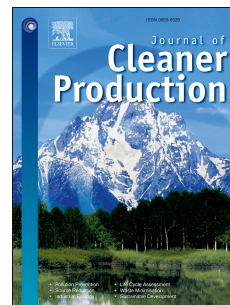


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**Advanced Oxidation Processes for *In-situ* production of Hydrogen
peroxide/Hydroxyl radical for Textile Wastewater Treatment: A Review**

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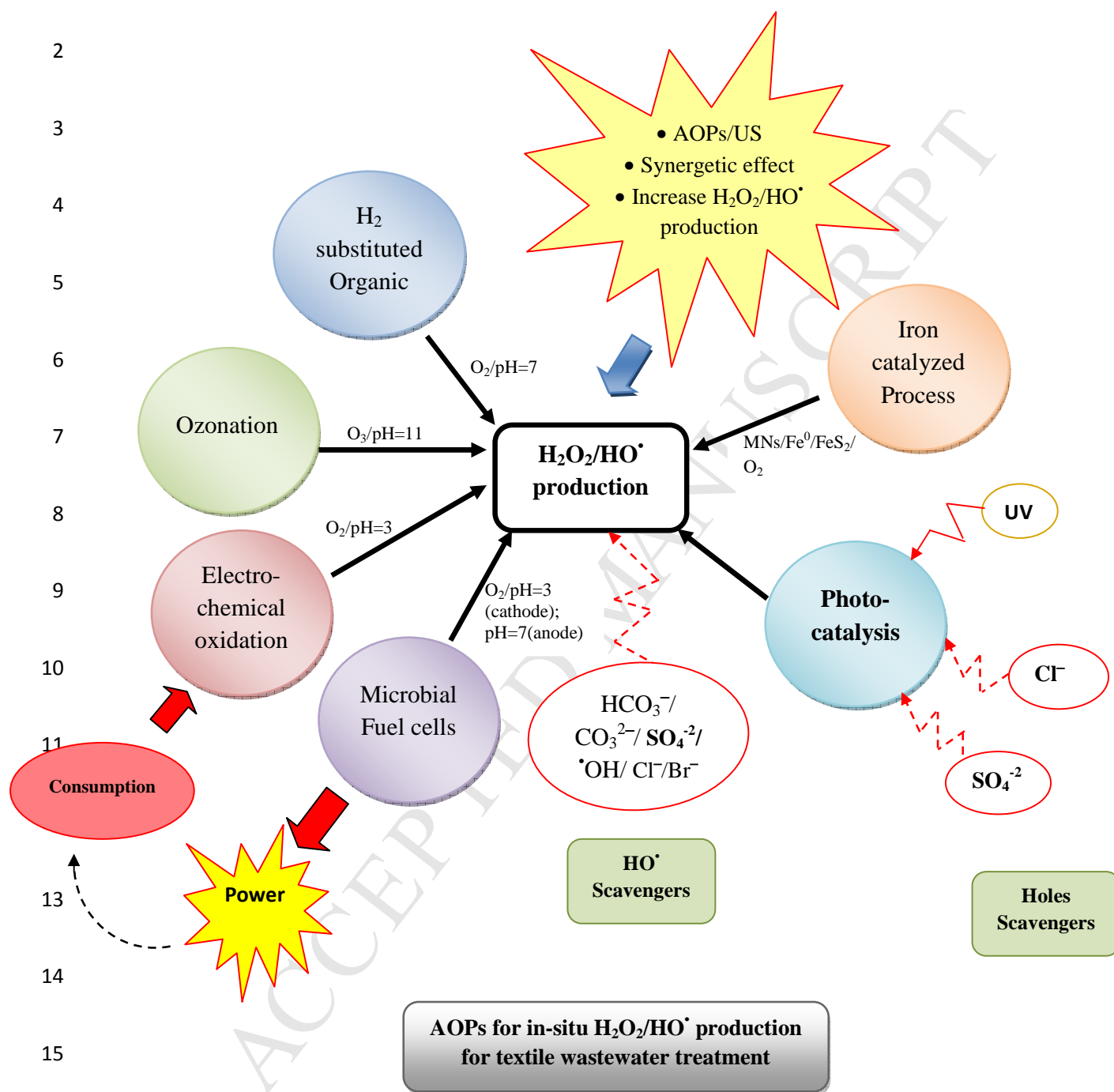
Abstract

Fenton Process, a type of Advanced Oxidation Processes is an efficient method for treating textile wastewaters. However, excessive use of hydrogen peroxide and catalyst has made this process economically non-feasible. Besides, industrial grade hydrogen peroxide costs \$390–500 per ton. One of the means to overcome this problem is the *in-situ* production of hydrogen peroxide. In this paper, a detailed review was conducted on the generation methods, degradation potential and optimum operating parameters for *in-situ* production of hydrogen peroxide/hydroxyl radicals. Additionally the scavenging aspect for hydroxyl radicals was also investigated. From this review, it can be concluded that hydroxyl radical is highly oxidative and non selective in nature and its *in-situ* production can be performed through application of catalyst, ozonation, photocatalysis, electro and microbial fuel cells. Furthermore, optimization of operating parameters can result in an increase in the yield of hydroxyl radicals/hydrogen peroxide. Sonolysis as an auxiliary tool have potential to induce synergetic effects in combination with Advanced Oxidation Processes to increase *in-situ* hydrogen peroxide production. However, the problem of the scavenging effect is an aspect that needs to be dealt with, as hydroxyl radicals are prone to deactivation by scavengers. Therefore based on the review, it is concluded that *in-situ* production of hydrogen peroxide/hydroxyl radical for treating textile wastewater is economically viable and practically feasible if careful selection of process is conducted through selective research.

Keywords

Hydrogen peroxide, Hydroxyl radicals, Fenton process, Textile wastewater, Advanced Oxidation Process, Sonolysis

Graphical Abstract



1. Introduction

Textile industry consumes immense amounts of process water and chemicals. Approximately 21-377m³ of water is consumed for one ton of textile product (Sahunin et al., 2006) and chemical consumption normally varies from 10% to over 100% of the weight of the cloth (Ozturk et al., 2009). Estimates indicate that approximately, 7×10⁵ tons of dyestuffs are produced annually and 280,000 tons of the textile dyes are discharged into water sinks through textile effluents (Eren, 2012; Jin et al., 2007). That, explains why textile effluent is characterized by high COD (150-10,000mg/L), BOD (100-4,000 mg/L), pH (6-10) and color content (50-2500) (Kalra et al., 2011). Moreover, discharge of even a small quantity (ca.1 mg/L) of dye is not acceptable and may produce toxic compounds at the end of treatment process (Ghodbane and Hamdaoui, 2009).

Since dyes are designed to resist degradation, these are chemically stable, non-biodegradable and exist as substances that possess toxic and carcinogenic characteristics (Turhan et al., 2012). Therefore, a proper treatment strategy is required to meet the pollution control requirements. Majority of the conventional treatment methods comprise of adsorption (Yeh et al., 2002), coagulation (Alinsafi et al., 2005), filtration (Métivier-Pignon et al., 2003) and biological treatment (Paprowicz and Słodczyk, 1988). These methods are less efficient because dyes are stable against biological degradation (Wu et al., 2008), which results in sludge formation, membrane fouling and incomplete mineralization (Yeh et al., 2002; Alinsafi et al., 2005; Liu et al., 2007).

Advanced Oxidation Processes (AOPs) comprise a series of methods including ozonation, photocatalysis, electrochemical oxidation, Fenton and Fenton-like processes. Although these processes use different reacting systems, all are characterized by similar chemical feature of

utilizing highly reactive oxidizing agent such as hydroxyl radical (HO^\bullet) with redox potential of 2.80eV (Krishnakumar and Swaminathan, 2011). However, the process that has gained attention is Fenton process because of rapid formation of HO^\bullet radicals in acidic medium according to the following chemical reaction:



Technical feasibility study of Fenton oxidation together with other AOPs has been discussed in detail (Chong et al., 2012). Nevertheless, there are various factors that hinders the efficacy of the process such as reaction parameters (Tosik, 2005), types of salt used (Ledakowicz et al., 2000), high cost of hydrogen peroxide (H_2O_2) and excess consumption of chemicals exclusively H_2O_2 (Hassan et al., 2012). Additionally, hazards associated with the transport, handling and storage of bulk quantities of H_2O_2 have made the process unsafe and economically challenging (Sheriff et al., 2007). It was also evident from the study conducted by Meric et al (2004) in which the authors reported that 400mg/L H_2O_2 and 100mg/L iron salt were consumed for degrading 100mg/L of synthetic dye. Similarly, Argun and Karastas (2011) used 2000mg/L of H_2O_2 for degrading 200mg/L of synthetic dye. High consumption of H_2O_2 is not economically viable and it intensifies the need to find some cost effective and technically feasible alternatives for textile wastewater treatment.

One such option is *in-situ* production of $\text{H}_2\text{O}_2/\text{HO}^\bullet$ or some other oxidants with redox potential comparable to HO^\bullet . In this context, several research groups have reported *in-situ* production of $\text{H}_2\text{O}_2/\text{HO}^\bullet$ (Tosik, 2005; Yang et al., 2010) and some other oxidants such as sulfate radicals ($\text{SO}_4^{\bullet-}$), permanganate (MnO_4^-), hypochlorite (ClO^-), chlorine dioxide (ClO_2) and ozone (O_3) for textile wastewater treatment (Anipsitakis and Dionysiou, 2003; Xu et al., 2005; Méndez-

Díaz et al., 2009; Turhan et al., 2012). Out of all these oxidants, *in-situ* production of $\text{H}_2\text{O}_2/\text{HO}^\bullet$ has received much attention because of its high redox potential and non-selective nature for most of the organic contaminants (Neyens and Baeyens, 2003). The redox potential of few oxidizing agents is provided in Table 1. Possible methods that are available in literature for *in-situ* production of $\text{H}_2\text{O}_2/\text{HO}^\bullet$ include AOPs such as ozonation, photocatalysis, electrochemical oxidation and microbial fuel cells. Therefore, this review aims at discussing literature relevant to *in-situ* $\text{H}_2\text{O}_2/\text{HO}^\bullet$ production by AOPs. However, there are some economical, technological and operational issues with commercial production of H_2O_2 that must be considered before going into the detail of *in-situ* production of $\text{H}_2\text{O}_2/\text{HO}^\bullet$.

