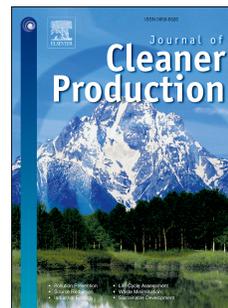


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Advanced Oxidation Processes for *In-situ* production of Hydrogen peroxide/Hydroxyl radical for Textile Wastewater Treatment: A Review

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

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1 Abstract

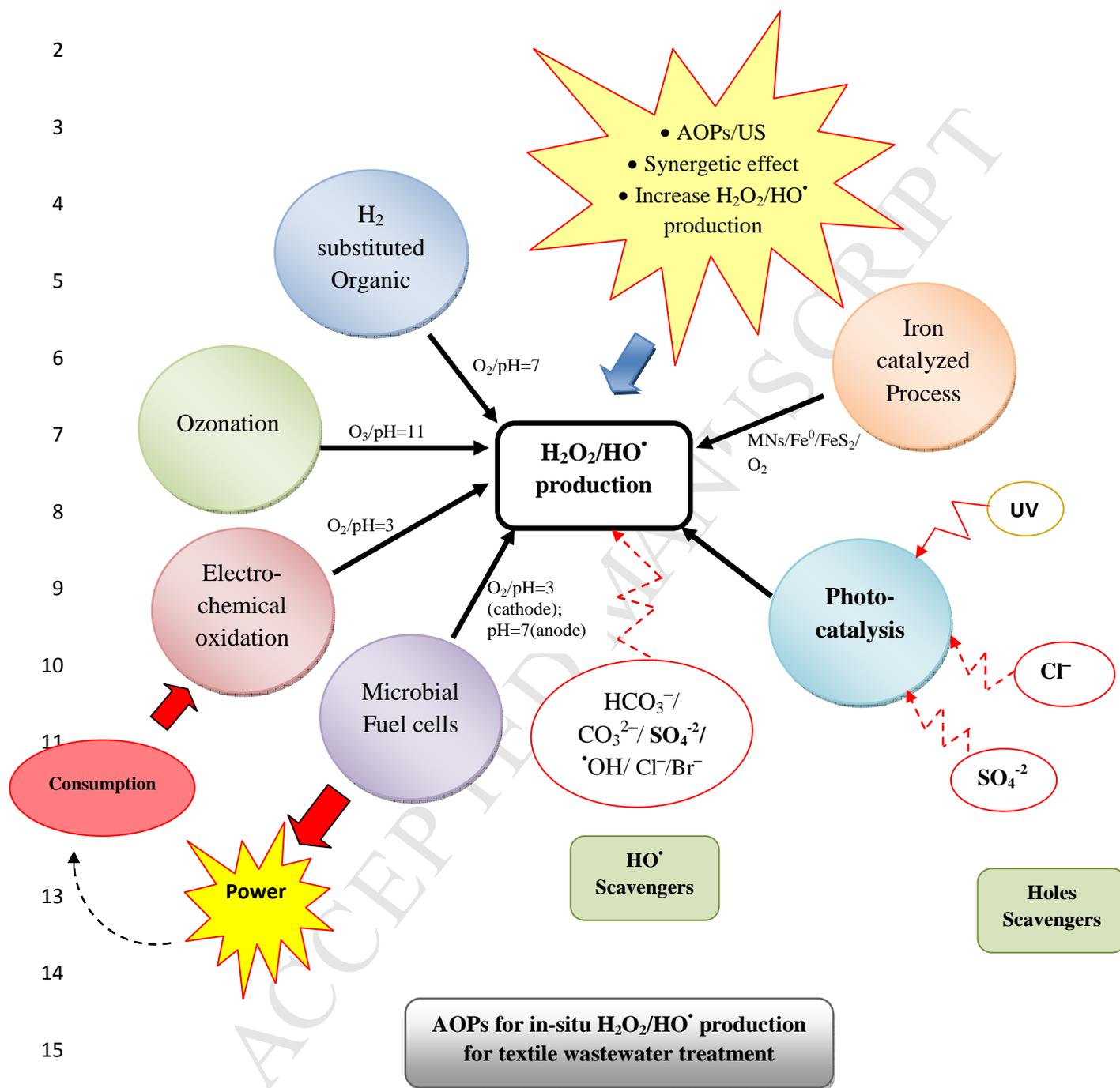
2 Fenton Process, a type of Advanced Oxidation Processes is an efficient method for treating
3 textile wastewaters. However, excessive use of hydrogen peroxide and catalyst has made this
4 process economically non-feasible. Besides, industrial grade hydrogen peroxide costs \$390–500
5 per ton. One of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

20 Keywords

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

23

1 Graphical Abstract



1 **1. Introduction**

2 Textile industry consumes immense amounts of process water and chemicals. Approximately
3 21-377m³ of water is consumed for one ton of textile product (Sahunin et al., 2006) and chemical
4 consumption normally varies from 10% to over 100% of the weight of the cloth (Ozturk et al.,
5 2009). Estimates indicate that approximately, 7×10⁵ tons of dyestuffs are produced annually and
6 280,000 tons of the textile dyes are discharged into water sinks through textile effluents (Eren,
7 2012; Jin et al., 2007). That, explains why textile effluent is characterized by high COD (150-
8 10,000mg/L), BOD (100-4,000 mg/L), pH (6-10) and color content (50-2500) (Kalra et al., 2011).
9 Moreover, discharge of even a small quantity (ca.1 mg/L) of dye is not acceptable and may
10 produce toxic compounds at the end of treatment process (Ghodbane and Hamdaoui, 2009).

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

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

1 utilizing highly reactive oxidizing agent such as hydroxyl radical (HO^\bullet) with redox potential of
2 2.80eV (Krishnakumar and Swaminathan, 2011). However, the process that has gained attention
3 is Fenton process because of rapid formation of HO^\bullet radicals in acidic medium according to the
4 following chemical reaction:



6 Technical feasibility study of Fenton oxidation together with other AOPs has been discussed
7 in detail (Chong et al., 2012). Nevertheless, there are various factors that hinders the efficacy of
8 the process such as reaction parameters (Tosik, 2005), types of salt used (Ledakowicz et al.,
9 2000), high cost of hydrogen peroxide (H_2O_2) and excess consumption of chemicals exclusively
10 H_2O_2 (Hassan et al., 2012). Additionally, hazards associated with the transport, handling and
11 storage of bulk quantities of H_2O_2 have made the process unsafe and economically challenging
12 (Sheriff et al., 2007). It was also evident from the study conducted by Meric et al (2004) in
13 which the authors reported that 400mg/L H_2O_2 and 100mg/L iron salt were consumed for
14 degrading 100mg/L of synthetic dye. Similarly, Argun and Karastas (2011) used 2000mg/L of
15 H_2O_2 for degrading 200mg/L of synthetic dye. High consumption of H_2O_2 is not economically
16 viable and it intensifies the need to find some cost effective and technically feasible alternatives
17 for textile wastewater treatment.

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

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

10 **1.1.Challenges with Commercially Available H_2O_2**

11 Hydroxyl radical (HO^\bullet) is unstable in nature that is why for wastewater treatment
12 applications commercially available H_2O_2 is used as a source of HO^\bullet production. It is one of the
13 cleanest and ideal oxidants for the degradation of dyes and organic contaminants present in
14 wastewater (Sheriff et al., 2007). Globally, demand for H_2O_2 has increased. According to the
15 statistical report published by ICON Group, H_2O_2 with the total worth of US\$ 383,067 (Parker,
16 2004) was exported in 2005 which was increased by 37% in 2011(Parker, 2010). This group
17 also discussed the breakdown of market in context of its supply and consumption in different
18 regions of the world as shown in Fig.1.

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

1 selective and highly active Pd/Al₂O₃ (Chen, 2006). However, energy requirement of the process
2 is still higher. This is because, for trade purposes, the product formed must be concentrated up to
3 70% (Campos-Martin et al., 2006) which makes the process energy intensive and increase the
4 cost of the product

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

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

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

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

1 found that MnO_4^- was efficient for decolorization and could be used as pre-treatment step for
2 biological processes. However, concentration of MnO_4^- and pH is important to control for
3 achieving high decolorization efficiencies. In another study, Mendez-Diaz et al (2009) collated
4 the performance of conventional oxidizing agents (ClO^- , ClO_2 , KMnO_4), O_3 , $\text{O}_3/\text{H}_2\text{O}_2$,
5 O_3 /activated carbon for the removal of sodium dodecylbenzenesulphonate (SDBS) and achieved
6 80% SDBS removal within 30 minutes with O_3/PAC while others showed insignificant results.

Table 1. Redox potential of oxidizing agents

7
8 It is suggested that conventional oxidizing agents are more suitable to perform decolorization
9 than mineralization (Xu et al., 2005). Limited works have been conducted on conventional
10 oxidizing agents in this decade. Although, $\text{SO}_4^{\bullet-}$ has redox potential comparable to HO^\bullet (Table
11 1), its selective nature for organic contaminants hinders its practical application. Therefore, it is
12 concluded that HO^\bullet is the most suitable option for textile or any other wastewater treatment.
13 Therefore, this study was attempted to review and conclude all aspects of literature that
14 determine the feasibility of *in-situ* production of $\text{H}_2\text{O}_2/\text{HO}^\bullet$ for textile wastewater treatment by
15 using common AOPs.

