THE EFFECT OF OPERATIONAL PARAMETERS ON DECOLOURISATION OF TEXTILE DYES AND COMPARISON EFFICIENCIES OF THE UV/H₂O₂, FENTON AND PHOTO-FENTON PROCESSES: A REVIEW

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Abstract. In this review article, we summarize the current knowledge about the applicability of advanced oxidation processes (AOPs) such as UV/H₂O₂, Fenton and photo-Fenton for removal of textile dyes from wastewater and the effect of operational parameters (initial dye concentration, initial H₂O₂ concentration, initial Fe²⁺ concentration and initial pH) on these processes. Numerous studies have reported the use of AOPs for degradation of textile dyes, and the results show that they are very effective. By comparing the results of the previous studies, it seems that the photo-Fenton process is more efficient than the Fenton and UV/H₂O₂ process.

Key words: advanced oxidation processes (AOPs), textile dyes, wastewater treatment, UV/H₂O₂, Fenton, photo-Fenton

1. INTRODUCTION

Synthetic dyes are major industrial pollutants and water contaminants (Brown et al., 1981). Synthetic dyes are widely used in the textile and dyestuff industries for textile dyeing, paper printing, food, cosmetics, pharmaceutical and colour photography (Padmavathy et al., 2003). Wastewaters from textile and dye industries are highly coloured with a significant amount of auxiliary chemicals. Estimates indicate that approximately 10-15% of the synthetic textile dyes used are lost in waste streams during manufacturing or processing.

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operations (Madalina et al., 2009). Discharge of wastewater introduced intensive colour and toxicity to the aquatic environment causing serious environmental problem (Pierce, 1994). Due to their complex structure, most of the dyes are resistant to biodegradation (Ohashi et al., 2012). Dyes in wastewaters cause aesthetic problems, absorb and scatter sunlight and thus affect the aquatic ecosystem (Gomathi Devi et al., 2009).

According to their mode of application, textile dyes can be classified as acid, reactive, metal complex, disperse, vat, mordant, direct, basic and sulphur dyes (Parsons, 2004). Azo dyes account for some 60–70% of the 10,000 commercial dyes currently in use (Neamtu et al., 2002; Méndez-Paz et al., 2005; Sun et al., 2007). This compound contains one or more azo groups (−N=N−) mostly linked to benzene or naphthalene rings (Zollinger, 2003). Some azo dyes via metabolic cleavage of azo linkage can produce potentially carcinogenic aromatic amines (Habibi et al., 2005).

Thus, there is a need to remove dyes from wastewaters before discharging them to receiving waters. Nowadays, various chemical and physical processes, such as elimination by adsorption onto activated carbon, coagulation by a chemical agent, ozone oxidation, hypochlorite oxidation, electrochemical method, etc. are applied for the treatment of dye waste effluents. Nevertheless, these (traditional methods) processes are usually non-destructive, inefficient, costly and result in the production of secondary waste products. Therefore, it is necessary to find an effective treatment technology that leads to complete destruction of the dye molecules (Yoshida et al., 1999; Tanaka et al., 2000; Shen et al., 2001).

Advanced oxidation processes (AOPs) such as homogeneous and heterogeneous photocatalysis are promising technologies for the decolourisation and mineralization of a wide range of dyes to stable inorganic compounds or, at least, their transformation into biodegradable or harmless products (Matthews, 1991; Tang, 1995; Andreozzi et al., 1999). AOPs are based on the generation of hydroxyl radicals in water, which are highly reactive and nonselective oxidants able to oxidize organic compounds such as azo dyes. The use of homogeneous degradation or photodegradation systems such as UV/H$_2$O$_2$, Fe$^{2+}$/H$_2$O$_2$ (Fenton) and Fe$^{2+}$/H$_2$O$_2$/UV (photo-Fenton) have attracted much attention due to their high efficiency in the oxidation of different pollutants including dyes (Hsueh et al., 2005; Daneshvar and Khataee, 2006). Some of the advantages of using AOPs in comparison to other systems are no sludge formation, no salt formation, considerable safety and easy operation, short reaction time, reduction of COD (Marechal et al., 1997).

