H_2O_2 decomposition to adsorbed $HO_2^\bullet$ and leaving surface iron ions as Fe^{2+} that can provoke further H_2O_2 decomposition leading to generation of $HO^\bullet$ capable of attacking nearby dye molecules. In the course of the reaction, the surface Fe^{2+} ions end up dissolving because they have a much higher solubility than Fe^{3+}. Dissolved Fe^{2+} ions then also propagate the conventional homogeneous Fenton mechanism with the remaining H_2O_2.

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