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

17 *In-situ* production of $\text{H}_2\text{O}_2/\text{HO}^\bullet$ means its production at the time of treatment. From
18 literature, possible methods that can be employed are AOPs comprising of iron catalyzed
19 reaction, ozonation, photocatalysis, electrochemical or microbial fuel cells. Thus, this review is
20 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

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

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

4 Fang et al (2013) exploited the reductive property of magnetic nano-particles for
5 transformation of oxygen into H_2O_2 . Here, transformation of oxygen into H_2O_2 takes place in
6 two consecutive single electron transfers steps from MNPs sorbed Fe^{+2} with subsequent
7 protonation with H^+ . Then H_2O_2 reacts with dissolved Fe^{+2} in bulk medium to produce HO^\bullet
8 radical through Fenton reaction. From reaction mechanism, it was observed that pH has a
9 profound effect on the type of oxidizing species available in reaction medium. As shown in Fig.
10 4, superoxide radical ($\text{O}_2^{\bullet -}$) is dominant at alkaline pH while HO^\bullet is dominant at acidic
11 condition.

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

15 **Fig. 4.** Reaction pathways for *in-situ* production of $\text{HO}^\bullet/\text{H}_2\text{O}_2$ utilizing MNPs

16 (Fang et al., 2013)

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

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



5 Wang et al (2010) reported that under oxic conditions, high COD removal was obtained
6 because of the combined effect of oxidation and adsorption of dyes on iron hydroxides,
7 generated from Fe⁰ oxidation. From above mentioned reaction equations, it can be inferred that
8 the efficacy of Fe⁰ depends on the transfer of electron from the iron surface to the targeted
9 contaminants. Lee et al (2007) investigated the oxidation of Fe⁰ accelerated by peroxometalate
10 (POM) as electron shuttle to improve the catalytic performance of the Fe⁰. POM is not suitable
11 for the degradation of dyes waste; however quinone intermediates can possibly be used to
12 accelerate the transfer of electrons.

13 Among aforementioned alternatives, iron catalyzed production of *in-situ* H₂O₂/HO[•] is a
14 viable option for textile wastewater treatment. Moreover, it has some advantages over hydrogen
15 substituted organic compound as there may be incomplete conversion of organic compound in
16 later option, no matter produced H₂O₂ is utilized *in-situ* or *ex-situ*. Furthermore, iron catalyzed
17 *in-situ* production of H₂O₂/HO[•] is also cost effective because single catalyst can be used for
18 oxidant production as well as for degradation of dyes in textile wastewater. As evident from one
19 study, the operating cost for Remazol Brilliant blue R (RBBR) degradation by Fe⁰/air reduced
20 from 0.015US\$/g of dye (Fenton process) to 0.00113 US\$/g of dye(Chang et al. 2009).

1 **2.3. Ozonation for *in-situ* H₂O₂/HO[•] production**

2 Ozonation is an environmentally sound technique because of no sludge formation; potential to
3 perform decolorization and degradation in a single step; decomposition of residual ozone into
4 water and oxygen; less space requirement for equipment installation; less hazardous as no stock
5 of H₂O₂ is required for the oxidation step and ease of operation (Chu and Ma, 2000; Oguz et al.,
6 2005). Therefore, it is recommended to consider it an efficient option for *in-situ* production of
7 H₂O₂/ HO[•] for dye degradation.

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

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

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

1 that the time required for complete decolorization of Acid Red 88 (AR88) by ozonation
2 increased till pH 7 and then decreased which clearly indicates the decomposition of O₃ into HO[•].
3 The COD value obtained as a result of regression analysis at alkaline pH was 64% according to
4 the study done by Muthukumar et al (2004).

5 From this review, it can therefore be concluded that pH is the key parameter for accelerating
6 *in-situ* production of HO[•]. Few investigations have discussed analogous results. For example, De
7 Souza et al (2010) and Tehrani-Bagha et al (2010) reported slight change in dye degradation
8 efficiencies at high pH values as compared to acidic conditions. They supported this result by
9 arguing that it was buffered or non-buffered solution that played a role in promoting *in-situ*
10 HO[•] production at high pH values. They explained that in non-buffered solution, pH value
11 decreased because of the formation of acidic products and left no effects at the end. To
12 overcome this problem, catalytic ozonation is an efficient alternative because ozone can
13 decompose itself to produce HO[•] in the presence of catalyst. Furthermore, use of catalyst also
14 promotes controlled decomposition of ozone into HO[•] resulting in effective mineralization of dye
15 and organic contaminants (Nawrocki and Kasprzyk-Hordern, 2010; Kasprzyk-Hordern et al.,
16 2003).

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

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

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

12 Thus, ozonation can be an efficient alternative for *in-situ* production of H₂O₂ as evident from
13 the examples discussed in Table 2 that with ozonation maximum COD removal achieved was
14 60.2%. However, there are several problems that must be dealt in for its industrial applications.
15 These include intense energy requirement for *in-situ* ozone generation, selectivity for organic
16 substrates, pH sensitivity (Song et al., 2007), mass transfer limitations, high consumption rate of
17 ozone and increase in turbidity level of effluents (Ince and Tezcanlí, 2001). It has been reported
18 that energy consumption for ozonation of Congo red dye increases linearly and to achieve 80%
19 TOC removal, 528kWh/m³ power was consumed which was 254kWh/m³ for electrochemical
20 oxidation process (Faouzi Elahmadi et al., 2009).

| |
|--|
| Table 2. Application of AOPs for <i>in-situ</i> production of H ₂ O ₂ /HO [•] for textile wastewater treatment |
|--|

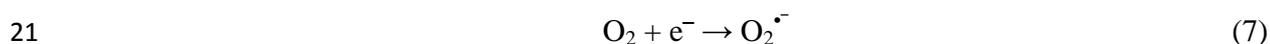
1 2.4. Photocatalysis

2 Photocatalysis makes the use of semiconducting materials to generate holes and free radicals
3 for degradation of recalcitrant organic contaminants. These radicals include HO^\bullet , $\text{O}_2^{\bullet-}$, HOO^\bullet ,
4 produced based on the interaction with the oxidizing species (Lachheb et al., 2002; Tanaka et al.,
5 2000). Semiconducting oxides like TiO_2 , ZnO , Fe_2O_3 , ZnS and CdS can be used as photocatalyst
6 (Umar and Aziz, 2013). Among all, TiO_2 has been probed frequently for observing reductive as
7 well as oxidative reactions on its surface (Chong et al., 2010).

8 In wastewater treatment applications, semiconductors (ZnO , TiO_2 etc) have the potential to
9 perform degradation of organic contaminants directly as well as through production of
10 chemically active species i.e. HO^\bullet (Boroski et al., 2009). It is well established that holes in
11 valence band and electrons in conduction band are formed when semiconducting material is
12 exposed to photons with energy higher than band gap energy. The radical generation mechanism
13 has been presented in Fig. 6. Holes are oxidizing agents that have capability to oxidize organic
14 compounds and H_2O into mineralization products and HO^\bullet respectively [Eq. 6] (Boroski et al.,
15 2009).



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



1

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

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

9 (Stylidi et al., 2003)

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

22 **Fig. 6.** Electron transfer in presence of POM

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

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

18 Furthermore, TiO₂ can only absorb ultraviolet light which is only 4% of the solar light (Ni et
19 al., 2007). To avoid it, TiO₂ is usually doped with other semiconducting material such as Cu₂O, a
20 p-type semiconductor which has narrow band gap but high conduction band (Yu et al., 2004).
21 When exposed to visible light, electrons in conduction band of Cu₂O transfer to that of TiO₂ and
22 thus increase the photocatalytic degradation of TiO₂ (Zhang et al., 2007).

1 Photocatalysis has been demonstrated successfully by several authors for production of HO[•]
2 along with the degradation of textile waste. This process has the potential to achieve maximum
3 of 80% COD and 90% color removal efficiencies (Table 2) with modifications. However, it
4 cannot be considered as an alternative for *in-situ* H₂O₂ production because: 1) it is energy
5 intensive. For instance, it consumed 8×10⁴ kW power reactive azo dye treatment (Mahamuni and
6 Adewuyi, 2010) which is several times of ozonation (Mehrjouei et al., 2014) 2) Textile
7 wastewater is highly variable in concentration and photocatalysis is limited for small streams and
8 low concentration of dyes.

9 **2.5. Electrochemical and Microbial fuel cells**

10 Electrochemical oxidation is an effective alternative as it employs either direct or indirect
11 oxidation approach for wastewater treatment (Fu et al., 2010). In direct electrochemical
12 oxidation, degradation is carried out through adsorption of the contaminants on the anode surface
13 without any involvement of oxidizing agent. However, indirect oxidation in electrochemical fuel
14 cells employs the sparging of oxygen in cathode chamber to produce H₂O₂ through direct
15 application of electric current (Panizza and Cerisola, 2009). This mechanism has been
16 successfully applied in textile wastewater treatment in several investigations as clear from Table
17 3.

18 High degradation rates and complete mineralization at optimum conditions are the main
19 features of the process but intense energy requirement hinders its practical application for *in-situ*
20 H₂O₂/HO[•] production (Fu et al., 2010; Martínez and Uribe, 2012). In one investigation, it has also
21 been found that electrochemical oxidation is more economic in comparison with ozonation in
22 terms of energy consumption for *in-situ* H₂O₂ production (Faouzi Elahmadi et al., 2009). The

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

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

21 Rozendal et al (2009) investigated the production of H_2O_2 in cathode chamber by using
22 oxygen as an electron acceptor. At applied voltage of 0.5V, about 1.9 to 2 kg $H_2O_2/m^3/day$ was
23 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 H₂O₂ 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 H₂O₂ 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* H₂O₂ 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* H₂O₂ 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* H₂O₂ 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 H₂O₂. 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.