For economic degradation of dyes from wastewaters by UV/H$_2$O$_2$, Fenton and photo-Fenton processes, there is a need to determine the optimal conditions of experimental parameters. Based on the results of previous studies, the aim of the present review is to investigate the influence of pH, dosages of H$_2$O$_2$ and Fe$^{2+}$ ions and the initial concentration of dyes on the degradation of dyes. Comparison efficiencies of UV/H$_2$O$_2$, Fenton and photo-Fenton processes on degradation of the textile dyes were also evaluated.

2. UV/H$_2$O$_2$ PROCESS

The UV/H$_2$O$_2$ process is of particular interest for potential application to water treatment, because it ensures complete oxidation of organic pollutants by generation of OH radicals (Legrini et al., 1993). Combination of UV and H$_2$O$_2$ is necessary for production of hydroxyl radicals by photolysis of the hydrogen peroxide (Namboodri and
Walsh, 1996). Many studies have shown that neither H₂O₂ nor UV alone was able to degrade organic dyes (Behnajady et al., 2004; Muruganandham, 2004a; Alebohey et al., 2005; Guettaï and Ait Amar, 2005; Haji et al., 2011). Hydroxyl radical is a non-selective and very powerful oxidizer with an oxidation potential of 2.8 V and can initiate decolourisation by reacting with the dye molecules (Legrini et al., 1993). The decolourisation of the dyes by the UV–H₂O₂ process proceeds according to the following reaction:

\[ H_2O_2 + \text{hv} \rightarrow 2 \cdot \text{OH} \]  
(1)

\[ \cdot \text{OH} + \text{dye} \rightarrow \text{dye intermediate} \]  
(2)

\[ \cdot \text{OH} + \text{dye intermediate} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{mineralisation products} \]  
(3)

### 2.1. The effect of concentration of H₂O₂ on the UV/H₂O₂ process

Hydrogen peroxide concentration is an important parameter for the degradation of dyes treated with the UV/H₂O₂ process. A lot of researchers have investigated the effect of H₂O₂ on the decolourisation of dyes. The optimal H₂O₂ concentrations for the UV/H₂O₂ process are shown in Table 1.

As we can see from these studies, decolourisation of dyes increases with addition of H₂O₂ to a certain value, after which decolourisation decreases.

The enhancement of decolourisation by addition of H₂O₂ is due to the increase in the hydroxyl radical concentration (Eq. 1). At low concentration H₂O₂ cannot generate enough hydroxyl radicals and the removal rate is limited (Muruganandham, 2004a).

However, the excess of H₂O₂ probably promoted the reaction of the produced \( \cdot \text{OH} \) radicals with the H₂O₂ molecules to form radicals that were of less oxidizing power (hydroperoxyl radicals) according to the following reaction (Haji et al., 2011):

\[ \cdot \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \]  
(4)

\( \text{HO}_2^- \) radicals can also react with \( \cdot \text{OH} \), thus reducing the concentration of \( \cdot \text{OH} \) radicals, and hence decolourisation of dyes decreases.

\[ \text{HO}_2^- + \cdot \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2 \]  
(5)

This phenomenon where an excess of H₂O₂ could lead to the consumption of the active oxidizing \( \cdot \text{OH} \) radicals and, consequently, reduce the rate of the latter reaction, was also reported in the literature and was referred to as scavenging effect (Kabir et al., 2006; Tokumura et al., 2006).