1.1.Challenges with Commercially Available H_2O_2

Hydroxyl radical (HO^\bullet) is unstable in nature that is why for wastewater treatment applications commercially available H_2O_2 is used as a source of HO^\bullet production. It is one of the cleanest and ideal oxidants for the degradation of dyes and organic contaminants present in wastewater (Sheriff et al., 2007). Globally, demand for H_2O_2 has increased. According to the statistical report published by ICON Group, H_2O_2 with the total worth of US\$ 383,067 (Parker, 2004) was exported in 2005 which was increased by 37% in 2011(Parker, 2010). This group also discussed the breakdown of market in context of its supply and consumption in different regions of the world as shown in Fig.1.

Besides increase in demand, the cost of commercially available H_2O_2 is also high. Industrial grade H_2O_2 costs \$390-500 per ton (Zhu and Logan, 2013a). Commercially, H_2O_2 is produced by the oxidation of anthrahydroquinone as shown in Fig. 2. Successive developments in this technology have reduced the cost of chemicals by replacing conventional Raney-Ni by highly

selective and highly active Pd/Al₂O₃ (Chen, 2006). However, energy requirement of the process is still higher. This is because, for trade purposes, the product formed must be concentrated up to 70% (Campos-Martin et al., 2006) which makes the process energy intensive and increase the cost of the product

Fig. 1. World supplies of Exported Hydrogen Peroxide (2005)

Fig. 2. Conventional method for H₂O₂ production (Campos-Martin et al., 2006)

Direct method is another option where direct contact of hydrogen and oxygen over the surface of catalyst leads to the formation of H₂O₂. It is a simple process as oxygen and hydrogen are naturally available. But there are several problems that must be dealt with such as side reactions, decomposition of H₂O₂ over the surface of catalyst (Campos-Martin et al., 2006) and formation of explosive mixture from hydrogen and oxygen (Voloshin et al., 2007). Possible ways to overcome these limiting issues have also been proposed but their practical applications have not been realized (Voloshin et al., 2007; Lunsford, 2003).

Several authors have also studied the potential of other oxidizing agents such as SO₄^{•-}, O₃, MnO₄⁻ etc based on their redox potential as given in Table 1. It is observed that most of the oxidizing agents have redox potential comparable to the H₂O₂ and HO[•]. Thus it is possible to use these oxidants for textile wastewater treatment. In order to confirm it, Co⁺²/PMS system as a source of SO₄^{•-} free radical was investigated for the degradation of Acid Red 88 (AR88) dye. In this study, it was found that SO₄^{•-} widens the pH range of the system but its selective nature for most of the oxidizing agents limit its application. Moreover, oxone which is used as a source of SO₄^{•-} is two times as costly as H₂O₂ (Anipsitakis and Dionysiou, 2003; Madhavan et al., 2009). Xu et al (2005) examined decolorization efficiency of ten different dyes by utilizing KMnO₄ and

found that MnO_4^- was efficient for decolorization and could be used as pre-treatment step for biological processes. However, concentration of MnO_4^- and pH is important to control for achieving high decolorization efficiencies. In another study, Mendez-Diaz et al (2009) collated the performance of conventional oxidizing agents (ClO^- , ClO_2 , KMnO_4), O_3 , $\text{O}_3/\text{H}_2\text{O}_2$, O_3 /activated carbon for the removal of sodium dodecylbenzenesulphonate (SDBS) and achieved 80% SDBS removal within 30 minutes with O_3 /PAC while others showed insignificant results.

Table 1. Redox potential of oxidizing agents

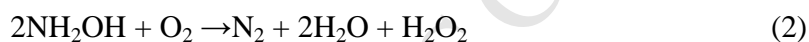
It is suggested that conventional oxidizing agents are more suitable to perform decolorization than mineralization (Xu et al., 2005). Limited works have been conducted on conventional oxidizing agents in this decade. Although, $\text{SO}_4^{\bullet-}$ has redox potential comparable to HO^\bullet (Table 1), its selective nature for organic contaminants hinders its practical application. Therefore, it is concluded that HO^\bullet is the most suitable option for textile or any other wastewater treatment. Therefore, this study was attempted to review and conclude all aspects of literature that determine the feasibility of *in-situ* production of $\text{H}_2\text{O}_2/\text{HO}^\bullet$ for textile wastewater treatment by using common AOPs.

2. *In-situ* Production of Hydrogen Peroxide/Hydroxyl radical from AOPs

In-situ production of $\text{H}_2\text{O}_2/\text{HO}^\bullet$ means its production at the time of treatment. From literature, possible methods that can be employed are AOPs comprising of iron catalyzed reaction, ozonation, photocatalysis, electrochemical or microbial fuel cells. Thus, this review is attempted to summarize AOPs studies that only focus on *in-situ* $\text{H}_2\text{O}_2/\text{HO}^\bullet$ production.

2.1. Hydrogen substituted organic compounds as a source of H₂O₂

The concept of hydrogen substituted organic compound for *in-situ* H₂O₂ production has been suggested to overcome the shortcomings of direct method such as formation of explosive mixture of hydrogen and oxygen (Voloshin et al., 2007). Choudhary and Jana (2007) employed hydroxylamine as a source of hydrogen to react with oxygen to form H₂O₂ over Pd/Al₂O₃ catalyst [Eq. 2-3].



This process was characterized by high reaction rates at neutral pH. However, net formation of H₂O₂ was decreased with increase in reaction time because of the decomposition of H₂O₂ over the surface of catalyst (Choudhary and Jana, 2007). However, Br⁻ or Cl⁻ ions can possibly be used as inhibitors to suppress the decomposition of H₂O₂. But excess concentrations of Cl⁻ ions act as scavengers for HO[•] formed within the system (Ledakowicz et al., 2000). Park et al (2000) discussed novel idea of catalyst loaded with organic compound for *in-situ* H₂O₂ production. They reported 1.5 times higher activity of zeolite beta supported Pd adsorbed with hydroquinone compared to zeolite beta supported with Pd alone.

Yalfani et al (2011) compared the performance of hydrazine, formic acid and hydroxylamine as hydrogen substitutes for H₂O₂ production. Among all, formic acid was observed to be the least efficient for H₂O₂ production. However, efficacy of the process was improved when H₂O₂ produced was utilized at the same time. Moreover, hydrazine was found to be dependent on acidic conditions which cause the corrosion of catalyst. Furthermore, its decomposition over

1 catalyst surface resulted in rapid formation of H_2O_2 which in turn decomposed rapidly rather
2 than participating in oxidation process (Yalfani, Contreras et al., 2011).

3 Since this method has been successfully applied for the treatment of organic contaminants; it
4 can possibly be used for textile wastewater. Although, it can overcome the limitations
5 encountered in direct method, incomplete conversion of organic compound may increase the
6 toxicity of the treated textile wastewater. Also, there may be the reaction between organic
7 compound and *in-situ* HO^\bullet (conversion of *in-situ* H_2O_2 to HO^\bullet in the presence of Fe^{+2}) which
8 lowers the process efficiency (Choudhary and Jana, 2007). Thus, it is suggested to use this
9 process if organic compound (source of H_2O_2) is already present in the textile wastewater.

10 2.2. Iron Catalyzed H_2O_2 Production

11 Among transition metals, iron is known as a suitable catalyst for generation of HO^\bullet radicals
12 through Fenton process (Anipsitakis and Dionysiou, 2004). Its role in *in-situ* production of
13 $\text{H}_2\text{O}_2/\text{HO}^\bullet$ was explored in the last decade.

14 Borda et al (2003) explored the catalytic ability of iron pyrite to produce HO^\bullet radical.
15 According to the study, water adsorbed on the catalyst surface dissociates on sulfur deficient
16 sites and forms HO^\bullet radical in oxygen free medium. Later, in 2012, Wang et al (2012) extended
17 the idea of Borda and his co-workers for *in-situ* production of HO^\bullet radicals. The report suggested
18 that in the presence of oxygen, pyrite was thermodynamically unstable and either dissolved
19 oxygen or Fe^{+2} ions was available in suspension for the production of oxidizing agents as shown
20 in Fig. 3. Moreover, Fe^{+2} ions formed Fenton reagent system with H_2O_2 for degradation of
21 organic contaminants (Wang et al., 2012). In both studies, it was found that production of sulfate

ions SO_4^{2-} is an inevitable phenomenon and it may affect the yield of HO^\bullet radicals by scavenging process (Liu et al., 2012).

Fig. 3. *In-situ* production of H_2O_2 / HO^\bullet by iron pyrite (Wang et al., 2012)

Fang et al (2013) exploited the reductive property of magnetic nano-particles for transformation of oxygen into H_2O_2 . Here, transformation of oxygen into H_2O_2 takes place in two consecutive single electron transfers steps from MNPs sorbed Fe^{+2} with subsequent protonation with H^+ . Then H_2O_2 reacts with dissolved Fe^{+2} in bulk medium to produce HO^\bullet radical through Fenton reaction. From reaction mechanism, it was observed that pH has a profound effect on the type of oxidizing species available in reaction medium. As shown in Fig. 4, superoxide radical ($\text{O}_2^{\bullet -}$) is dominant at alkaline pH while HO^\bullet is dominant at acidic condition.