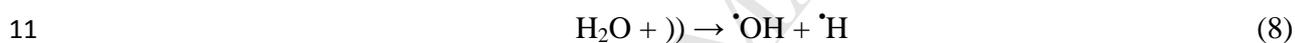
1 Electrode material must have good electrical conductivity, high surface area, chemical stability
2 and appropriate strength and toughness (Zhou et al., 2011). Many authors have collated different
3 electrodes such as graphite, platinum, IrO₂, RuO₂, PbO₂ and boron-doped diamond electrodes in
4 their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

11 Microbial fuel cell is a versatile technology because electricity production is accompanied by
12 the production of H₂O₂ in cathode chamber (Li et al., 2010, Rozendal et al., 2009). Much work
13 has been done on improving the production of electricity to-date (Feng et al., 2010a; Feng et al.,
14 2010b). To-date, power produced has been used as a low power source for operating
15 electrochemical fuel cells (Zhu and Logan, 2013b). Alternatively, power produced can also be
16 used for the aeration of cathode chamber, which would provide an environmental friendly and
17 cost effective solution for textile wastewater treatment through *in-situ* H₂O₂ (*in-situ* Fenton
18 oxidation). Being at initial stages of the process, maximum TOC removal of 76% has been
19 obtained through microbial fuel cell application at low concentrations of pollutant (Table 3). It is
20 lesser than that obtained in electrochemical oxidation thus highlighting the need of optimizing
21 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[•]

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

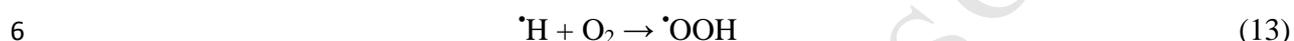
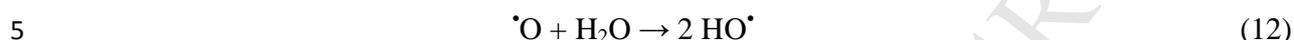
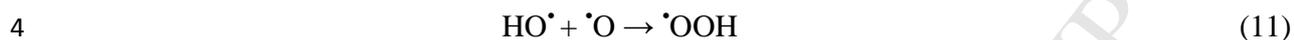
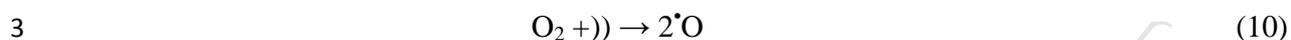
2 Sono-chemical degradation of dyes is considered as AOPs (Vončina and Majcen-Le-
 3 Marechal, 2003) because of its potential to produce HO[•] radical by homogeneous reactions or
 4 enhancing the activity of catalyst in heterogeneous reactions. In aqueous medium, ultrasound
 5 waves (‘’)) provoke the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



13 Dyes are highly hydrophilic so they can be degraded in bulk in comparison with the volatile
 14 organic compounds which can only be degraded thermally inside the gas bubble (Adewuyi,
 15 2001). However, reactive azo dyes are non-volatile, water soluble and their reaction at interface
 16 is not observed (Vajnhandl and Le Marechal, 2007). It indicates that dye interaction with HO[•]
 17 radicals can only be possible in the bulk solution. However, if hydrophilic organic compounds
 18 are concentrated in the solution additional degradation mechanism then quickly takes place at
 19 gas-liquid interface (Okitsu et al., 2005).

20 Concentration of HO[•] radicals is reported to be improved in bulk dye solution in the presence
 21 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 [•]OH 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

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

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

11

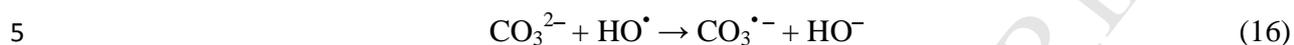
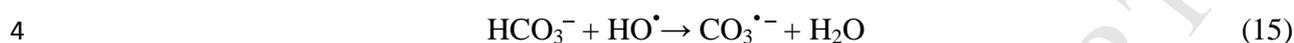
12 **4. Considerations during the *in-situ* $\text{H}_2\text{O}_2/\text{HO}^\bullet$ production process**

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

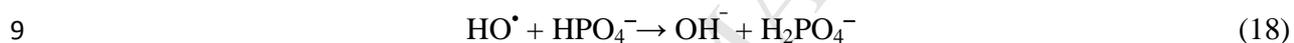
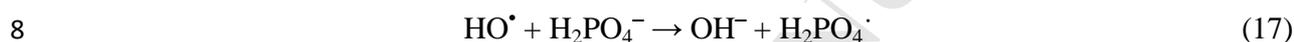


18 Bicarbonates and carbonates are the most commonly available anions in wastewater and can
19 easily scavenge radicals available for textile wastewater treatment [Eq. 15-16]. Faria et al (2009)

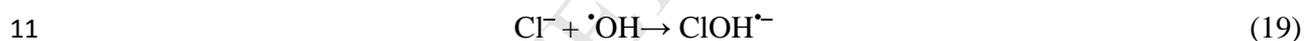
1 reported the influence of carbonates and bicarbonates as HO[•] scavenger on the efficacy of the
 2 process. It was found that scavenging effect of carbonate ions was more as compared to
 3 bicarbonate ions at both moderate and high pH value.



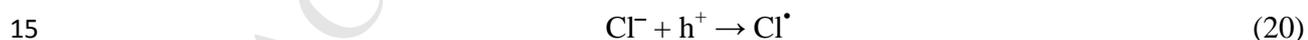
6 Moreover, presence of di-hydrogen phosphate ion H₂PO₄⁻ and mono hydrogen phosphate ion
 7 HPO₄⁻ also lowers the efficiency by scavenging HO[•] (Karthikeyan et al., 2011) [Eq. 17-18].



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

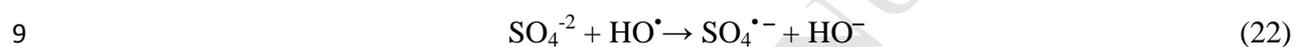
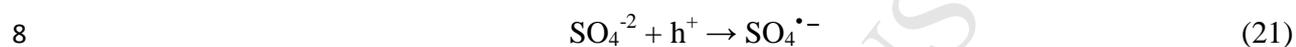


12 That is why FeSO₄·7H₂O is always preferred over FeCl₂·4H₂O in Fenton process. Moreover,
 13 Cl⁻ ions can also scavenge the holes in photocatalysis system and reduce the yield of the *in-situ*
 14 hydrogen peroxide formation [Eq. 20]:



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

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



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

14 **5. Conclusion**

15 Fenton process is an efficient method for degradation of dyes and recalcitrant organic
16 contaminants present in textile wastewater. However, excessive use of reagents, acidic
17 conditions, and high cost of hydrogen peroxide hinder its industrial applications. It is also unsafe
18 to transport and store bulk quantities of H_2O_2 . To overcome this problem, *in-situ* $\text{H}_2\text{O}_2/\text{HO}^\bullet$
19 production by Advanced Oxidation Processes including iron-catalyzed processes, ozonation,
20 photocatalysis, electrochemical oxidation and microbial fuel cells is an option worth
21 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

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

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

9 **Acknowledgement**

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13 **Abbreviations**

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

22

1 Reference

- 2 Adewuyi, Y.G., 2001. Sonochemistry: Environmental Science and Engineering Applications.
3 *Ind. Eng. Chem. Res.* 40, 4681-4715.
- 4 Aguedach, A., Brosillon, S., Morvan, J., Lhadi, E.K., 2008. Influence of ionic strength in the
5 adsorption and during photocatalysis of reactive black 5 azo dye on TiO₂ coated on non woven
6 paper with SiO₂ as a binder. *J. Hazard. Mater.* 150, 250-256.
- 7 Akyol, A., Bayramoglu, M., 2008. The degradation of an azo dye in a batch slurry photocatalytic
8 reactor. *Chem. Eng. Process.* 47, 2150-2156.
- 9 Alinsafi, A., Khemis, M., Pons, M.N., Leclerc, J.P., Yaacoubi, A., Benhammou, A., Nejmeddine,
10 A., 2005. Electro-coagulation of reactive textile dyes and textile wastewater. *Chem. Eng.*
11 *Process.* 44, 461-470.
- 12 Anipsitakis, G.P., Dionysiou, D.D., 2003. Degradation of Organic Contaminants in Water with
13 Sulfate Radicals Generated by the Conjunction of Peroxymonosulfate with Cobalt. *Environ. Sci.*
14 *Technol.* 37, 4790-4797.
- 15 Anipsitakis, G.P., Dionysiou, D.D., 2004. Radical Generation by the Interaction of Transition
16 Metals with Common Oxidants. *Environ. Sci. Technol.* 38, 3705-3712.
- 17 Arami-Niya, A., Wan Daud, W.M.A., S. Mjalli, F., Abnisa, F., Shafeeyan, M.S., 2012.
18 Production of microporous palm shell based activated carbon for methane adsorption: Modeling
19 and optimization using response surface methodology. *Chem. Eng. Res. Des.* 90, 776-784.
- 20 Baban, A., Yediler, A., Lienert, D., Kemerdere, N., Kettrup, A., 2003. Ozonation of high
21 strength segregated effluents from a woollen textile dyeing and finishing plant. *Dyes Pigm.* 58,
22 93-98.
- 23 Barakat, M.A., 2011. Adsorption and photodegradation of Procion yellow H-EXL dye in textile
24 wastewater over TiO₂ suspension. *J. Hydro-Environ. Res.* 5, 137-142.
- 25 Bejarano-Pérez, N.J., Suárez-Herrera, M.F., 2007. Sonophotocatalytic degradation of congo red
26 and methyl orange in the presence of TiO₂ as a catalyst. *Ultrason. Sonochem.* 14, 589-595.
- 27 Bensalah, N., Alfaro, M.A.Q., Martínez-Huitle, C.A., 2009. Electrochemical treatment of
28 synthetic wastewaters containing Alphazurine A dye. *Chem. Eng. J.* 149, 348-352.
- 29 Borda, M.J., Elsetinow, A.R., Strongin, D.R., Schoonen, M.A., 2003. A mechanism for the
30 production of hydroxyl radical at surface defect sites on pyrite. *Geochim. Cosmochim. Acta* 67,
31 935-939.