Therefore, an important step in the optimization of the method is the determination of the adequate amount of concentration of H₂O₂ to avoid an excess of the reagent that can retard the decolourisation. The results from Table 1 show that in most cases the optimum concentration of H₂O₂ is about 20-50 mmol/dm³.
| Dye                 | Dye conc. (mg dm$^{-3}$) | Optimal H$_2$O$_2$ conc. (mmol dm$^{-3}$) | Optimal pH | Reference                      |
|---------------------|--------------------------|--------------------------------------------|------------|--------------------------------|
| Methyl Orange       | 25.53                    | 45.80                                      | /          | (Haji et al., 2011)            |
| Reactive Orange 4   | 390.73                   | 20.00                                      | 2-3        | (Muruganandham, 2004a)         |
| Acid Blue 74        | 32.64                    | 50.00                                      | 3.5-5.5    | (Aleboyeh et al., 2005)        |
| Reactive Yellow 14  | 334.51                   | 20.00                                      | /          | (Muruganandham and Swaminathan, 2006) |
| Mordant Red 73      | 24.04                    | 2.50                                       | 2-9        | (Elmorsi et al., 2010)         |
| Reactive Green 19   | 89.96                    | 30.00                                      | 6          | (Zuorro and Lavecchia, 2013)   |
| Reactive Red 195A   | 100.00                   | 44.12                                      | 3-8        | (Sudarjanto and Keller, 2005)  |
| Reactive Red 198    | 1013.70                  | 97.90                                      | 3-10       | (Ribeiro et al., 2014)         |
| Reactive Orange 16  | 50.00                    | 25.00                                      | 7          | (Mitrović et al., 2012)        |
| Reactive Orange 4   | 50.00                    | 30.00                                      | 7          | (Radovic et al., 2015)         |
| Reactive Blue 19    | 50.00                    | 30.00                                      | 7          | (Radovic et al., 2015)         |
| Reactive Blue 181   | 500.00                   | 14.71                                      | 3          | (Basturk and Karatas, 2015)     |
| Alizarin Yellow R   | 250.00                   | 250.00                                     | 4.95       | (Narayanasamy and Murugesan, 2014) |
| Acid Red 94         | 5.25                     | 42.00                                      | 6.6        | (Rauf et al., 2008)            |
| Reactive Red 35     | 46.60                    | 20.50                                      | 7.6        | (Velmurugan et al., 2013)       |

### 2.2. The effect of pH on the UV/H$_2$O$_2$ process

The reactivity of hydrogen peroxide depends on the pH of the medium. At low pH, the removal rate is limited due to the hydroxyl radical scavenging effects of H$^+$ ion (Eq. 6) (Spinks and Woods, 1990).

\[ \cdot \text{OH} + \cdot \text{H}^+ + e^- \rightarrow \text{H}_2\text{O} \]  

In acidic pHs, where the acidity of a solution comes from the presence of HCl, a certain amount of conjugated base is also present in the solution. The anion Cl$^-$ is able to react with hydroxyl radicals leading to inorganic radical ions (Eq. 7) (Ga~lindo et al., 2001).

\[ \text{Cl}^- + \cdot \text{OH} \rightarrow \text{CIHO}^+ \]

Therefore, Cl$^-$ ions react with $\cdot \text{OH}$ radicals and produce inorganic radical ions. These inorganic radical anions show a much lower reactivity than $\cdot \text{OH}$ radicals, so that they do not participate in dye decolourisation. Hence, Eq. 7 indicates that the decrease in concentration of $\cdot \text{OH}$ radicals as a consequence of pH reduction results in lowering the decolourisation rate of the dye.

The lowering of the removal rate in alkaline pH range is due to the reduction of hydroxyl radical concentration. Under this condition H$_2$O$_2$ undergoes photodecomposition to water and oxygen rather than to hydroxyl radicals (Eq. 8) (Ga~lindo and Kalt, 1999).

\[ 2\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\text{H}_2\text{O} + \text{O}_2^* \]

In an alkaline medium the oxidizing species hydroperoxy anion (HO$_2^-$) is also formed (HO$_2^-$ anion is the conjugated base of H$_2$O$_2$). This HO$_2^-$ anion reacts with $\cdot \text{OH}$ radical and residual H$_2$O$_2$ (Eqs. 9 and 10) and, consequently, lowers the removal rate because the reactivity of O$_2^*$ and HO$_2^-$ with organic pollutants is very low (Braun et al., 1991).
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\begin{equation}
\text{HO}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{OH}^-
\end{equation}
\begin{equation}
\text{HO}_2^- + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2^-
\end{equation}