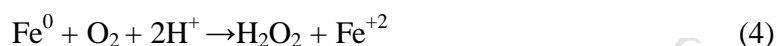
Although the application of above mentioned processes have not yet been investigated for textile wastewater treatment, comparison of these techniques with conventional Fenton oxidation processes portrays the feasibility of these methods for textile wastewater treatment.

Fig. 4. Reaction pathways for *in-situ* production of HO^\bullet / H_2O_2 utilizing MNPs

(Fang et al., 2013)

Besides, zero valent iron (Fe^0) has potential for *in-situ* generation of H_2O_2 . Degradation phenomenon by Fe^0 is attributed to the direct transfer of electron from metal surface to the dye or organic contaminant prior to *in-situ* production of H_2O_2 , (Cao et al., 1999). This degradation step takes place via oxidizing agents such as H_2O_2 and other oxidative species depending on pH in

oxic condition which in turn produce HO^\bullet radical for decolorization of dyes through Fenton process [Eq. 4, 1 & 5] (Yang et al.,2010).



Wang et al (2010) reported that under oxic conditions, high COD removal was obtained because of the combined effect of oxidation and adsorption of dyes on iron hydroxides, generated from Fe^0 oxidation. From above mentioned reaction equations, it can be inferred that the efficacy of Fe^0 depends on the transfer of electron from the iron surface to the targeted contaminants. Lee et al (2007) investigated the oxidation of Fe^0 accelerated by peroxometalate (POM) as electron shuttle to improve the catalytic performance of the Fe^0 . POM is not suitable for the degradation of dyes waste; however quinone intermediates can possibly be used to accelerate the transfer of electrons.

Among aforementioned alternatives, iron catalyzed production of *in-situ* $\text{H}_2\text{O}_2/\text{HO}^\bullet$ is a viable option for textile wastewater treatment. Moreover, it has some advantages over hydrogen substituted organic compound as there may be incomplete conversion of organic compound in later option, no matter produced H_2O_2 is utilized *in-situ* or *ex-situ*. Furthermore, iron catalyzed *in-situ* production of $\text{H}_2\text{O}_2/\text{HO}^\bullet$ is also cost effective because single catalyst can be used for oxidant production as well as for degradation of dyes in textile wastewater. As evident from one study, the operating cost for Remazol Brilliant blue R (RBBR) degradation by Fe^0/air reduced from 0.015US\$/g of dye (Fenton process) to 0.00113 US\$/g of dye(Chang et al. 2009).

2.3. Ozonation for *in-situ* H₂O₂/HO[•] production

Ozonation is an environmentally sound technique because of no sludge formation; potential to perform decolorization and degradation in a single step; decomposition of residual ozone into water and oxygen; less space requirement for equipment installation; less hazardous as no stock of H₂O₂ is required for the oxidation step and ease of operation (Chu and Ma, 2000; Oguz et al., 2005). Therefore, it is recommended to consider it an efficient option for *in-situ* production of H₂O₂/ HO[•] for dye degradation.

Ozonation is suitable for complete decolorization rather than mineralization (Tosik, 2005). Ozonation process follows two different routes for degradation of textile dyes based on pH value. Under acidic conditions, ozone selectively attacks the aromatic and conjugated double bonds of chromophores in dye structures (Turhan et al., 2012) and leads to the formation of aldehydes, carboxylic acids and other by-products (Nawrocki and Kasprzyk-Hordern, 2010).

However, at high pH values, ozonation mechanism changes from direct ozonation to complex chain mechanism. As a result, HO[•], HO₂[•] and HO₄[•] radicals are formed (Glaze, Kang and Chapin, 1987). Among these, HO[•] is dominant and it has a potential to open aromatic rings of dye present in textile wastewater (Chu and Ma, 2000). It was also explained by the findings of Turhan et al (2012) that the reported COD removal of direct dyestuff in wastewater at pH 6.5 was 23.33% after 2 hrs of ozone bubbling which increased to 64.96% when pH value increased to 12.

Moreover, pH also effects the time required for complete decolorization. For example, time required for decolorizing direct dye stuff reduced to 59.62% when pH increased from 2 to 12 (Turhan et al., 2012). In another experimental study by Muthukumar et al (2004), it was reported

that the time required for complete decolorization of Acid Red 88 (AR88) by ozonation increased till pH 7 and then decreased which clearly indicates the decomposition of O_3 into HO^\bullet . The COD value obtained as a result of regression analysis at alkaline pH was 64% according to the study done by Muthukumar et al (2004).

From this review, it can therefore be concluded that pH is the key parameter for accelerating *in-situ* production of HO^\bullet . Few investigations have discussed analogous results. For example, De Souza et al (2010) and Tehrani-Bagha et al (2010) reported slight change in dye degradation efficiencies at high pH values as compared to acidic conditions. They supported this result by arguing that it was buffered or non-buffered solution that played a role in promoting *in-situ* HO^\bullet production at high pH values. They explained that in non-buffered solution, pH value decreased because of the formation of acidic products and left no effects at the end. To overcome this problem, catalytic ozonation is an efficient alternative because ozone can decompose itself to produce HO^\bullet in the presence of catalyst. Furthermore, use of catalyst also promotes controlled decomposition of ozone into HO^\bullet resulting in effective mineralization of dye and organic contaminants (Nawrocki and Kasprzyk-Hordern, 2010; Kasprzyk-Hordern et al., 2003).

Wu et al (2008) compared catalytic ozonation for homogeneous (Mn(II)) and heterogeneous (UV/TiO₂ & MnO₂) catalytic system for degradation of Reactive Red 2 (RR2) with subsequent mechanisms. And they observed high degradation of RR2 as a result of radical chain reaction and surface mechanism.

Performance of catalytic ozonation can further be improved in the presence of activated carbon as it enhances the chances of *in-situ* HO^\bullet radical formation. For this, Faria et al (2009)

demonstrated the activity of composite AC₀-Ce-O for ozonation of one acid and two reactive dyes. They observed that improvement in the performance of ozonation was due to the adsorption and accelerated decomposition of O₃ into HO[•]. Moreover, this decomposition step depends on textural properties of activated carbon i.e. type of functional groups present, ash content, pore volume, surface area and pre-treatment of activated surface (Rivera-Utrilla and Sánchez-Polo, 2002; Sánchez-Polo et al., 2005). To realize it, Sanchez et al (2005) treated the activated carbon with urea and detected the presence of pyrodine and pyrrol groups on carbon surface with increased surface area. It was elucidated that pyrrolic groups present on activated carbon surface yield N-oxide type groups and hydroperoxide radical in presence of O₃ (Sánchez-Polo et al., 2005) and thus enhances decomposition rate to form HO[•] for mineralization of recalcitrant intermediates (Staehelin and Hoigne, 1982).

Thus, ozonation can be an efficient alternative for *in-situ* production of H₂O₂ as evident from the examples discussed in Table 2 that with ozonation maximum COD removal achieved was 60.2%. However, there are several problems that must be dealt in for its industrial applications. These include intense energy requirement for *in-situ* ozone generation, selectivity for organic substrates, pH sensitivity (Song et al., 2007), mass transfer limitations, high consumption rate of ozone and increase in turbidity level of effluents (Ince and Tezcanlı, 2001). It has been reported that energy consumption for ozonation of Congo red dye increases linearly and to achieve 80% TOC removal, 528kWh/m³ power was consumed which was 254kWh/m³ for electrochemical oxidation process (Faouzi Elahmadi et al., 2009).

Table 2. Application of AOPs for *in-situ* production of H₂O₂/HO[•] for textile wastewater treatment

2.4. Photocatalysis

Photocatalysis makes the use of semiconducting materials to generate holes and free radicals for degradation of recalcitrant organic contaminants. These radicals include HO^\bullet , $\text{O}_2^{\bullet-}$, HOO^\bullet , produced based on the interaction with the oxidizing species (Lachheb et al., 2002; Tanaka et al., 2000). Semiconducting oxides like TiO_2 , ZnO , Fe_2O_3 , ZnS and CdS can be used as photocatalyst (Umar and Aziz, 2013). Among all, TiO_2 has been probed frequently for observing reductive as well as oxidative reactions on its surface (Chong et al., 2010).

In wastewater treatment applications, semiconductors (ZnO , TiO_2 etc) have the potential to perform degradation of organic contaminants directly as well as through production of chemically active species i.e. HO^\bullet (Boroski et al., 2009). It is well established that holes in valence band and electrons in conduction band are formed when semiconducting material is exposed to photons with energy higher than band gap energy. The radical generation mechanism has been presented in Fig. 6. Holes are oxidizing agents that have capability to oxidize organic compounds and H_2O into mineralization products and HO^\bullet respectively [Eq. 6] (Boroski et al., 2009).



Electrons present in conductive band react with O_2 as a reducing agent and form superoxide [Eq. 7], which has wonderful chemistry not only for the production of H_2O_2 but also for the degradation of intermediates depending on pH (Fang et al., 2013; Boroski et al., 2009). Thus pH plays a key role for *in-situ* production of HO^\bullet .



The role of ZnO is the same as that of TiO₂ for *in-situ* HO[•] production for textile wastewater treatment. Peternel et al (2007) collated the performance of TiO₂ and ZnO for degradation of C.I. Reactive red 45(RR45) and observed same mechanism for both. The observed decolorization efficiency with TiO₂ was 71% at pH 3 while it was only 60.1% at neutral pH with 5 times more dosage of ZnO. Although ZnO has been found to be more efficient than TiO₂, it has disadvantage of photo-corrosion when exposed to UV light (Kaur and Singh, 2007).