- 1 Boroski, M., Rodrigues, A.C., Garcia, J.C., Sampaio, L.C., Nozaki, J., Hioka, N., 2009.
2 Combined electrocoagulation and TiO₂ photoassisted treatment applied to wastewater effluents
3 from pharmaceutical and cosmetic industries. *J. Hazard. Mater.* 162, 448-454.
- 4 Campos-Martin, J.M., Blanco-Brieva, G., Fierro, J.L.G., 2006. Hydrogen Peroxide Synthesis: An
5 Outlook beyond the Anthraquinone Process. *Angew. Chem. Int. Ed.* 45, 6962-6984.
- 6 Cao, J., Wei, L., Huang, Q., Wang, L., Han, S., 1999. Reducing degradation of azo dye by zero-
7 valent iron in aqueous solution. *Chemosphere* 38, 565-571.
- 8 Cao, Y., Hu, Y., Sun, J., Hou, B., 2010. Explore various co-substrates for simultaneous
9 electricity generation and Congo red degradation in air-cathode single-chamber microbial fuel
10 cell. *Bioelectrochemistry* 79, 71-76.
- 11 Chakrabarti, S., Dutta, B.K., 2004. Photocatalytic degradation of model textile dyes in
12 wastewater using ZnO as semiconductor catalyst. *J. Hazard. Mater.* 112, 269-278.
- 13 Chang, S.-H., Chuang, S.-H., Li, H.-C., Liang, H.-H., Huang, L.-C., 2009. Comparative study on
14 the degradation of I.C. Remazol Brilliant Blue R and I.C. Acid Black 1 by Fenton oxidation and
15 Fe⁰/air process and toxicity evaluation. *J. Hazard. Mater.* 166, 1279-1288.
- 16 Chen Q., 2006. Towards cleaner production of hydrogen peroxide in China. *J. Clean. Prod.* 14,
17 708-712.
- 18 Chen, Y., Yang, S., Wang, K., Lou, L., 2005. Role of primary active species and TiO₂ surface
19 characteristic in UV-illuminated photodegradation of Acid Orange 7. *Photochem. Photobiol. A.*
20 *Chem.* 172, 47-54.
- 21 Chiang, Y.-J., Lin, C.-C., 2013. Photocatalytic decolorization of methylene blue in aqueous
22 solutions using coupled ZnO/SnO₂ photocatalysts. *Powder Technol.* 246, 137-143.
- 23 Chitra, S., Paramasivan, K., Sinha, P.K., Lal, K.B., 2004. Ultrasonic treatment of liquid waste
24 containing EDTA. *J. Clean. Prod.* 12, 429- 436
- 25 Chong, M.N., Jin, B., Chow, C.W.K., Saint, C., 2010. Recent developments in photocatalytic
26 water treatment technology: A review. *Water Res.* 44, 2997-3027.
- 27 Chong, M.N., Sharma, A.K., Burn, S., Saint, C.P., 2012. Feasibility study on the application of
28 advanced oxidation technologies for decentralised wastewater treatment. *J. Clean. Prod.* 35, 230-
29 238.
- 30 Choudhary, V.R., Jana, P., 2007. In situ generation of hydrogen peroxide from reaction of O₂
31 with hydroxylamine from hydroxylammonium salt in neutral aqueous or non-aqueous medium
32 using reusable Pd/Al₂O₃ catalyst. *Catal. Commun.* 8, 1578-1582.

- 1 Chu, L.-B., Xing, X.-H., Yu, A.-F., Zhou, Y.-N., Sun, X.-L., Jurcik, B., 2007. Enhanced
2 ozonation of simulated dyestuff wastewater by microbubbles. *Chemosphere* 68, 1854-1860.
- 3 Chu, W., Ma, C.-W., 2000. Quantitative prediction of direct and indirect dye ozonation kinetics.
4 *Water Res.* 34, 3153-3160.
- 5 de Souza, S.M.d.A.G.U., Bonilla, K.A.S., de Souza, A.A.U., 2010. Removal of COD and color
6 from hydrolyzed textile azo dye by combined ozonation and biological treatment. *J. Hazard.*
7 *Meter.* 179, 35-42.
- 8 Destailats, H., Colussi, A.J., Joseph, J.M., Hoffmann, M.R., 2000. Synergistic Effects of
9 Sonolysis Combined with Ozonolysis for the Oxidation of Azobenzene and Methyl Orange. *The*
10 *J. Phys. Chem. A* 104, 8930-8935.
- 11 Ding, H., Li, Y., Lu, A., Jin, S., Quan, C., Wang, C., Wang, X., Zeng, C., Yan, Y., 2010.
12 Photocatalytically improved azo dye reduction in a microbial fuel cell with rutile-cathode.
13 *Bioresour. Technol.* 101, 3500-3505.
- 14 Du, Z., Li, H., Gu, T., 2007. A state of the art review on microbial fuel cells: A promising
15 technology for wastewater treatment and bioenergy. *Biotechnol. Adv.* 25, 464-482.
- 16 Eren, Z., 2012. Ultrasound as a basic and auxiliary process for dye remediation: A review.
17 *Journal of Environmental Management* 104, 127-141.
- 18 Eren, Z., Ince, N.H., 2010. Sonolytic and sonocatalytic degradation of azo dyes by low and high
19 frequency ultrasound. *J. Hazard. Meter.* 177, 1019-1024.
- 20 Fang, G.-D., Zhou, D.-M., Dionysiou, D.D., 2013. Superoxide mediated production of hydroxyl
21 radicals by magnetite nanoparticles: Demonstration in the degradation of 2-chlorobiphenyl. *J.*
22 *Hazard. Meter.* 250-251, 68-75.
- 23 Faouzi Elahmadi, M., Bensalah, N., Gadri, A., 2009. Treatment of aqueous wastes contaminated
24 with Congo Red dye by electrochemical oxidation and ozonation processes. *J. Hazard. Meter.*
25 168, 1163-1169.
- 26 Faria, P.C.C., Órfão, J.J.M., Pereira, M.F.R., 2009. Activated carbon and ceria catalysts applied
27 to the catalytic ozonation of dyes and textile effluents. *Appl. Catal. B. Environ.* 88, 341-350.
- 28 Feng, C., Ma, L., Li, F., Mai, H., Lang, X., Fan, S., 2010a. A polypyrrole/anthraquinone-2,6-
29 disulphonic disodium salt (PPy/AQDS)-modified anode to improve performance of microbial
30 fuel cells. *Biosens. Bioelectron.* 25, 1516-1520.
- 31 Feng, Y., Yang, Q., Wang, X., Logan, B.E., 2010b. Treatment of carbon fiber brush anodes for
32 improving power generation in air-cathode microbial fuel cells. *J. Power Sources* 195, 1841-
33 1844.