The self-decomposition rate of hydrogen peroxide is strongly dependent on pH. In practice, H\textsubscript{2}O\textsubscript{2} is supplied in slightly acid condition (pH=5), because of its self-decomposition rate is higher in alkaline medium (Chu, 2001).

\begin{equation}
2 \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2
\end{equation}

The decolourisation of dyes with UV/H\textsubscript{2}O\textsubscript{2} process also depends on their structure, but most frequently the largest degree of decolourisation is at neutral and weakly acidic pH values, which is confirmed by the results of previous reports showed in Table 1.

2.3. The effect of the initial dye concentration on the UV/H\textsubscript{2}O\textsubscript{2} process

The pollutant concentration is one of the most important parameters in the UV/H\textsubscript{2}O\textsubscript{2} process. The effect of the initial dyes concentrations on the efficiency of dye degradation was investigated by many researchers and the obtained results were the same (Muruganandham, 2004a; Aleboyeh et al., 2005; Haji et al., 2011; Basturk and Karatas, 2015). The decolourisation rates of dyes show decreases with the increases of dyes concentrations. Hydroxyl radical is mainly responsible for dyes decolourisation and its concentration remains constant for all dyes concentrations. The increase in dyes concentrations increases the number of dyes molecules and not the \textsuperscript{'}OH radical concentration and so the decolourisation rate decreases.

Moreover, decreases in decolourisation can be explained by considering the fact that both the aromatic dyes and H\textsubscript{2}O\textsubscript{2} absorb UV radiation in the range emitted by the lamp. However, the molar absorption coefficient of dyes is higher than that of H\textsubscript{2}O\textsubscript{2}, so that an increase in dyes concentrations induces a rise of the internal optical density and the solution becomes more and more impermeable to UV radiation. Then, H\textsubscript{2}O\textsubscript{2} can only be irradiated by a smaller portion of UV light and forms lower \textsuperscript{'}OH radicals such that the decolourisation of dyes decreases (Aleboyeh et al., 2005).

3. FENTON AND PHOTO-FENTON PROCESSES

As described above, the decolourisation of dyes was mainly initiated by the production of \textsuperscript{'}OH radicals resulting from direct photolysis of H\textsubscript{2}O\textsubscript{2}. The oxidation power of Fenton and photo-Fenton reagent is due to the generation of \textsuperscript{'}OH during the Fe\textsuperscript{2+} catalysed decomposition of H\textsubscript{2}O\textsubscript{2} in an acid medium (Eq. 12) and decomposition of H\textsubscript{2}O\textsubscript{2} by UV light (Eq. 1) (only for the photo-Fenton process) (Chamarro, 2001).

The mechanism of the Fenton’s process can be summarized by the following steps:

1) First step is production of \textsuperscript{'}OH radicals by the reaction of H\textsubscript{2}O\textsubscript{2} with Fe\textsuperscript{3+} ions according to Eq. 12 (Chen and Pignatello, 1997; Kang et al., 2002). They can attack and initiate the oxidation of organic pollutant molecule by several degradation mechanisms as shown above (Eqs. 2 and 3).

\begin{equation}
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{'OH}
\end{equation}
2) As a $\text{Fe}^{2+}$ ion acts as a catalyst, it has to be regenerated, which happens through the following scheme (Herney-Ramirez et al., 2010):

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightleftharpoons \text{Fe}^{2+} \cdot \text{O}_2\text{H}^+ + \text{H}^+
\]  

(13)

\[
\text{Fe}^{2+} \cdot \text{O}_2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{HO}_2^+
\]  

(14)

The rate of pollutants degradation can be considerably increased via photochemical reactions in the UV/Fenton process (photo-Fenton) (Tarr, 2003; Parsons, 2004; Núñez et al., 2007). In this process, in addition to the above reaction, the formation of $\cdot\text{OH}$ radicals occurs in the presence of light by the following reactions (Papić et al., 2009):

\[
\text{H}_2\text{O}_2 + h\nu \rightarrow 2\cdot\text{OH}
\]  