Fig. 5. Schematic presentation of mechanism of oxidative species production

(Stylidi et al., 2003)

Photocatalysis can potentially be used for *in-situ* H₂O₂/HO[•] productions but there are several factors that must be considered. One of the issues with TiO₂ is the difficult separation of the particles. For this, Sathishkumar et al (2013) investigated CoFe₂O₄ loaded TiO₂ nano-particles for degradation of Reactive red 184 (RR184) and successfully achieved both Photocatalytic as well as magnetic properties. The purpose of enhanced magnetic properties is to achieve easy separation just by applying the magnetic field. Another common problem that has been frequently highlighted in several investigations is the recombination of electrons and holes. In order to resolve it, Ozer and Ferry (2001) successfully investigated the performance of Polyoxomethalate (POM) anions as electron shuttle and explained the mechanism as shown in Fig. 6. As discussed earlier, quinone groups are known to serve as electron shuttles for aromatic compounds such as azo dyes. Hence, improved production of photocatalytically induced *in-situ* HO[•] can possibly be observed for textile wastewater treatment (Lee et al., 2007).

Fig. 6. Electron transfer in presence of POM

Apart from the above mentioned constraints, catalyst loading and dye concentration have to be optimized for enhanced production of HO^\bullet . Initial increase in the catalyst loading is directly proportional to the dye degradation. Above optimum value, catalyst loading results in decrease in the dye degradation. The reason for such behavior is an increase in the number of active sites at lower concentrations which in turn increase the production of primary and active HO^\bullet . Increase in the catalyst loading results in either agglomeration of the particles in the suspension or reflectance of light which reduces the HO^\bullet production. This is in exact agreement with the results achieved by Krishnakumar and Swaminathan (2011) and Sun et al (2008) while degrading Acid Violet 7 (AV7) and Orange G (OG) respectively.

It has also been reported by Krishnakumar and Swaminathan (2011) that increasing dye degradation, reduces the probability of dye molecules to react with the HO^\bullet as concentration of catalyst and intensity of UV light are the same. Same reason has been addressed in another way by Muruganandham and Swaminathan (2006). It has been reported that degradation of Orange G (OG) dye decreased from 98.79% to 23.91% above optimum concentration of dye. It was reported that above some optimum value, dye molecules affected the catalytic activity of the catalyst. Additionally, high concentrations also decrease the path length of the photon entering which reduces the photocatalytically produced *in-situ* HO^\bullet .

Furthermore, TiO_2 can only absorb ultraviolet light which is only 4% of the solar light (Ni et al., 2007). To avoid it, TiO_2 is usually doped with other semiconducting material such as Cu_2O , a p-type semiconductor which has narrow band gap but high conduction band (Yu et al., 2004). When exposed to visible light, electrons in conduction band of Cu_2O transfer to that of TiO_2 and thus increase the photocatalytic degradation of TiO_2 (Zhang et al., 2007).

Photocatalysis has been demonstrated successfully by several authors for production of HO^\bullet along with the degradation of textile waste. This process has the potential to achieve maximum of 80% COD and 90% color removal efficiencies (Table 2) with modifications. However, it cannot be considered as an alternative for *in-situ* H_2O_2 production because: 1) it is energy intensive. For instance, it consumed 8×10^4 kW power reactive azo dye treatment (Mahamuni and Adewuyi, 2010) which is several times of ozonation (Mehrlouei et al., 2014) 2) Textile wastewater is highly variable in concentration and photocatalysis is limited for small streams and low concentration of dyes.

2.5. Electrochemical and Microbial fuel cells

Electrochemical oxidation is an effective alternative as it employs either direct or indirect oxidation approach for wastewater treatment (Fu et al., 2010). In direct electrochemical oxidation, degradation is carried out through adsorption of the contaminants on the anode surface without any involvement of oxidizing agent. However, indirect oxidation in electrochemical fuel cells employs the sparging of oxygen in cathode chamber to produce H_2O_2 through direct application of electric current (Panizza and Cerisola, 2009). This mechanism has been successfully applied in textile wastewater treatment in several investigations as clear from Table 3.

High degradation rates and complete mineralization at optimum conditions are the main features of the process but intense energy requirement hinders its practical application for *in-situ* $\text{H}_2\text{O}_2/\text{HO}^\bullet$ production (Fu et al., 2010; Martínez and Uribe, 2012). In one investigation, it has also been found that electrochemical oxidation is more economic in comparison with ozonation in terms of energy consumption for *in-situ* H_2O_2 production (Faouzi Elahmadi et al., 2009). The

possible reason may be the use of modified boron doped diamond electrode. Thus there is an intense need of alternative that requires less energy and must be environmental friendly.

Wastewater can be a renewable energy source for the production of electricity, fuels and chemicals (Rozendal et al., 2008). Recently, several findings have explored the potential of wastewater for the *in-situ* production of H_2O_2 (hence *in-situ* Fenton oxidation) in microbial fuel cells (Fu et al., 2010; Kalathil et al., 2011; Li et al., 2010; Modin and Fukushi, 2013). However, it has been frequently investigated for the generation of electricity from wastewater and many authors have also reported the production of water in cathode chamber (Du et al., 2007; Rabaey et al., 2003; Han et al., 2010). For *in-situ* production of H_2O_2/HO^\bullet , bacterial species present in the wastewater (in anode chamber) plays an important role. It is confirmed by R. Bond and Lovely (2002) and his co-worker that among all bacterial species, presence of *Geobacter Sulfurreducens* in anode compartment favors the production of H_2O_2 in cathode compartment. However, *G. Sulfurreducens* species are highly sensitive to oxygen therefore, Fernantez de Dios et al (2013) suggested the use of *Shewanella* species which is facultative exoelectrogen and obtained 82% mineralization of dye mixture through H_2O_2 production (*in-situ* Fenton oxidation) in cathode chamber of WBMFCs. Thus, microbial fuel cells use electrochemically active microorganisms (Rozendal et al., 2008) present in the wastewater to convert the chemical energy stored in organic compounds into electrical energy (Gil et al., 2003; Moon et al., 2006). This oxidation step is coupled by *in-situ* production of H_2O_2 for the degradation of refractory waste in cathode compartment (Zhu and Ni, 2009).

Rozendal et al (2009) investigated the production of H_2O_2 in cathode chamber by using oxygen as an electron acceptor. At applied voltage of 0.5V, about 1.9 to 2 kg $H_2O_2/m^3/day$ was successfully produced. In this study, voltage was applied to accelerate the production of

1 electrons and start-up time. It is in agreement with the findings of Wang et al (2009) according to
2 which applied voltage enhanced the production of electricity in microbial fuel cells.

3 The study conducted by Rozendal et al (2009) was not based on the *in-situ* production of
4 H_2O_2 but it is still beneficial to estimate the potential of microbial fuel cell for degradation of dye
5 in future investigations. It can be proved by the findings of Fu et al (2010), who examined the
6 *in-situ* generation of H_2O_2 for degradation of azo dye (amaranth) under neutral cathodic
7 conditions and reported that by utilizing 0.5 mmole/L Fe^{+3} as catalyst 76.5% degradation
8 efficiency could be achieved within one hour.

9 The literature concerning *in-situ* H_2O_2 production in microbial fuel cells has frequently
10 discussed the dual chamber configuration. It has been reported that performance of dual chamber
11 MFCs is affected by high internal resistance caused by proton exchange membrane (Zhu and
12 Logan, 2013a). Thus, with an attention of reducing the cost and eliminating the effect of
13 membrane, membrane-less single chamber microbial fuel cell was suggested to use as a low
14 power source for performing *in-situ* H_2O_2 production in electro-Fenton reactor (Zhu and Logan,
15 2013b). However, distances between anode and cathode may contribute to an increase in the
16 resistance of the microbial fuel cell. Therefore, *in-situ* H_2O_2 production in microbial fuel cells
17 should be further explored to increase the efficiency of the process.

18 Performance of microbial fuel cells also depends on several other factors that must be taken
19 into account while discussing the *in-situ* production of H_2O_2 . These include hydraulic retention
20 time, pH, characteristic of effluent, external resistance, type of co-substrates (Solanki et al.,
21 2013), start up times (Liu et al., 2011) and irreversible nature of the reactions (Rismani-Yazdi et
22 al., 2008). However, the cost and properties of electrode material have significant importance.

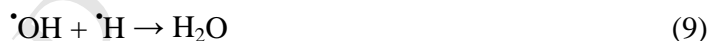
Electrode material must have good electrical conductivity, high surface area, chemical stability and appropriate strength and toughness (Zhou et al., 2011). Many authors have collated different electrodes such as graphite, platinum, IrO₂, RuO₂, PbO₂ and boron-doped diamond electrodes in their investigations. It has been found that IrO₂ and RuO₂ electrodes have low reactivity for organic oxidation and graphite electrodes are inexpensive but all of them have low current efficiencies (Tan et al., 2011). Platinum exhibits excellent electro catalytic properties (Jaccoud et al., 2006) but its high cost always limits its application (Du et al., 2007). To improve the performance of microbial fuel cell, simple graphite anode was heated and used in single chamber microbial fuel cell and 75% of the recalcitrant contaminant was mineralized through *in-situ* H₂O₂ (hence *in-situ* Fenton oxidation).

Microbial fuel cell is a versatile technology because electricity production is accompanied by the production of H₂O₂ in cathode chamber (Li et al., 2010, Rozendal et al., 2009). Much work has been done on improving the production of electricity to-date (Feng et al., 2010a; Feng et al., 2010b). To-date, power produced has been used as a low power source for operating electrochemical fuel cells (Zhu and Logan, 2013b). Alternatively, power produced can also be used for the aeration of cathode chamber, which would provide an environmental friendly and cost effective solution for textile wastewater treatment through *in-situ* H₂O₂ (*in-situ* Fenton oxidation). Being at initial stages of the process, maximum TOC removal of 76% has been obtained through microbial fuel cell application at low concentrations of pollutant (Table 3). It is lesser than that obtained in electrochemical oxidation thus highlighting the need of optimizing the operating parameters for achieving results comparable to electrochemical oxidation process.