- 1 Fernández de Dios, M.Á., del Campo, A.G., Fernández, F.J., Rodrigo, M., Pazos, M., Sanromán,
2 M.Á., 2013. Bacterial–fungal interactions enhance power generation in microbial fuel cells and
3 drive dye decolourisation by an ex situ and in situ electro-Fenton process. *Bioresour. Technol.*
4 148, 39-46.
- 5 Fu, L., You, S.-J., Zhang, G.-q., Yang, F.-L., Fang, X.-h., 2010. Degradation of azo dyes using
6 in-situ Fenton reaction incorporated into H₂O₂-producing microbial fuel cell. *Chem. Eng. J.* 160,
7 164-169.
- 8 Fujishima, A., N. Rao, T., A. Tryk, D., 2000. Titanium dioxide photocatalysis. *J. Photochem.*
9 *Photobiol. C. Photochem. Rev.* 1, 1-21.
- 10 Gao, M., Zeng, Z., Sun, B., Zou, H., Chen, J., Shao, L., 2012. Ozonation of azo dye Acid Red 14
11 in a microporous tube-in-tube microchannel reactor: Decolorization and mechanism.
12 *Chemosphere* 89, 190-197.
- 13 Ghodbane, H., Hamdaoui, O., 2009. Intensification of sonochemical decolorization of
14 anthraquinonic dye Acid Blue 25 using carbon tetrachloride. *Ultrason. Sonochem.* 16, 455-461.
- 15 Gil, G.-C., Chang, I.-S., Kim, B.H., Kim, M., Jang, J.-K., Park, H.S., Kim, H.J., 2003.
16 Operational parameters affecting the performance of a mediator-less microbial fuel cell.
17 *Biosens. Bioelectron.* 18, 327-334.
- 18 Gillham, R.W., O'Hannesin, S.F., 1994. Enhanced Degradation of Halogenated Aliphatics by
19 Zero-Valent Iron. *Ground Water* 32, 958-967.
- 20 Glaze, W.H., Kang, J.-W., Chapin, D.H., 1987. The Chemistry of Water Treatment Processes
21 Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation. *Ozone Sci. Eng.* 9, 335-352.
- 22 González, A.S., Martínez, S.S., 2008. Study of the sonophotocatalytic degradation of basic blue
23 9 industrial textile dye over slurry titanium dioxide and influencing factors. *Ultrason. Sonochem.*
24 15, 1038-1042.
- 25 Gul, S., Ozcan, O., Erbatur, O., 2007. Ozonation of C.I. Reactive Red 194 and C.I. Reactive
26 Yellow 145 in aqueous solution in the presence of granular activated carbon. *Dyes Pigm.* 75,
27 426-431.
- 28 Gültekin, I., Tezcanli-Güyer, G., Ince, N.H., 2009. Sonochemical decay of C.I. Acid Orange 8:
29 Effects of CCl₄ and t-butyl alcohol. *Ultrason. Sonochem.* 16, 577-581.
- 30 Han, J.-L., Wang, C.-T., Hu, Y.-C., Liu, Y., Chen, W.-M., Chang, C.-T., Xu, H.-Z., Chen, B.-Y.,
31 2010. Exploring power generation of single-chamber microbial fuel cell using mixed and pure
32 cultures. *J. Taiwan Inst. Chem. Eng.* 41, 606-611.
- 33 Hassan, D.U.B., Aziz, A.R.A., Daud, W.M.A.W., 2012. On the Limitation of Fenton Oxidation
34 Operational Parameters: A Review. *Int. J. Chem. React. Eng.* 10.

- 1 He, Z., Lin, L., Song, S., Xia, M., Xu, L., Ying, H., Chen, J., 2008. Mineralization of C.I.
2 Reactive Blue 19 by ozonation combined with sonolysis: Performance optimization and
3 degradation mechanism. *Sep. Purif. Technol.* 62, 376-381.
- 4 He, Z., Song, S., Xia, M., Qiu, J., Ying, H., Lü, B., Jiang, Y., Chen, J., 2007. Mineralization of
5 C.I. Reactive Yellow 84 in aqueous solution by sonolytic ozonation. *Chemosphere* 69, 191-199.
- 6 Huang, K.-C., Zhao, Z., Hoag, G.E., Dahmani, A., Block, P.A., 2005. Degradation of volatile
7 organic compounds with thermally activated persulfate oxidation. *Chemosphere* 61, 551-560.
- 8 Ince, N.H., Tezcanlı, G., 2001. Reactive dyestuff degradation by combined sonolysis and
9 ozonation. *Dyes Pigm.* 49, 145-153.
- 10 Jaccoud, A., Fóti, G., Comninellis, C., 2006. Electrochemical investigation of platinum electrode
11 in solid electrolyte cell. *Electrochim. Acta* 51, 1264-1273.
- 12 Jin, X.C., Liu, G.Q., Xu, Z.H., Tao, W.Y., 2007. Decolorization of a dye industry effluent by
13 *Aspergillus fumigatus* XC6. *Appl. Microbiol. Biotechnol.* 74, 239-243.
- 14 Kalathil, S., Lee, J., Cho, M.H., 2011. Granular activated carbon based microbial fuel cell for
15 simultaneous decolorization of real dye wastewater and electricity generation. *New Biotechnol.*
16 29, 32-37.
- 17 Kalra, S.S., Mohan, S., Sinha, A., Singh, G., 2011. Advance Oxidation processes for Treatment
18 of textile and dye Wastewater: A Review 2nd International Conference on Environmental
19 Science and Development IACSIT Press, Singapore.
- 20 Karthikeyan, S., Titus, A., Gnanamani, A., Mandal, A.B., Sekaran, G., 2011. Treatment of textile
21 wastewater by homogeneous and heterogeneous Fenton oxidation processes. *Desalination* 281,
22 438-445.
- 23 Kasprzyk-Hordern, B., Ziółek, M., Nawrocki, J., 2003. Catalytic ozonation and methods of
24 enhancing molecular ozone reactions in water treatment. *Appl. Catal. B. Environ* 46, 639-669.
- 25 Kaur, S., Singh, V., 2007. Visible light induced sonophotocatalytic degradation of Reactive Red
26 dye 198 using dye sensitized TiO₂. *Ultrason. Sonochem.* 14, 531-537.
- 27 Kelley, K., Marley, M., Sperry, K., 2003. In Situ Chemical Oxidation, in: Moyer, E., Kostecki,
28 P. (Eds.), *MTBE Remediation Handbook*. Springer US, pp. 223-241.
- 29 Khatee, A., Sheydaei, M., Hassani, A., Taseidifar, M., Karaca, S., 2015. Sonocatalytic removal of
30 an organic dye using TiO₂/Montmorillonite nano-compoiste. *Ultrason. Sonochem.* 22, 404-411.
- 31 Krishnakumar, B., Swaminathan, M., 2011. Influence of operational parameters on
32 photocatalytic degradation of a genotoxic azo dye Acid Violet 7 in aqueous ZnO suspensions.
33 *Spectrochim. Acta A. Mol. Biomol. Spectrosc.* 81, 739-744.

- 1 Lachheb, H., Puzenat, E., Houas, A., Ksibi, M., Elaloui, E., Guillard, C., Herrmann, J.-M., 2002.
2 Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red,
3 Congo Red, Methylene Blue) in water by UV-irradiated titania. *Appl. Catal. B. Environ.* 39, 75-
4 90.
- 5 Ledakowicz, S., Maciejewska, R., Gebicka, L., Perkowski, J., 2000. Kinetics of the
6 Decolorization by Fenton's Reagent. *Ozone Sci. Eng.* 22, 195-205.
- 7 Lee, J., Kim, J., Choi, W., 2007. Oxidation on Zerovalent Iron Promoted by Polyoxometalate as
8 an Electron Shuttle. *Environ. Sci. Technol.* 41, 3335-3340.
- 9 Li, Z., Zhang, X., Lin, J., Han, S., Lei, L., 2010. Azo dye treatment with simultaneous electricity
10 production in an anaerobic-aerobic sequential reactor and microbial fuel cell coupled system.
11 *Bioresour. Technol.* 101, 4440-4445.
- 12 Liang, C., Lee, I.L., 2008. In situ iron activated persulfate oxidative fluid sparging treatment of
13 TCE contamination — A proof of concept study. *J. Contam. Hydrol.* 100, 91-100.
- 14 Liu, C.-H., Wu, J.-S., Chiu, H.-C., Suen, S.-Y., Chu, K.H., 2007a. Removal of anionic reactive
15 dyes from water using anion exchange membranes as adsorbers. *Water Res.* 41, 1491-1500.
- 16 Liu, G., Yates, M.D., Cheng, S., Call, D.F., Sun, D., Logan, B.E., 2011. Examination of
17 microbial fuel cell start-up times with domestic wastewater and additional amendments.
18 *Bioresour. Technol.* 102, 7301-7306.
- 19 Liu, H., Li, G., Qu, J., Liu, H., 2007b. Degradation of azo dye Acid Orange 7 in water by
20 Fe⁰/granular activated carbon system in the presence of ultrasound. *J. Hazard. Mater.* 144, 180-
21 186.
- 22 Liu, Y., Yu, H., Lv, Z., Zhan, S., Yang, J., Peng, X., Ren, Y., Wu, X., 2012. Simulated-sunlight-
23 activated photocatalysis of Methylene Blue using cerium-doped SiO₂/TiO₂ nanostructured
24 fibers. *J. Environ. Sci.* 24, 1867-1875.
- 25 Lunsford, J.H., 2003. The direct formation of H₂O₂ from H₂ and O₂ over palladium catalysts. *J.*
26 *Catal.* 216, 455-460.
- 27 Ma, C.Y., Xu, J.Y., Liu, X.J., 2006. Decomposition of an azo dye in aqueous solution by
28 combination of ultrasound and visible light. *Ultrason.* 44, 375-378.
- 29 Madhavan, J., Maruthamuthu, P., Murugesan, S., Ashokkumar, M., 2009. Kinetics of
30 degradation of acid red 88 in the presence of Co²⁺-ion/peroxomonosulphate reagent. *Appl. Catal.*
31 *A. Gen.* 368, 35-39.
- 32 Maezawa, A., Nakadoi, H., Suzuki, K., Furusawa, T., Suzuki, Y., Uchida, S., 2007. Treatment of
33 dye wastewater by using photo-catalytic oxidation with sonication. *Ultrason. Sonochem.* 14,
34 615-620.