(15)

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 + h\nu \rightarrow \text{Fe}^{2+} + \cdot\text{OH} + \cdot\text{OH}
\]  

(16)

In the photo-Fenton process, the regeneration of $\text{Fe}^{2+}$ with a production of new $\cdot\text{OH}$ radicals, follows the photoreduction process (Papić et al., 2009):

\[
\text{Fe}^{3+} + \text{H}_2\text{O} \rightarrow \text{FeOH}^{2+} + \text{H}^+
\]  

(17)

\[
\text{FeOH}^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \cdot\text{OH} \text{ (≤ 410 nm)}
\]  

(18)

The reason for the higher efficiency of the photo-Fenton compared to the Fenton process are additional reactions under light irradiation which produce $\cdot\text{OH}$ radicals (Eqs. 15, 16 and 18), and regenerate $\text{Fe}^{2+}$ ions (Eqs. 16 and 18).

Table 2. Optimal parameters for decolourisation of textile dyes by the Fenton process.

| Dye           | Dye conc. | Optimal $\text{Fe}^{2+}$ conc. (mmol dm$^{-3}$) | Optimal $\text{H}_2\text{O}_2$ conc. (mmol dm$^{-3}$) | Optimal pH | Reference               |
|---------------|-----------|-----------------------------------------------|------------------------------------------------|------------|-------------------------|
| Acid Blue 161 | 39.44     | 0.10                                          | 1.10                                           | 3-3.5      | (Trovó et al., 2016)    |
| Carmoisine    | 20.00     | 0.015                                         | 0.15                                           | 3.5        | (Sohrabi et al., 2014)  |
| Reactive Orange 4 | 390.73  | 0.10                                          | 15.00                                          | 3          | (Muruganandham, 2004b)  |
| Acid Yellow 23 | 40.00     | 0.10                                          | 14.71                                          | 3          | (Modirshahla et al., 2007) |
| Reactive Yellow 14 | 334.51 | 0.075                                         | 15.00                                          | /          | (Muruganandham and Swaminathan, 2006) |
| Reactive Yellow 3 | 100.00   | 0.50                                          | 20.00                                          | /          | (Papić et al., 2009)    |
| Reactive Blue 2 |         |                                               |                                               |            |                         |
| Reactive Violet 2 |         |                                               |                                               |            |                         |
| Acid Orange 8 | 3.64      | 0.02                                          | 10.00                                          | 3          | (Abo-Farha, 2010)       |
| Acid Red 17   | 5.02      | 0.01                                          | 5.00                                           |            |                         |
| Ponceau 4R    | 60.00     | 0.27                                          | 4.41                                           | 3          | (Benincá et al., 2012)  |
| Reactive Orange 4 | 50      | 0.1                                           | 25                                             | /          | (Radovic et al., 2015)  |
| Reactive Blue 19 |         |                                               |                                               |            |                         |
| Sunzol Black DN | 100.00   | 0.05                                          | 4.00                                           | 3.5        | (Daud et al., 2012)     |
| Reactive Blue 114 | 60.00   | 0.89                                          | 14.71                                          | 3          | (Karatas et al., 2012)  |
| Procion Red H-E7B | 100.00  | 0.18                                          | 2.94                                           | /          | (Núñez et al., 2007)    |
| Cibacron Red FN-R |         |                                               | 7.35                                           |            |                         |
3.1. The effect of Fe$^{2+}$ on the Fenton and photo-Fenton processes

One of the main parameters for decolourisation of dyes by the Fenton and photo-Fenton processes is concentration of Fe$^{2+}$ ions. The effect of addition of Fe$^{2+}$ ions have been investigated in many studies to determine the optimal Fe$^{2+}$ ions concentration (Table 2 and 3).