Table 3. Electrochemical and microbial fuel cells for *in-situ* production of H₂O₂/HO[•]

3. Improvements for *in-situ* H₂O₂/HO[•] production through sonolysis

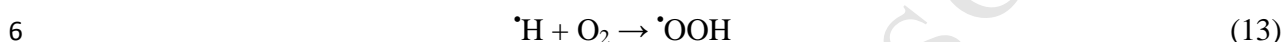
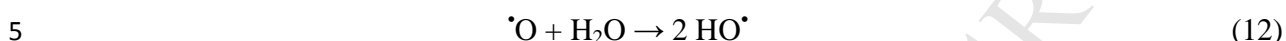
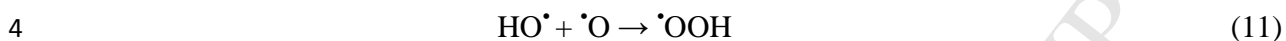
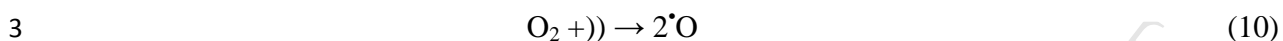
Sono-chemical degradation of dyes is considered as AOPs (Vončina and Majcen-Le-Marechal, 2003) because of its potential to produce HO[•] radical by homogeneous reactions or enhancing the activity of catalyst in heterogeneous reactions. In aqueous medium, ultrasound waves (‘’))’ provoke the formation and collapse of cavitation bubbles. Cavitation produces hot spots of high temperature and pressure for shorter time which during collapsing phase cause splitting of water molecules into HO[•] and H[•] radical (Chitra, 2004). Local concentration of HO[•] and H[•] radical is high but an estimated 80% of H[•] and HO[•] radicals recombine and reduces the bulk concentration of these radicals (Stock, Peller et al., 2000; Gültekin et al., 2009). Thus, major portion of the mechanical energy is lost due to recombination reaction.



Dyes are highly hydrophilic so they can be degraded in bulk in comparison with the volatile organic compounds which can only be degraded thermally inside the gas bubble (Adewuyi, 2001). However, reactive azo dyes are non-volatile, water soluble and their reaction at interface is not observed (Vajnhandl and Le Marechal, 2007). It indicates that dye interaction with HO[•] radicals can only be possible in the bulk solution. However, if hydrophilic organic compounds are concentrated in the solution additional degradation mechanism then quickly takes place at gas-liquid interface (Okitsu et al., 2005).

Concentration of HO[•] radicals is reported to be improved in bulk dye solution in the presence of dissolved oxygen, ozone or catalyst. Thermal decomposition of dissolved oxygen and water

1 produce more HO[•] and other chemical reactive species [Eq. 8, 10-13]. However, recombination
 2 phenomenon still cannot be overcome (Destailats et al., 2000).



7 In several investigations, it has been suggested that sonolysis should combine with ozonation
 8 for *in-situ* H₂O₂/ HO[•] production without alkaline conditions as discussed in Table 4. When
 9 sonicated liquid is bubbled with ozone, mass transfer rates of the ozone is improved which is the
 10 main issue with ozonation alone. In the presence of O₃ alone 30% mineralization can be achieved
 11 with methyle orange. In combination with Ultrasound, synergetic effect is produced and
 12 mineralization achieved exceeds 80% within pH range of 5.5-6.5 (Destailats et al., 2000).
 13 Reason for this synergetic effect is that every O₃ molecule decomposes to yield two molecules of
 14 HO[•] radicals in the presence of Sonolysis (Vecitis et al., 2010).

15 Aside from homogeneous reaction, activity of the catalytic process has been observed to
 16 improve because of the synergized effect induced by the ultrasound waves. As mentioned before
 17 Fe⁰ deactivates due to the precipitation of hydroxyl/iron oxides which results in the decrease in
 18 the porosity of the catalyst with time (Gillham and O'Hannesin, 1994). However, US/Fe⁰ not
 19 only increases the active surface area of catalyst by rupture or pitting, but also increase the
 20 concentration of HO[•] at increased loading of the iron catalyst. That is the reason that

1 decolorization of the C.I. Acid Orange 7 (AO7) improved from 63% to 91% due in a study done
2 by Zhang et al (2005). However, with zero-valent copper (Cu^0), the efficiency is lower in
3 comparison with Fe^0 regardless of dye concentration and sound frequency. It may be because of
4 the acidic conditions which cause protonated dyes to repel the catalyst surface (positively
5 charged) and Cu has less potential than iron species (Eren and Ince, 2010).

6 Photocatalyst mainly TiO_2 and ZnO intensify *in-situ* production of HO^\bullet by dissociating water
7 molecule because of combined effect of UV and US. Table 4 summarizes the ultrasound
8 conditions, dye concentration and subsequent outcomes for AOPs demonstrated by several
9 authors specifically for HO^\bullet radical production. An increase in HO^\bullet radical production in
10 combinative process may be attributed to the accelerated mass transfer of reactants and products
11 to and from the catalyst surface. It may also be caused by an increase in the activity of the
12 catalyst by particle disaggregation which increases the surface area of the catalyst (Stock et al.,
13 2000). However, effect of US, UV and photocatalyst are more significant than either
14 combination with the photocatalyst. For example Acid Orange 8 dye has completely been
15 degraded within 4 hrs under sonophotocatalysis while in the absence of US, 79% degradation has
16 been achieved (Selli, 2002). It has also been reported that synergetic effect of ultrasound waves
17 convert H_2O_2 into more HO^\bullet radicals which makes this process efficient. Therefore, dye and
18 catalyst concentrations are equally sensitive for combined process (González and Martínez,
19 2008; Bejarano-Pérez and Suárez-Herrera, 2007).

20 Sonolysis is an auxiliary tool for *in-situ* HO^\bullet radicals production for textile wastewater
21 treatment through AOPs. Economic analysis conducted by Adewuyi (2001) states that overall
22 cost for sonolysis alone is not economically acceptable on large scale. However, addition of

additive or combination of the US with AOPs is more economical. The cost for US combined with ozonation is 1.67×10^5 USD and for ultrasound it is 2.11×10^8 USD. For reactive azo dye degradation, the power consumed by sonolysis is 6.58×10^5 kW which is more than that of ozonation (Mahamuni and Adewuyi, 2010). There are several additional factors that must be dealt with before considering scale-up including properties of fluid and dissolved gases, amount and frequency of the sonication required for HO^\bullet production. In addition, nature of dye structure present in the textile wastewater will also affect the reaction rate (Thompson and Doraiswamy, 1999). These factors make large scale application of sonolysis doubtful because incoming textile wastewater contains variety of dyes with different concentrations and properties. So, optimization of operating parameters may be an issue for scale up.

Table 4. Ultrasound as an auxiliary tool for AOPs: *In-situ* production of $\text{H}_2\text{O}_2/\text{HO}^\bullet$

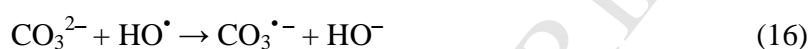
4. Considerations during the *in-situ* $\text{H}_2\text{O}_2/\text{HO}^\bullet$ production process

Real textile effluents contain carbonates, bicarbonates and chlorides in addition to dyes. These inorganic anions reduce the degradation efficiency of the dyes by scavenging the oxidizing agents. One of the most challenging scavenging phenomenon is the formation of H_2O_2 in the presence of excessive HO^\bullet [Eq. 14] (Borda et al., 2003).



Bicarbonates and carbonates are the most commonly available anions in wastewater and can easily scavenge radicals available for textile wastewater treatment [Eq. 15-16]. Faria et al (2009)

reported the influence of carbonates and bicarbonates as HO^\bullet scavenger on the efficacy of the process. It was found that scavenging effect of carbonate ions was more as compared to bicarbonate ions at both moderate and high pH value.



Moreover, presence of di-hydrogen phosphate ion H_2PO_4^- and mono hydrogen phosphate ion HPO_4^- also lowers the efficiency by scavenging HO^\bullet (Karthikeyan et al., 2011) [Eq. 17-18].



Halides ions have potential to scavenge the hydroxyl radicals as follows [Eq. 19]:



That is why $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is always preferred over $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in Fenton process. Moreover, Cl^- ions can also scavenge the holes in photocatalysis system and reduce the yield of the *in-situ* hydrogen peroxide formation [Eq. 20]:



In ozonation, the effect of inorganic ions is more pronounced as they inhibit the decomposition of ozone but it put positive impact on the decolorization of the dye because of the presence of molecular ozone (Tehrani-Bagha et al., 2010).

Same phenomenon can be observed in the presence of NO_3^- and SO_4^{2-} radicals. In the presence of sulfate ions, it seems difficult to decide either sulfate ions are scavengers or playing a productive role for formation of other radicals. According to reaction Eq. 21 & 22, sulfate ions are scavenging holes and HO^\bullet but at the same time transformation to $\text{SO}_4^{\bullet-}$ are also taking place. And $\text{SO}_4^{\bullet-}$ have redox potential comparable to the HO^\bullet (see Table 1) and can degrade the dyes present in the wastewater (Huang et al., 2005). But as they are less reactive as compared to HO^\bullet and holes so their role is more as scavengers as compared to promoter.



Scavenging of HO^\bullet is unavoidable because these anions are naturally present in wastewater. Separation of these anions is also not possible because this requires more sophisticated experimental setup and is not economically viable. This suggests the need to find some alternative to suppress the effect of anions as scavenger.