- 1 Mahamuni, N.N., Adewuyi, Y.G., 2010. Advanced oxidation processes (AOPs) involving
2 ultrasound for waste water treatment: A review with emphasis on cost estimation. *Ultrason.*
3 *Sonochem.* 17, 990-1003.
- 4 Mahmoodi, N.M., 2013. Photocatalytic ozonation of dyes using multiwalled carbon nanotube. *J.*
5 *Mol. Catal. A. Chem.* 366, 254-260.
- 6 Martínez, S.S., Uribe, E.V., 2012. Enhanced sonochemical degradation of azure B dye by the
7 electroFenton process. *Ultrason. Sonochem.* 19, 174-178.
- 8 McMullan, G., Meehan, C., Conneely, A., Kirby, N., Robinson, T., Nigam, P., Banat, I.M.,
9 Marchant, R., Smyth, W.F., 2001. Microbial decolourisation and degradation of textile dyes.
10 *Appl. Microbiol. Biotechnol.* 56, 81-87.
- 11 Mehrjouei, M., Muller, S., Moller, D., 2014. Energy consumption of three different advanced
12 oxidation methods for water treatment: a cost effectiveness study. *J. Clean. Prod.* 65, 178-183.
- 13 Méndez-Díaz, J.D., Sánchez-Polo, M., Rivera-Utrilla, J., Bautista-Toledo, M.I., 2009.
14 Effectiveness of different oxidizing agents for removing sodium dodecylbenzenesulphonate in
15 aqueous systems. *Water Res.* 43, 1621-1629.
- 16 Meric, S., Kaptan, D. Olmez, T., 2004. Color and COD removal from wastewater containing
17 Reactive Black 5 using Fenton's oxidation process. *Chemosphere* 54, 435- 441.
- 18 Métivier-Pignon, H., Faur-Brasquet, C., Jaouen, P., Le Cloirec, P., 2003. Coupling ultrafiltration
19 with an activated carbon cloth for the treatment of highly coloured wastewaters : A
20 techno-economic study. *Environ. Technol.* 24, 735-743.
- 21 Modin, O., Fukushi, K., 2013. Production of high concentrations of H₂O₂ in a bioelectrochemical
22 reactor fed with real municipal wastewater. *Environ. Technol.* 34, 2737-2742.
- 23 Moon, H., Chang, I.S., Kim, B.H., 2006. Continuous electricity production from artificial
24 wastewater using a mediator-less microbial fuel cell. *Bioresour. Technol.* 97, 621-627.
- 25 Muruganandham, M., Swaminathan, M., 2006. Photocatalytic decolourisation and degradation of
26 Reactive Orange 4 by TiO₂-UV process. *Dyes Pigm.* 68, 133-142.
- 27 Muthukumar, M., Sargunamani, D., Selvakumar, N., Venkata Rao, J., 2004. Optimisation of
28 ozone treatment for colour and COD removal of acid dye effluent using central composite design
29 experiment. *Dyes Pigm.* 63, 127-134.
- 30 Nawrocki, J., Kasprzyk-Hordern, B., 2010. The efficiency and mechanisms of catalytic
31 ozonation. *Appl. Catal. B. Environ.* 99, 27-42.
- 32 Neelavannan, M.G., Ahmed Basha, C., 2008. Electrochemical-assisted photocatalytic
33 degradation of textile washwater. *Sep. Purif. Technol.* 61, 168-174.

- 1 Neyens, E., Baeyens, J., 2003. A review of classic Fenton's peroxidation as an advanced
2 oxidation technique. *J. Hazard. Mater.* 98, 33-50.
- 3 Ni, M., Leung, M.K.H., Leung, D.Y.C., Sumathy, K., 2007. A review and recent developments
4 in photocatalytic water-splitting using for hydrogen production. *Sust. Energ. Rev.* 11, 401-425.
- 5 Oguz, E., Keskinler, B., Çelik, Z., 2005. Ozonation of aqueous Bomaplex Red CR-L dye in a
6 semi-batch reactor. *Dyes Pigm.* 64, 101-108.
- 7 Okitsu, K., Iwasaki, K., Yobiko, Y., Bandow, H., Nishimura, R., Maeda, Y., 2005. Sonochemical
8 degradation of azo dyes in aqueous solution: A new heterogeneous kinetics model taking into
9 account the local concentration of OH radicals and azo dyes. *Ultrason. Sonochem.* 12, 255-262.
- 10 Özcan, A., Oturan, M.A., Oturan, N., Şahin, Y., 2009. Removal of Acid Orange 7 from water by
11 electrochemically generated Fenton's reagent. *J. Hazard. Mater.* 163, 1213-1220.
- 12 Ozer, R.R., Ferry, J.L., 2001. Investigation of the Photocatalytic Activity of
13 TiO₂-Polyoxometalate Systems. *Environ. Sci. Technol.* 35, 3242-3246.
- 14 Ozturk, E., Yetis, U., Dilek, F.B., Demirer, G.N. 2009. A chemical substitution study for a wet
15 processing textile mill in Turkey. *J. Clean. Prod.* 17, 239- 247.
- 16 Panizza, M., Cerisola, G., 2009. Electro-Fenton degradation of synthetic dyes. *Water Res.* 43,
17 339-344.
- 18 Paprowicz, J., Słodczyk, S., 1988. Application of biologically activated sorptive columns for
19 textile waste water treatment. *Environ. Technol. Lett.* 9, 271-280.
- 20 Park, S.-E., Huang, L., Lee, C.W., Chang, J.-S., 2000. < Generation of H₂O₂ from H₂ and O₂
21 over zeolite beta containing Pd and heterogenized organic compounds. *Catal. Today* 61, 117-
22 122.
- 23 Parker, P.M., 2004. Global Trade Perspective 2005 - Hydrogen Peroxide. ICON Group
24 International, Inc., p. 1.
- 25 Parker, P.M., 2010. The 2011 Import and Export Market for Hydrogen Peroxide in Europe.
26 Regional Trade Reports, N.PAG.
- 27 Patil, B.N., Naik, D.B., Shrivastava, V.S., 2011. Photocatalytic degradation of hazardous
28 Ponceau-S dye from industrial wastewater using nanosized niobium pentoxide with carbon.
29 *Desalination* 269, 276-283.
- 30 Peng, X., Yu, H., Wang, X., Gao, N., Geng, L., Ai, L., 2013. Enhanced anode performance of
31 microbial fuel cells by adding nanosemiconductor goethite. *J. Power Sources* 223, 94-99.

- 1 Peralta-Hernández, J.M., Meas-Vong, Y., Rodríguez, F.J., Chapman, T.W., Maldonado, M.I.,
2 Godínez, L.A., 2008. Comparison of hydrogen peroxide-based processes for treating dye-
3 containing wastewater: Decolorization and destruction of Orange II azo dye in dilute solution.
4 *Dyes Pigm.* 76, 656-662.
- 5 Peternel, I.T., Koprivanac, N., Božić, A.M.L., Kušić, H.M., 2007. Comparative study of
6 UV/TiO₂, UV/ZnO and photo-Fenton processes for the organic reactive dye degradation in
7 aqueous solution. *J. Hazard. Mater.* 148, 477-484.
- 8 R. Bond, D., R. Lovley, D., 2002. Electricity Production by *Geobacter sulfurreducens* Attached
9 to Electrodes. *Appl. Environ. Microbiol.* 69, 1548-1555.
- 10 Rabaey, K., Lissens, G., Siciliano, S., Verstraete, W., 2003. A microbial fuel cell capable of
11 converting glucose to electricity at high rate and efficiency. *Biotechnol. Lett.* 25, 1531-1535.
- 12 Rismani-Yazdi, H., Carver, S.M., Christy, A.D., Tuovinen, O.H., 2008. Cathodic limitations in
13 microbial fuel cells: An overview. *J. Power Sources* 180, 683-694.
- 14 Rittmann, B.E., 2008. Opportunities for renewable bioenergy using microorganisms. *Biotechnol.*
15 *Bioeng.* 100, 203-212.
- 16 Rivera-Utrilla, J., Sánchez-Polo, M., 2002. Ozonation of 1,3,6-naphthalenetrisulphonic acid
17 catalysed by activated carbon in aqueous phase. *Appl. Catal. B. Environ.* 39, 319-329.
- 18 Robinson, T., McMullan, G., Marchant, R., Nigam, P., 2001. Remediation of dyes in textile
19 effluent: a critical review on current treatment technologies with a proposed alternative.
20 *Bioresour. Technol.* 77, 247-255.
- 21 Rozendal, R.A., Hamelers, H.V.M., Rabaey, K., Keller, J., Buisman, C.J.N., 2008. Towards
22 practical implementation of bioelectrochemical wastewater treatment. *Trends biotechnol.* 26,
23 450-459.
- 24 Rozendal, R.A., Leone, E., Keller, J., Rabaey, K., 2009. Efficient hydrogen peroxide generation
25 from organic matter in a bioelectrochemical system. *Electrochem. Commun.* 11, 1752-1755.
- 26 Ruiz, E.J., Arias, C., Brillas, E., Hernández-Ramírez, A., Peralta-Hernández, J.M., 2011.
27 Mineralization of Acid Yellow 36 azo dye by electro-Fenton and solar photoelectro-
28 Fenton processes with a boron-doped diamond anode. *Chemosphere* 82, 495-501.
- 29 Sahunin, C., Kaewboran, J., Hunsom, M., 2006. Treatment of textile dyeing wastewater by photo
30 oxidation using UV/H₂O₂/Fe⁺² Reagents. *Sci. Asia* 32, 181-186.
- 31 Sala, M., Gutierrez-Bouzan, M.C., 2014. Electrochemical treatment of industrial wastewater and
32 effluent reuse at laboratory and semi-industrial scale. *J. Clean. Prod.* 65, 458-464.