The results showed that decolourisation of dyes increases when the added Fe$^{2+}$ dose increases to a certain value. The reason for this increase is that more •OH radicals are produced with the increase in the concentration of Fe$^{2+}$.

On the other hand, further increases in the amount of Fe$^{2+}$ ions did not result in appreciable increases in the rate of decolourisation. Moreover, many studies have revealed that an excess of Fe$^{2+}$ ions may scavenge the formed •OH radicals (Eq. 19) and induce a decrease in the degradation rate of pollutants (Chen and Pignatello, 1997; Joseph et al., 2000).

$$\text{Fe}^{2+} + \cdot \text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^-$$

(19)

As it can be seen from Table 2 and 3, the optimum initial concentration of Fe$^{2+}$ ions in most cases is 0.05-0.2 mmol/dm$^3$.

### Table 3. Optimal parameters for decolourisation of textile dyes by the photo-Fenton process.

| Dye                  | Dye conc. (mg dm$^{-3}$) | Optimal Fe$^{2+}$ conc. (mmol dm$^{-3}$) | Optimal H$_2$O$_2$ conc. (mmol dm$^{-3}$) | Optimal pH | Reference                          |
|----------------------|--------------------------|------------------------------------------|-------------------------------------------|------------|------------------------------------|
| Yellow 5 (E102)      | 200.00                   | 1.00                                     | 17.13                                     | 3          | (GilPalvas et al., 2015)           |
| Reactive Blue 19     | 97.73                    | 0.09                                     | 48.95                                     | 4          | (Ercan et al., 2015)               |
| Reactive Red 21      | 29.69                    |                                          |                                           |            |                                    |
| Carmoisine           | 20.00                    | 0.0125                                   | 0.30                                      | 3.5        | (Sohrabi et al., 2014)             |
| Reactive Orange 4    | 390.73                   | 0.10                                     | 20.00                                     | 3          | (Muruganandham, 2004b)             |
| Acid Yellow 23       | 40.00                    | 0.10                                     | 20.59                                     | 3          | (Modirshahla et al., 2007)         |
| Reactive Yellow 14   | 334.51                   | 0.075                                    | 20.00                                     | /          | (Muruganandham and Swaminathan, 2006) |
| Acid Orange 8        | 3.64                     | 0.05                                     | 10.00                                     | 3          | (Abo-Farha, 2010)                  |
| Acid Red 17          | 5.02                     |                                          | 5.00                                      |            |                                    |
| Ponceau 4R           | 60.00                    | 0.27                                     | 4.41                                      | 3          | (Benincá et al., 2012)             |
| Reactive Orange 4    | 50.00                    | 0.10                                     | 25.00                                     | /          | (Radovic et al., 2015)             |
| Reactive Blue 19     | 99.18                    | 0.15                                     | 0.73                                      | 3          | (Lucas and Peres, 2006)            |

3.2. The effect of H$_2$O$_2$ on the Fenton and photo-Fenton processes

In a Fenton and photo-Fenton-based system, the oxidant concentration is a key factor that can significantly influence decolourisation of dyes. The H$_2$O$_2$ concentration is directly related to the number of •OH radicals generated, and hence to the performance achieved. Much research has been done to determine the effect of H$_2$O$_2$ dosage on the decolourisation of dyes by the Fenton and photo-Fenton processes, and results are shown in Table 2 and 3.

The results indicate that decolourisation of dyes increases by increasing the concentration of H$_2$O$_2$. This can be explained by the effect of additionally produced hydroxyl radicals. However,
high dosages of H$_2$O$_2$ cause no significant change in decolourisation, and in some cases cause reduction of decolourisation (Fig. 13). This is due to the fact that at higher H$_2$O$_2$ concentrations scavenging of $^\cdot$OH radicals will occur, as expressed by the following equations (Najjar et al., 2007; Chen et al., 2009):

\[ \text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \] (20)

\[ \cdot \text{OH} + \text{HO}_2^- \rightarrow \text{H}_2\text{O} + \text{O}_2 \] (21)

Based on the findings in the literature displayed in Table 2 and 3, it can be concluded that the optimal initial concentration of H$_2$O$_2$ for the Fenton and photo-Fenton processes is most frequently in the range from 5 to 25 mmol/dm$^3$.