5. Conclusion

Fenton process is an efficient method for degradation of dyes and recalcitrant organic contaminants present in textile wastewater. However, excessive use of reagents, acidic conditions, and high cost of hydrogen peroxide hinder its industrial applications. It is also unsafe to transport and store bulk quantities of H_2O_2 . To overcome this problem, *in-situ* $\text{H}_2\text{O}_2/\text{HO}^\bullet$ production by Advanced Oxidation Processes including iron-catalyzed processes, ozonation, photocatalysis, electrochemical oxidation and microbial fuel cells is an option worth consideration. Based on this review, the following main conclusions are drawn:

1 *In-situ* H₂O₂ production by iron catalyzed process has advantage of forming Fenton oxidation
2 system in itself. Economically, it is a suitable alternative as the operating cost has been found to
3 reduce from 0.015 to 0.00113 US\$/g of dye for RRB treatment with Fe⁰/air. However, zero
4 valent iron has been found to be deactivated with time. Similarly, ozonation follows radical chain
5 reaction mechanism to produce HO[•] radical either in alkaline conditions or in the presence of
6 catalyst, However, there are few constraints such as alkaline conditions, high power consumption
7 of 34.98kW/gallons of dye and mass transfer limitations that reduce the efficiency and economic
8 viability of the process.

9 Besides, Photocatalysis which is with an intense energy requirement of 80kW/gallon of dye can
10 efficiently induce dye degradation through *in-situ* HO[•] radical production. Replacing UV with
11 solar energy is economically beneficial but photocatalysis is limited for small and less
12 concentrated streams of the textile wastewater. Alternatively, smooth and efficient production of
13 HO[•] and high mineralization rates are achievable in electrochemical oxidation process. However,
14 its energy requirement is more intense than Photocatalysis which indicates the process is not
15 economically viable. The most viable solution to this problem is the use of microbes present in
16 the wastewater in microbial fuel cells to produce H₂O₂/HO[•] with simultaneous power production.
17 In this way, microbial fuel cell will be used as a low power source for electrochemical oxidation
18 or aeration of the cathode chamber of microbial fuel cell. Use of ultrasound in combination with
19 AOPs provokes the formation of HO[•] by following the splitting mechanism of water molecules.
20 According to the reported data, sonolysis requires 658kW energy/gallon of reactive dye treated.
21 It is a more economical option when combined with other AOPs such as ozonation and
22 Photocatalysis. However, types of the fluid, frequency and power of sonolysis need to be
23 determined for its application in *in-situ* HO[•] radical production. Apart from that, scavenging of

HO[•] by anions is unavoidable. This is because these anions are naturally present in real wastewater and their removal requires a few pre-treatment steps that increase the total cost of the treatment process.

Therefore, it is concluded that *in-situ* H₂O₂ is technically and economically viable for textile wastewater treatment. It may overcome issues currently linked with commercially available H₂O₂. Being under its developing stages, this concept requires further research in optimizing the operating parameters and methodology so that its commercial applications could be ensured in near future in the view of its economical and ecological importance.

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Abbreviations

AOPs: Advance Oxidation Processes; HO[•]: Hydroxyl radical; H₂O₂: Hydrogen Peroxide; SO₄^{•-}: Sulfate free radicals; MnO₄⁻: Permanganate; ClO⁻: Hypochlorite; ClO₂: Chlorine dioxide; Co⁺²: Cobalt ion; PMS: Peroxymonosulfate; AR88: Acid red 88; SDBS: Sodium Dodecylbenzenesulphonate; PAC: Powdered Activated Carbon; O₂^{•-}: Superoxide Radical; Fe⁰: Zero-valent iron; POM: Peroxometalate; RBBR: Remazol Brilliant Blue R; RR2: Reactive red 2; ACo: Activated Carbon; Ce-O: Cerium Oxide; ACo-Ce-O: Ceria-activated carbon composite; h⁺: Holes; e⁻: electrons; RR45: C.I. Reactive Red 45; RR184: C.I. Reactive Red 184; AV7: Acid Violet 7; OG: Orange G; AO7: C.I. Acid Orange 7.

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Table 1. Redox potential of oxidizing agents

Table 2. Application of AOPs for *in-situ* production of $\text{H}_2\text{O}_2/\text{HO}^\bullet$ for textile wastewater treatment

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Table 1. Redox potential of oxidizing agents

Oxidizing agent	Redox potential	Reference
Hydrogen peroxide(H_2O_2)	1.8	(Neyens and Baeyens, 2003; Kelley et al., 2003)
Hydroxyl radicals(HO^\bullet)	2.8	(Kelley et al., 2003)
Holes(h^+)	2.53	(Fujishima et al., 2000)
Sulfate free radicals($\text{SO}_4^{\bullet-}$)	2.5-3.1	(Kelley et al., 2003; Zhao et al., 2010)
Ozone(O_3)	2.1	(Kelley et al., 2003)
Persulfate anions($\text{S}_2\text{O}_8^{2-}$)	2.01	(Kelley et al., 2003; Liang and Lee, 2008)
Permanganate (MnO_4^-)	1.70	(Kelley et al., 2003)

Table 2. Application of AOPs for *in-situ* production of $\text{H}_2\text{O}_2/\text{HO}^\bullet$ for textile wastewater treatment

Dye	Catalyst/Oxidants	[Dye] mg/L	[Catalyst]/ [Oxidants]	pH/T(°C)	Color removal	COD/TOC	AOPs employed	Reference
AO7 RR120 AB9	$\text{Fe}^\circ/\text{air}$	100	0.0.3 g/L	3/-	>99%	COD: 97% COD: 87% COD: 93%	Catalytic (Zero valent iron)	(Yang et al., 2010)
RBBR AB1	$\text{Fe}^\circ/\text{air}$	100	50	3/-	>99% >99%	COD: 96% COD: 50%	Catalytic (Zero valent iron catalyst)	(Chang et al., 2009)
Calmagite	$\text{Mn(II)}/\text{Tiron}/\text{NH}_2\text{OH}$	0.1 mM	50 μM /1.50mM/ 100mM	8/20	-	-	H_2 substituted organic compound	(Sheriff et al., 2007)
-	$\text{Pd}/\text{Al}_2\text{O}_3$ with NH_2OH & O_2		0.001g	7/27	-	-	H_2 substituted organic compound	(Choudhary and Jana, 2007)
RB19	O_3	200	55g/m ³	7/25	100%	COD: 55% TOC: 17% (800 mg/L of dye)	Ozonation	(Tehrani-Bagha et al., 2010)
AR88	O_3	0.5 mM	2g/hr	3/- 11/-	98.2% -	- COD: 60.2%	Ozonation	(Muthukumar et al., 2004)
Dye bath effluent	O_3	2480 ^a	11 to 111 mg/L min	4.7/20	60~91%	13~22%	Ozonation	(Sevimli and Sarıkaya, 2005)
Plant Effluent	O_3	665 ^a	11 to 111 mg/L min	6.7/20	74%	11~33%	Ozonation	(Sevimli and Sarıkaya, 2005)
Raw wastewater	O_3	1700 ^a	18.5 mg/L	8.3/-	98-99%	7.64~15.88 %	Ozonation	(Baban et al., 2003)

Table 2. Continued

Dye	Catalyst/Oxidants	[Dye] mg/L	[Catalyst]/ [Oxidants]	pH/T(°C)	Color removal	COD/TOC	AOPs employed	Reference
Biologically treated wastewater	O ₃	450 ^a	18.5 mg/L	8.3/-	70-75%	18.88%	Ozonation	(Baban et al., 2003)
Congo red	O ₃ /O ₂	500	0.5L/min	12/25	-----	COD: 85% TOC: 81%	Ozonation	(Faouzi et al., 2009)
Reactive Black 5	O ₃ (micro-bubbles)	230	132mg/L	-/20	100%	TOC:80%	Ozonation	(Chu et al., 2007)
Acid Red 14	O ₃	200	19.26g/hr	-/25	98%	COD: 45%	Ozonation	(Gao et al., 2012)
C.I Reactive Red 2	O ₃ /UV/TiO ₂ Mn(II)/O ₃ MnO ₂ /O ₃	100	1 mg/L 0.1 mg/L 0.8 mg/L O ₃ : 200ml/min	6.9/- 2/- 2/-	>95%	17-21%	Catalytic ozonation	(Wu et al., 2008)
RR194	O ₃ /GAC	100	O ₃ : 28 mg/L GAC: 10 g/L	6.3/-		COD:80% TOC: 50%	Catalytic ozonation	(Gul et al., 2007)
RY145				5.9/-		COD:90% TOC: 50%		
Brilliant Red Dye	Cu ₂ O/MWNT/ FeSO ₄	200	1g/L 10mmol/L	6/-	-	-	solar light catalytic process	(Zhang et al., 2006)

Table 2. Continued

Dye	Catalyst/Oxidants	[Dye] mg/L	[Catalyst]/ [Oxidants]	pH/T(°C)	Color removal	COD/TOC	AOPs employed	Reference
AO7	TiO ₂ /UV	40	1g/L / 6 W lamp	6/20	-	-	Photocatalysis	(Chen et al., 2005)
RB5	TiO ₂ /SiO ₂ in the presence of ions	-	TiO ₂ /SiO ₂ : 1 (mass ratio)	5.8/21	-	-	Photocatalysis	(Aguedach et al., 2008)
RR45	UV/TiO ₂	80	0.5 g/L/ 125 W	5/ 25	59%	TOC: 23%	Photocatalysis	(Peternel et al., 2007)
	UV/ZnO	80	2.5 g/L/ 125W		58.3%	TOC: 22.4%	Photocatalysis	(Peternel et al., 2007)
MB	UV/SiO ₂ /TiO ₂ - Ce	2.5	250W/ 100 mg/L Ce:0.2%	11/25	-	-	Photocatalysis	(Liu et al., 2012)
Procion yellow H- EXL	UV/TiO ₂ (P-25)	50	100W mercury lamp/1g/L	5/-	~100%	COD: 89%	Photocatalysis	(Barakat, 2011)
Ponceau-S dye	Nb ₂ O ₅ /CAC	40	400W/5g/L/1 g/L	8/-		TOC:78.95% COD: 86.2%	Photocatalysis	(Patil et al., 2011)
MB	ZnO/SnO ₂	10	8W/ 0.50 g/L Air: 400ml/min	12/25	96%	-	Photocatalysis	(Chiang and Lin, 2013)
RR180	TiO ₂	150	24W/2g/L	7/25	97.17%	TOC: 83.05%	photocatalysis	(Akyol and Bayramoglu, 2008)