- 1 Sánchez-Polo, M., von Gunten, U., Rivera-Utrilla, J., 2005. Efficiency of activated carbon to
2 transform ozone into OH radicals: Influence of operational parameters. *Water Res.* 39, 3189-
3 3198.
- 4 Sathishkumar, P., Mangalaraja, R.V., Anandan, S., Ashokkumar, M., 2013. CoFe₂O₄/TiO₂
5 nanocatalysts for the photocatalytic degradation of Reactive Red 120 in aqueous solutions in the
6 presence and absence of electron acceptors. *Chem. Eng. J.* 220, 302-310.
- 7 Selli, E., 2002. Synergistic effects of sonolysis combined with photocatalysis in the degradation
8 of an azo dye. *Phys. Chem. Chem. Phys.* 4, 6123-6128.
- 9 Sevimli, M.F., Sarikaya, H.Z., 2005. Effect of Some Operational Parameters on the
10 Decolorization of Textile Effluents and Dye Solutions by Ozonation. *Environ. Technol.* 26, 135-
11 144.
- 12 Sheriff, T.S., Cope, S., Ekwegh, M., 2007. Calmagite dye oxidation using in situ generated
13 hydrogen peroxide catalysed by manganese(ii) ions. *Dalton Trans.* 5119.
- 14 Solanki, K., Subramanian, S., Basu, S., 2013. Microbial fuel cells for azo dye treatment with
15 electricity generation: A review. *Bioresour. Technol.* 131, 564-571.
- 16 Song, S., Xu, L., He, Z., Chen, J., Xiao, X., Yan, B., 2007a. Mechanism of the Photocatalytic
17 Degradation of C.I. Reactive Black 5 at pH 12.0 Using SrTiO₃/CeO₂ as the Catalyst.
18 *Environmental Science & Technology* 41, 5846-5853.
- 19 Song, S., Xu, L., He, Z., Ying, H., Chen, J., Xiao, X., Yan, B., 2008. Photocatalytic degradation
20 of C.I. Direct Red 23 in aqueous solutions under UV irradiation using SrTiO₃/CeO₂ composite as
21 the catalyst. *J. Hazard. Mater.* 152, 1301-1308.
- 22 Song, S., Ying, H., He, Z., Chen, J., 2007b. Mechanism of decolorization and degradation of CI
23 Direct Red 23 by ozonation combined with sonolysis. *Chemosphere* 66, 1782-1788.
- 24 Staehelin, J., Hoigne, J., 1982. Decomposition of ozone in water: rate of initiation by hydroxide
25 ions and hydrogen peroxide. *Environ. Sci. Technol.* 16, 676-681.
- 26 Stock, N.L., Peller, J., Vinodgopal, K., Kamat, P.V., 2000. Combinative Sonolysis and
27 Photocatalysis for Textile Dye Degradation. *Environ. Sci. Technol.* 34, 1747-1750.
- 28 Styliidi, M., Kondarides, D.I., Verykios, X.E., 2003. Pathways of solar light-induced
29 photocatalytic degradation of azo dyes in aqueous TiO₂ suspensions. *Appl. Catal. B. Environ.*
30 40, 271-286.
- 31 Sun, J., Bi, Z., Hou, B., Cao, Y.-q., Hu, Y.-y., 2011. Further treatment of decolorization liquid of
32 azo dye coupled with increased power production using microbial fuel cell equipped with an
33 aerobic biocathode. *Water Res.* 45, 283-291.

- 1 Sun, J., Qiao, L., Sun, S., Wang, G., 2008. Photocatalytic degradation of Orange G on nitrogen-
2 doped TiO₂ catalysts under visible light and sunlight irradiation. *J. Hazard. Mater.* 155, 312-319.
- 3 Tan, C., Xiang, B., Li, Y., Fang, J., Huang, M., 2011. Preparation and characteristics of a nano-
4 PbO₂ anode for organic wastewater treatment. *Chem. Eng. J.* 166, 15-21.
- 5 Tanaka, K., Padermpole, K., Hisanaga, T., 2000. Photocatalytic degradation of commercial azo
6 dyes. *Water Res.* 34, 327-333.
- 7 Tavares, M.G., da Silva, L.V.A., Sales Solano, A.M., Tonholo, J., Martínez-Huitle, C.A., Zanta,
8 C.L.P.S., 2012. Electrochemical oxidation of Methyl Red using Ti/Ru_{0.3}Ti_{0.7}O₂ and Ti/Pt
9 anodes. *Chem. Eng. J.* 204–206, 141-150.
- 10 Tehrani-Bagha, A.R., Mahmoodi, N.M., Menger, F.M., 2010. Degradation of a persistent organic
11 dye from colored textile wastewater by ozonation. *Desalination* 260, 34-38.
- 12 Tezcanli-Güyer, G., Ince, N.H., 2004. Individual and combined effects of ultrasound, ozone and
13 UV irradiation: A case study with textile dyes. *Ultrasonics* 42, 603-609.
- 14 Thompson, L.H., Doraiswamy, L.K., 1999. Sonochemistry: Science and Engineering. *Ind. Eng.*
15 *Chem. Res.* 38, 1215-1249.
- 16 Tosik, R., 2005. Dyes Color Removal by Ozone and Hydrogen Peroxide: Some Aspects and
17 Problems. *Ozone Sci. Eng.* 27, 265-271.
- 18 Turhan, K., Durukan, I., Ozturkcan, S.A., Turgut, Z., 2012. Decolorization of textile basic dye in
19 aqueous solution by ozone. *Dyes Pigm.* 92, 897-901.
- 20 Umar, M., Aziz, H.A., 2013. Photocatalytic Degradation of Organic Pollutants in Water.
- 21 Vajnhandl, S., Le Marechal, A.M., 2007. Case study of the sonochemical decolouration of textile
22 azo dye Reactive Black 5. *J. Hazard. Mater.* 141, 329-335.
- 23 Vecitis, C.D., Lesko, T., Colussi, A.J., Hoffmann, M.R., 2010. Sonolytic Decomposition of
24 Aqueous Bioxalate in the Presence of Ozone. *J. Phys. Chem. A.* 114, 4968-4980.
- 25 Vlyssides, A.G., Papaioannou, D., Loizidou, M., Karlis, P.K., Zorpas, A.A., 2000. Testing an
26 electrochemical method for treatment of textile dye wastewater. *Waste Manage.* 20, 569-574.
- 27 Voloshin, Y., Halder, R., Lawal, A., 2007. Kinetics of hydrogen peroxide synthesis by direct
28 combination of H₂ and O₂ in a microreactor. *Catal. Today* 125, 40-47.
- 29 Vončina, D.B., Majcen-Le-Marechal, A., 2003. Reactive dye decolorization using combined
30 ultrasound/H₂O₂. *Dyes Pigm.* 59, 173-179.

- 1 Wang, A., Guo, W., Hao, F., Yue, X., Leng, Y., 2014. Degradation of Acid Orange 7 in aqueous
2 solution by zero-valent aluminium under ultrasonic irradiation. *Ultrason. Sonochem.* 21, 572-
3 575.
- 4 Wang, W., Qu, Y., Yang, B., Liu, X., Su, W., 2012. Lactate oxidation in pyrite suspension: A
5 Fenton-like process in situ generating H₂O₂. *Chemosphere* 86, 376-382.
- 6 Wang, X., Feng, Y., Ren, N., Wang, H., Lee, H., Li, N., Zhao, Q., 2009. Accelerated start-up of
7 two-chambered microbial fuel cells: Effect of anodic positive poised potential. *Electrochim. Acta*
8 54, 1109-1114.
- 9 Wu, C., Kuo, C., Chang, C., 2008. Decolorization of C.I. Reactive Red 2 by catalytic ozonation
10 processes. *J. Hazard. Mater.* 153, 1052-1058.
- 11 Wu, C.H., 2008. Effects of sonication on decolorization of C.I. Reactive Red 198 in UV/ZnO
12 system. *J. Hazard. Mater.* 153, 1254-1261.
- 13 Xu, X.-R., Li, H.-B., Wang, W.-H., Gu, J.-D., 2005. Decolorization of dyes and textile
14 wastewater by potassium permanganate. *Chemosphere* 59, 893-898.
- 15 Yadav, A.K., Dash, P., Mohanty, A., Abbassi, R., Mishra, B.K., 2012. Performance assessment
16 of innovative constructed wetland-microbial fuel cell for electricity production and dye removal.
17 *Ecol. Eng.* 47, 126-131.
- 18 Yalfani, M.S., Contreras, S., Medina, F., Sueiras, J.E., 2011. Hydrogen substitutes for the in situ
19 generation of H₂O₂: An application in the Fenton reaction. *J. Hazard. Mater.* 192, 340-346.
- 20 Yang, S., Wang, P., Yang, X., Shan, L., Zhang, W., Shao, X., Niu, R., 2010. Degradation
21 efficiencies of azo dye Acid Orange 7 by the interaction of heat, UV and anions with common
22 oxidants: Persulfate, peroxymonosulfate and hydrogen peroxide. *J. Hazard. Mater.* 179, 552-
23 558.
- 24 Yeh, R.Y.-L., Hung, Y.-T., Liu, R.L.-H., Chiu, H.-M., Thomas, A., 2002. Textile Wastewater
25 Treatment With Activated Sludge And Powdered Activated Carbon. *Int. J. Environ. Stud.* 59,
26 607-622.
- 27 Yu, Y., Du, F.-P., Yu, J.C., Zhuang, Y.-Y., Wong, P.-K., 2004. One-dimensional shape-
28 controlled preparation of porous Cu₂O nano-whiskers by using CTAB as a template. *J. Solid
29 State Chem.* 177, 4640-4647.
- 30 Zhang, H., Duan, L., Zhang, Y., Wu, F., 2005. The use of ultrasound to enhance the
31 decolorization of the C.I. Acid Orange 7 by zero-valent iron. *Dyes Pigm.* 65, 39-43.
- 32 Zhang, L., Li, J., Chen, Z., Tang, Y., Yu, Y., 2006. Preparation of Fenton reagent with H₂O₂
33 generated by solar light-illuminated nano-Cu₂O/MWNTs composites. *Appl. Catal. A. Gen.* 299,
34 292-297.