### 3.3. The effect of pH on the Fenton and photo-Fenton processes

The pH of a solution is an important parameter for the Fenton and photo-Fenton oxidation processes, controlling the production rate of the hydroxyl radical and the concentration of Fe$^{2+}$. The studies which results for optimal parameters of Fenton and photo-Fenton process are presented in Table 2 and 3, show that an increase in the pH of the solution from 1 to 3-4 increases decolourisation sharply. Further increase of pH decreases the decolourisation of dyes. Hence, pH 3 is found to be the optimum pH for both processes.

At pH below 3, the reactions according to Eq. 12 could be slowed down because hydrogen peroxide can stay stable probably by solvating a proton to form an oxonium ion (Eq. 22). An oxonium ion makes hydrogen peroxide electrophilic to enhance its stability and presumably to reduce substantially the reactivity with Fe$^{2+}$ ions (Kwon et al., 1999).

At the same time, the formed complex species [Fe(H$_2$O)$_6$]$^{2+}$ and [Fe(H$_2$O)$_6$]$^{3+}$ also react more slowly with hydrogen peroxide (Bossmann et al., 1998). In addition, at low pH the removal rate is limited due to the hydroxyl radical scavenging effects of H$^+$ ion (Eq. 6) (Spinks and Woods, 1990).

\[ \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{H}_3\text{O}_2^+ \] (22)

In the Fenton and photo-Fenton processes the decrease in decolourisation at pH above 3 is due to deactivation of a Fe$^{2+}$ catalyst with the formation of Fe$^{3+}$ hydroxide complexes leading to a reduction of $^\cdot$OH radical (Solozhenko et al., 1995).

### 3.4. The effect of the initial dye concentration on the Fenton and photo-Fenton processes

Many researchers have investigated the effect of the initial concentration of a pollutant as it is of importance in any process of wastewater treatment. For the Fenton and photo-Fenton processes it has been observed that decolourisation decreases with increasing the initial concentrations of dyes (Muruganantham, 2004b; Lucas and Peres, 2006; Modirshahla et al., 2007; Sun et al., 2007).

The presumed reason is that when the initial concentrations of dyes are increased, the hydroxyl radical concentration remains constant for all dyes molecules so the removal rate decreases. Once the concentrations of dyes are increased, dyes molecules absorb light and photons never reach the photo-catalyst surface, so the photodegradation efficiency decreases (Daneshvar et al., 2005).
4. COMPARISON OF THE EFFICIENCIES OF THE UV/H₂O₂, FENTON AND PHOTO-FENTON PROCESSES

The experimental data have demonstrated that the UV/H₂O₂, Fenton and photo-Fenton processes are promising techniques for degradation of dyes from an aqueous solution. Comparison efficiencies of these processes for decolourisation of different dyes solutions have been performed by a lot of researchers, and the results are presented in Table 4.

| Dye               | Dye concentration (mg dm⁻³) | Time (min) | Decolourisation (%) by UV/H₂O₂ | Decolourisation (%) by Fe²⁺/H₂O₂ | Decolourisation (%) by UV/Fe²⁺/H₂O₂ | References                |
|-------------------|-----------------------------|------------|---------------------------------|----------------------------------|-------------------------------------|---------------------------|
| Reactive Yellow 14| 334.51                      | 40         | 34.2                            | 84.2                             | 94.8                                | (Muruganandham and Swamininathan, 2006) |
| Acid Red 14       | 50.00                       | 4          | 51.5                            | 82                               | 95.9                                | (Daneshvar and Khataee, 2006)         |
| Procion Navy H-exl| 75.00                       | 7          | 85                              | 96                               | 99                                  | (Riga et al., 2007)                  |
| Reactive Black 5  | 99.18                       | 7.5        | 14                              | 90.9                             | 93.6                                | (Lucas and Peres, 2006)              |
| Reactive Orange 4 | 390.73                      | 40         | 44                              | 79.89                            | 95.5                                | (Muruganandham, 2004b)               |
| Acid Orange 8     | 3.64                        | 55         | /                               | 89                               | 99.5                                | (Abo-Farha, 2010)                   |
| Acid Red 17       | 5.02                        | /          |                                 | 78                               | 95                                  |                                         |
| Reactive Yellow 3 | 100.00                      | 5          | /                               | 84                               | 87                                  | (Papić et al., 2009)                |
| Reactive Blue 2   | 92                          |            |                                 |                                  |                                     |                                         |
| Reactive Violet 2 | 95                          |            |                                 |                                  |                                     |                                         |