Table 2. Continued

Dye	Catalyst/Oxidants	[Dye] mg/L	[Catalyst]/ [Oxidants]	pH/T(°C)	Color removal	COD/TOC	AOPs employed	Reference
C.I. Direct Red 23	SrTiO ₃ /CeO ₂	100	250W/1.5g/L	12/25	97%	COD: 69%	Photocatalysis	(Song et al., 2008)
Methylene Blue	TiO ₂ /Cu ₂ O with FeSO ₄ & EDTA	100	2	4/-			Catalytic/ Photocatalytic	(Zhang et al., 2007)
Reactive Black 5	SrTiO ₃ /CeO ₂	100	200W/ 0.02g/L ⁻¹ / 0.2m ³ hr ⁻¹	12/-	100%	TOC:57%	Catalytic/ Photocatalytic	(Song et al., 2007)
Procion blue dye	Titanium anode coated with 70TiO ₂ /30RuO ₂ / TiO ₂ catalysts	100	6W/2A/dm ³ /65 mg/L	3.5/-	100%	COD: 90%	Electro- photocatalytic	(Neelavannan et al., 2008)
Acid Violet 7	ZnO/UV/air	5×10 ⁻⁴ M	2g/L/ 8W/ 8.1mL/s	9/-	-----	COD: 94.4%	Photocatalytic	(Krishnakumar and Swaminathan, 2011)
Eosin Y	ZnO/UV	50	0.4g/16W	6.9/30	39%	COD: 8.1%	Photocatalytic	(Chakrabarti and Dutta, 2004)
Methylene Blue	ZnO/UV	50	0.4g/16W	6.9/30	58%	COD: 24%	Photocatalytic	(Chakrabarti and Dutta, 2004)
RR2	O ₃ /Fe(II)	0.45mM	10mg/hr/ 0.9mM	7/25	k ₂ : 2248M/s***	-	Catalytic ozonation	(Zhang et al., 2013b)
MB	O ₃ /CNTs	30mg/L	5g/hr/0.1g	11/20	100%	TOC: 80%	Catalytic ozonation	(Zhang et al., 2013b)

Table 2. Continued

Dye	Catalyst/Oxidants	[Dye] mg/L	[Catalyst]/ [Oxidants]	pH/T(°C)	Color removal	COD/TOC	AOPs employed	Reference
RR198/ DG6	UV/O ₃ /MWNTs	150	9W/0.03g/L	3/25	100%	-	Photocatalytic ozonation	(Mahmoodi, 2013)

*AO7: Acid Orange 7; RR120: Reactive Red 120; AB9: Acid blue 9; RBBR: I.C Remazol Brilliant Blue; AB1: C.I Acid Black 1; RB19: C.I Reactive 19; AR88: Acid Red 88; RR2: C.I. Reactive Red 2 ; CR: Congo Red; RR194: C.I. Reactive Red 194; RR145: C.I. Reactive Red 145; AO7: Acid Orange 7; RB5: Reactive Black 5; RR45: C.I Reactive Red 45; MB: Methylene Blue; RR180: Remazol red F-3B; R23: C.I. Direct Red 23; 4BS: C.I. Direct Red 23; AV7: Acid Violet 7; RR2: Reactive Red 2; MB: Methylene Blue; RR198: Reactive red 198; DG: Direct Green

^a Concentration of real wastewater is always reported in terms of COD value.

**Rate constant

Table 3. Electrochemical and microbial fuel cells for *in-situ* production of H₂O₂/HO[•]

Dye	Anode	Cathode	[Dye] (mg/L)	[Catalyst]/ [Oxidant]	pH/T (°C)	Color removal	COD/TOC	Methods	Reference
AZ	Boron doped diamond	zirconium	500*	I: 30 mA/cm ²	-/25	100%	COD: 95%	Electrochemical oxidation	(Bensalah, et al., 2009)
MR	Ti/Pt	Titanium plates	100	40mA/cm ²	-/25	100%	TOC: 50%	Electrochemical oxidation	(Tavares et al., 2012)
MR	Ti/Ru _{0.3} /Ti _{0.7} O ₂	Titanium plates	100	40mA/cm ²	-/25	100%	TOC: 10-35%	Electrochemical oxidation	(Tavares et al., 2012)
Alizarin Red	Pt Grid	GDE	120	Fe ⁺² : 1mM Air: 20mL/s	3/35		TOC: 93%	Electrochemical oxidation	(Panizza and Cerisola, 2009)
TDFW	Titanium alloy	Stainless Steel	1250*	-	5/42	100%	90%	Electrochemical oxidation	(Vlyssides et al., 2000)
DW	Titanium alloy	Stainless Steel	3325*	-	5/42	100%	77%	Electrochemical oxidation	(Vlyssides et al., 2000)
CR	Boron doped diamond	Stainless steel	500	I: 30mA/cm ²	7/25	----	TOC:100% COD:100%	Electrochemical oxidation	(Faouzi Elahmadi et al., 2009)
AO7	carbon felt	carbon felt	0.10 mM	Fe ⁺³ : 0.1mM/ 0.3A	3-2.8/-		TOC: 92%	Electro fenton	(Özcan et al., 2009)
OG-II	Graphite cloth	Graphite cloth	50	Fe ⁺² : 0.2mM; UV:75mW/m ² I: 300mA/cm ²	3/-	100%	TOC: 80%	Photo-electro fenton	(Peralta-Hernández et al., 2008)
OG-II	Graphite cloth	Graphite cloth	50	Fe ⁺² : 0.2mM; I: 300mA/cm ²	3/-	100%	TOC: 63%	Electro Fenton	(Peralta-Hernández et al., 2008)

Table 3. Continued

Dye	Anode	Cathode	[Dye] (mg/L)	[Catalyst]/ [Oxidant]	pH/T (°C)	Color removal	COD/TOC	Methods	Reference
AY36	Boron doped diamond	carbon-PTFE air diffusion cathode	108	Fe ⁺² : 0.5mM/3A	3/35	100%	TOC: 71%	Electro-Fenton	(Ruiz et al., 2011)
AY36	Boron doped diamond	carbon-PTFE air diffusion cathode	108	Fe ⁺² : 0.5mM/3A	3/35	100%	TOC: 95%	Solar Photo- Electro Fenton	(Ruiz et al., 2011)
MO	Graphite	Rutile coated graphite	10	Vis Light	2.4/25	73.4%	----	Microbial fuel Cells	(Ding et al., 2010)
Azo dye	Granular graphite	SPG rod	75	Fe ⁺² :1 mmole/L Fe ⁺³ :0.5 mmole/L	7/20	90%	TOC: 31 %	Microbial fuel cells	(Fu et al., 2010)
Real dye waste	Granular carbon	Granular carbon	2080*	Air: 200L/min	12.4/30	Anode: 73% Cathode: 77%	COD:76%	Microbial fuel cells	(Kalathil et al., 2011)
ABRX3B	Porous carbon	Porous carbon	300	-----	-/30	----	COD:24.8%	Microbial fuel cells	(Sun et al., 2011)
RhB	Carbon Felt	Fe@Fe ₂ O ₃ /NFC	15	-----	3/-	-----	TOC: 90%	Microbial fuel cells	(Zhuang et al., 2010)
Lissamine Green B	Graphite rod	Graphite rod	10	Air: 2L/min Fe ⁺² : 0.05 mole/L	6-8	-----	TOC: 82%	In-situ Microbial fuel cells	(Fernandez de Dios et al., 2013)

Table 3 Continued

Dye	Anode	Cathode	[Dye] (mg/L)	[Catalyst]/ [Oxidant]	pH/T (°C)	Color removal	COD/TOC	Methods	Reference
Crystal Violet	Graphite rod	Graphite rod	10	Air: 2L/min Fe ⁺² : 0.05 mole/L	6-8	-----	TOC: 72%	In-situ Microbial fuel cells	(Fernandez de Dios et al., 2013)

* Red; TDFW: Wastewater from total dyeing and finishing stages; DW: Wastewater from dyeing stages Alphazurine A: AZA; MR:

Methylene; OG-II: Orange II; AY36: Acid Yellow 36; MO: Methylene Orange; ABRX3: Active Brilliant Red X-3B; RhB: Rhodamine

Table 4. Ultrasound as an auxiliary tool for AOPs: *In-situ* production of H₂O₂/HO[•]

Dye	Catalyst/Oxidant	[Dye] (mg/L)	[Catalyst]/[Oxidant]	Frequency (kHz)	pH/T(°C)	Color removal	COD/TOC	Method	Reference
AO7	Fe ⁰ /GAC	1000	12g/2.3g	40	4/22	80%	TOC: 57%	Iron catalyzed	(Liu et al., 2007)
R5	O ₃	363	3.36 g/L	520	7/20	-----	TOC: 76%	Ozonation	(Ince and Tezcanlı, 2001)
RY84	O ₃	500	4.5 g/h	20	4.5/25	----	TOC: 56%	Ozonation	(He et al., 2007)
AB & MO	O ₃	10μM	-----	500	6.5/15		TOC; 80%	Ozonation	(Destailats et al., 2000)
4BS	O ₃	100	3.2g/h	20	8/-	100%	-----	Ozonation	(Song et al., 2007)
RB19	US/O ₃	500	3.8g/h	20	8/-	100%	TOC: 65%	Ozonation	(He et al., 2008)
Azure B dye	Fe ⁺² ; carbon electrode	5×10 ⁻⁴ mol/L	0.8×10 ⁻³ mol/L	23	2.8/25		COD: ~85%	Electro-Fenton	(Martínez and Uribe, 2012)
RR198	ZnO/UV	20	1g/L/ 15W	40	7/30	-----	TOC: 75%	photocatalytic	(Wu, 2008)
AO7	UV/O ₃	50 μM	18W/40g/m ₃	520	5.5/25		TOC: 45%	photo-ozonation	(Tezcanli-Güyer and Ince, 2004)
AO7	UV	50	100mW/mm ₂	20	-/22	65%	-----	photolysis	(Ma et al., 2006)
AO52	UV/TiO ₂	25	20/0.6g/L	200	-/25	100%	TOC: 35%	photocatalysis	(Maezawa et al., 2007)
BB3	TiO ₂ /MM	10	1g/L/300W	-	7/25	80%	-	Photocatalysis	(Khataee et al., 2015)
AO7	ZVAI	20	2g/L/300W	20	2.5/25	96%	-	Ultrasound	(Wang et al., 2014)

*AO7: Acid Orange 7; R5: C.I. Reactive 5; RY84: Reactive Yellow 84; AB: Azo Benzene dye; MO: Methylene Orange; 4BS: C.I.