It can be observed that relative efficiencies of the above processes are in the following order: photo-Fenton > Fenton > UV/H₂O₂. The differences in decolourisation rate in these processes are mainly due to the difference in hydroxyl radical generation in each process. The application of H₂O₂ at appropriate dosages with UV light leads to total dye decolourisation, but the UV/H₂O₂ process is quite slow when compared to the other two processes.

Despite the advantages of the Fenton and photo-Fenton processes in comparison to UV/H₂O₂, they have certain drawbacks. During the Fenton and photo-Fenton processes in water, Fe²⁺ ions are also added, which later, despite the relatively low concentration, have to be removed from the water, thus complicating the process of water purification. Also, the Fenton and photo-Fenton processes must be performed at pH 3 after which it is necessary to neutralize the solution. On the other hand, during the UV/H₂O₂ process no salt is introduced into water and further treatment is not necessary.
5. Conclusion

After analyzing and comparing the results of the previous studies that focus on the usage of advanced oxidation processes for removal of textile dyes from wastewater, it can be concluded that all three processes (UV/H₂O₂, Fenton and photo-Fenton) can efficiently be used for decolourisation of textile dyes. The observations of these investigations clearly demonstrate the importance of choosing the optimum decolourisation parameters to obtain a high reaction rate. The optimal dosage of H₂O₂ for UV/H₂O₂ process is 20-50 mmol/dm³. The UV/H₂O₂ process also depends on pH such that it is faster on neutral or weakly acid pH values. An increase in dye concentration decreases decolourisation of dyes treated with the UV/H₂O₂, Fenton and photo-Fenton processes. The highest decolourisation rate of dyes treated with the Fenton and photo-Fenton processes is at pH 3. The optimum concentrations of H₂O₂ and Fe²⁺ ions are 5-25 mmol/dm³ and 0.05-0.2 mmol/dm³, respectively. The photo-Fenton process is found to be the most efficient for decolourisation of dyes.

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UTICAJ PARAMETARA PROCESA NA DEKOLORIZACIJU TEKSTILNIH BOJA I POREĐENJE EFIKASNOSTI UV/H₂O₂, FENTON I FOTO-FENTON PROCESA: PREGLEDNI RAD

U ovom preglednom članku, pokušali smo da sumiramo rezultate dosadašnjih proučavanja vezanih za primenu unapređenih oksidacionih procesa (UOP) kakvi su UV/H₂O₂, Fenton i foto-Fenton za uklanjanje tekstilnih boja iz otpadnih voda. Predstavljen je i uticaj parametara kao što su početna koncentracija boje, početna koncentracija H₂O₂, početna koncentracija Fe²⁺ jona i početna pH vrednost rastvora na efikasnost ovih procesa. Do sada je objavljen eliki broj radova u kojima su unapređeni oksidacioni procesi korišćeni za degradaciju tekstilnih boja i rezultati su pokazali da su ovi procesi veoma efikasni. Poređenjem rezultata prethodnih studija, čini se da je foto-Fenton proces efikasniji od Fenton i UV/H₂O₂ procesa.

Ključne reči: unapređeni oksidacioni procesi, tekstilne boje, prečišćavanje otpadnih voda, UV/H₂O₂, Fenton, foto-Fenton