Direct Red 23; RR198: C.I. Reactive Red 198; AO52: C.I. Acid Orange 52; GAC: Granular Activated Carbon; BB3: Basic Blue;

TiO₂/MM: TiO₂/ montmorillonite; AO7: Acid Orange 7; Zero-valent iron: ZVAI

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Fig. 5. Schematic presentation of mechanism of oxidative species production

Fig. 6. Electron transfer in presence of POM

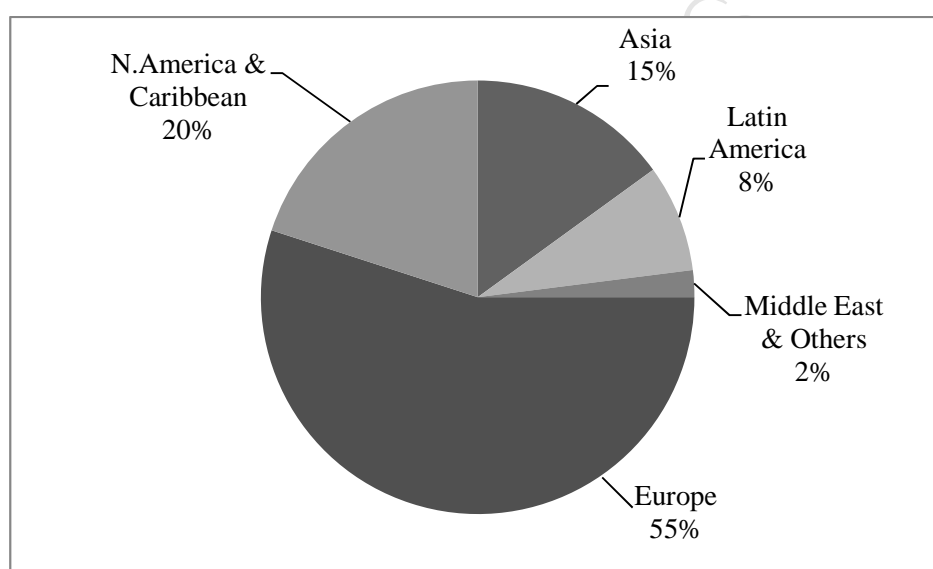


Fig. 1. World supplies of Exported Hydrogen Peroxide (2005)

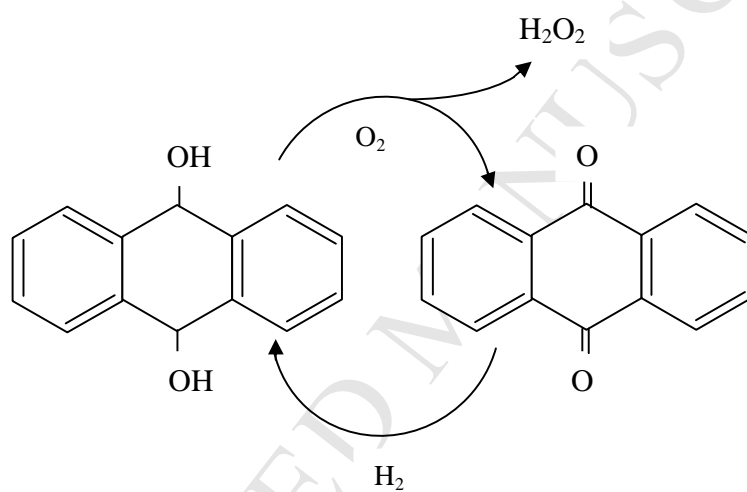


Fig. 2. Conventional method for H_2O_2 production (Campos-Martin et al., 2006)

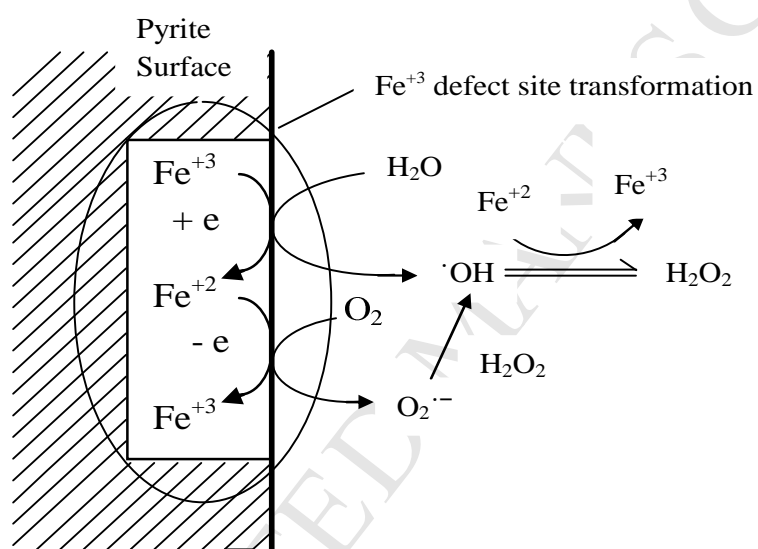


Fig. 3. *In-situ* production of $\text{H}_2\text{O}_2/\text{HO}^\bullet$ by iron pyrite (Wang et al., 2012)

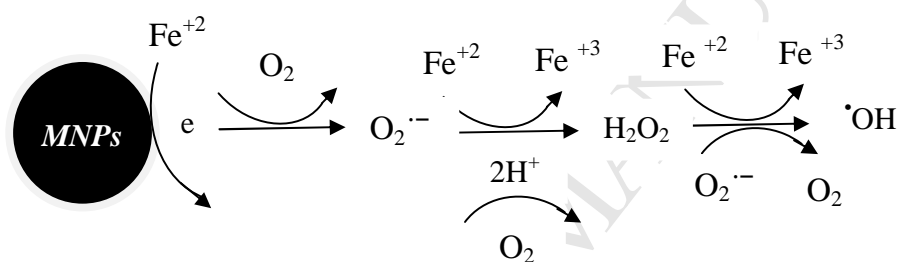


Fig. 4. Reaction pathways for *in-situ* production of $\text{HO}^\bullet/\text{H}_2\text{O}_2$ utilizing MNPs (Fang et al., 2013)

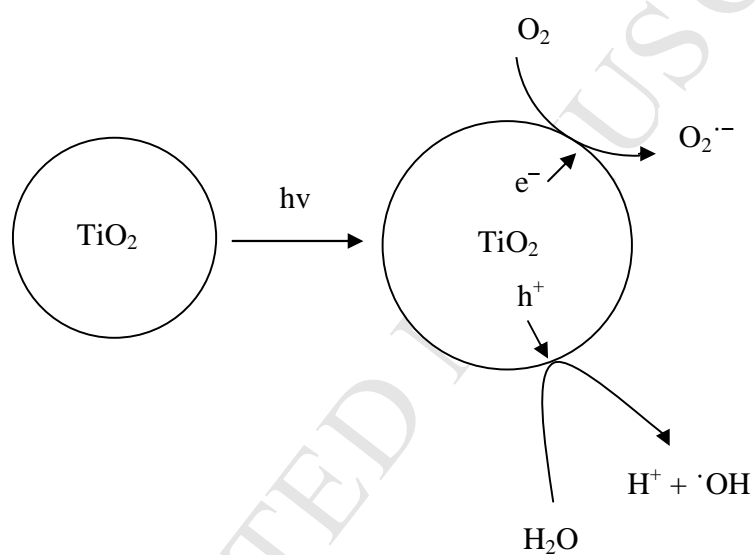


Fig. 5. Schematic presentation of mechanism of oxidative species production

(Stylidi et al., 2003)

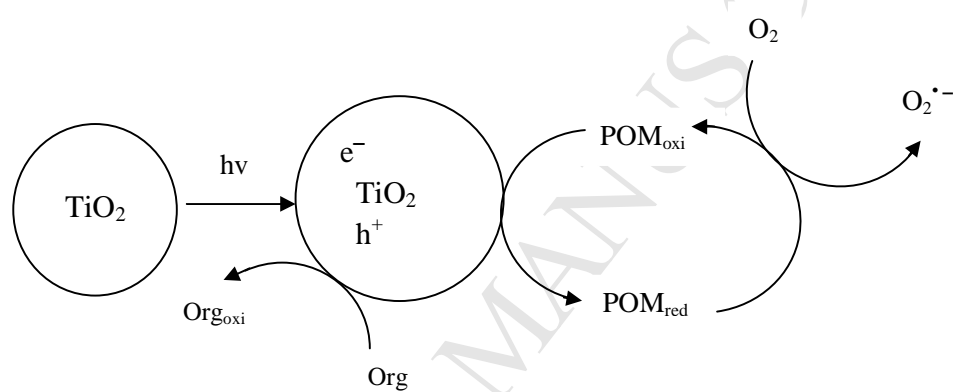


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