- 1 Zhang, S., Wang, D., Zhang, S., Zhang, X., Fan, P., 2013a. Ozonation and carbon-assisted
2 Ozonation of Methylene Blue as Model Compound: Effect of solution pH. *Procedia Environ.*
3 *Sci.* 18, 493-502.
- 4 Zhang, X.b., Dong, W.-y., Yang, W., 2013b. Decolorization efficiency and kinetics of typical
5 reactive azo dye RR2 in the homogeneous Fe(II) catalyzed ozonation process. *Chem. Eng. J.*
6 233, 14-23.
- 7 Zhang, Y.-G., MA, L.-L., Li, J.-L., YU, Y., 2007. In Situ Fenton Reagent Generated From
8 TiO₂/Cu₂O Composite Film: a New Way to Utilize TiO₂ Under Visible Light Irradiation
9 *Environ. Sci. Technol.*
- 10 Zhao, J., Zhang, Y., Quan, X., Chen, S., 2010. Enhanced oxidation of 4-chlorophenol using
11 sulfate radicals generated from zero-valent iron and peroxydisulfate at ambient temperature. *Sep.*
12 *Purif. Technol.* 71, 302-307.
- 13 Zhou, M., Chi, M., Luo, J., He, H., Jin, T., 2011. An overview of electrode materials in microbial
14 fuel cells. *J. Power Sources* 196, 4427-4435.
- 15 Zhu, X., Logan, B.E., 2013a. Using single-chamber microbial fuel cells as renewable power
16 sources of electro-Fenton reactors for organic pollutant treatment. *J. Hazard. Mater.* 252-253,
17 198-203.
- 18 Zhu, X., Logan, B.E., 2013b. Using single-chamber microbial fuel cells as renewable power
19 sources of electro-Fenton reactors for organic pollutant treatment. *J. Hazard. Mater.* 252-253,
20 198-203.
- 21 Zhu, X., Ni, J., 2009. Simultaneous processes of electricity generation and p-nitrophenol
22 degradation in a microbial fuel cell. *Electrochem. Commun.* 11, 274-277.
- 23 Zhuang, L., Zhou, S., Yuan, Y., Liu, M., Wang, Y., 2010. A novel bioelectro-Fenton system for
24 coupling anodic COD removal with cathodic dye degradation. *Chem. Eng. J.* 163, 160-163.

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27

List of Table Captions

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

Table 3. Electrochemical and microbial fuel cells for *in-situ* production of $\text{H}_2\text{O}_2/\text{HO}^\bullet$

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

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 H₂O₂/HO[•] 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 | Fe ⁰ /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 | Fe ⁰ /air | 100 | 50 | 3/- | >99% >99% | COD: 96% COD: 50% | Catalytic (Zero valent iron catalyst) | (Chang et al., 2009) |
| Calmagite | Mn(II)/Tiron/ NH ₂ OH | 0.1 mM | 50μM/1.50mM/ 100mM | 8/20 | - | - | H ₂ substituted organic compound | (Sheriff et al., 2007) |
| - | Pd/Al ₂ O ₃ with NH ₂ OH & 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

List of Figure Captions

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

Fig. 2. Conventional method for H₂O₂ production

Fig. 3. *In-situ* production of H₂O₂/ HO[•] by iron pyrite

Fig. 4. Reaction pathways for *in-situ* production of HO[•]/H₂O₂ utilizing MNPs

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

Fig. 6. Electron transfer in presence of POM

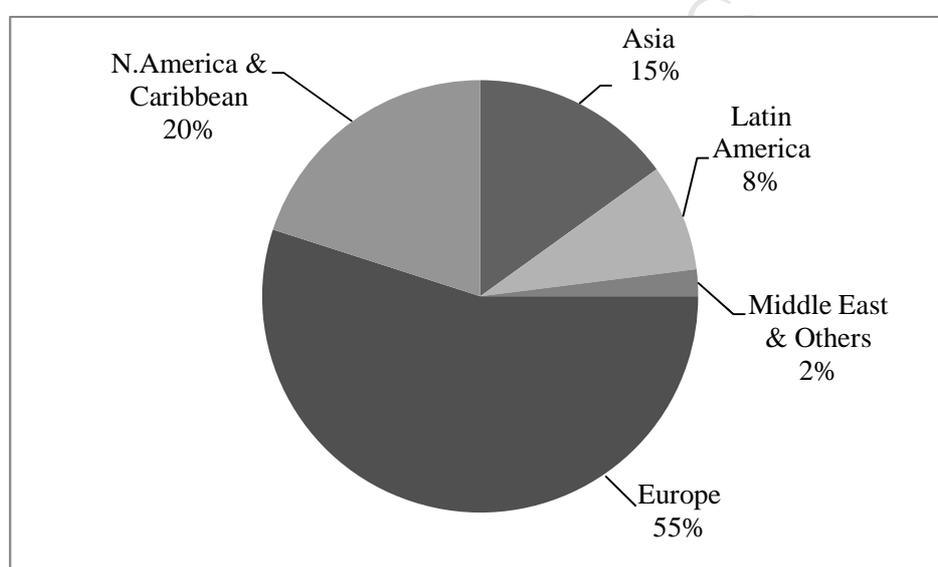


Fig. 1. World supplies of Exported Hydrogen Peroxide (2005)

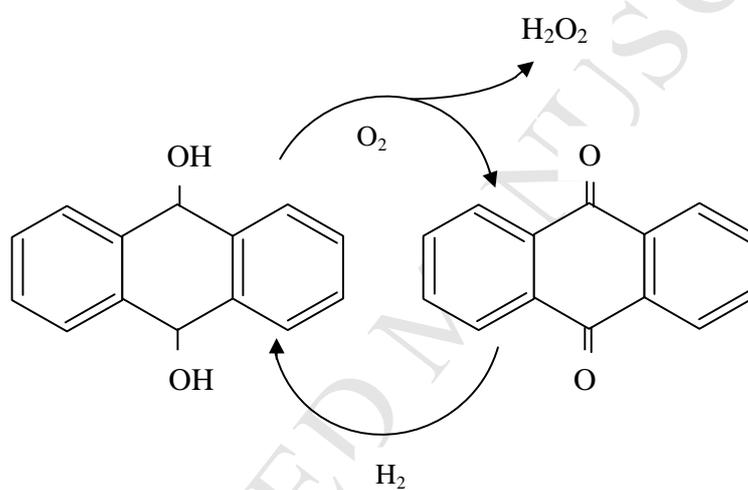


Fig. 2. Conventional method for H_2O_2 production (Campos-Martin et al., 2006)

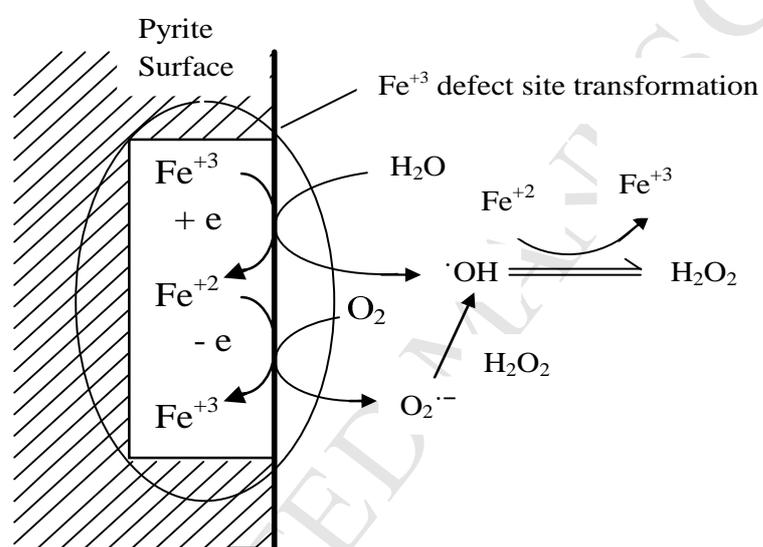


Fig. 3. *In-situ* production of $\text{H}_2\text{O}_2/\text{HO}^\bullet$ by iron pyrite (Wang et al., 2012)

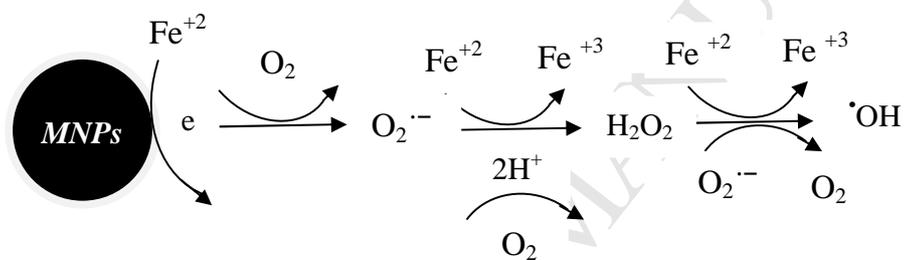


Fig. 4. Reaction pathways for *in-situ* production of HO[•]/H₂O₂ utilizing MNPs (Fang et al., 2013)

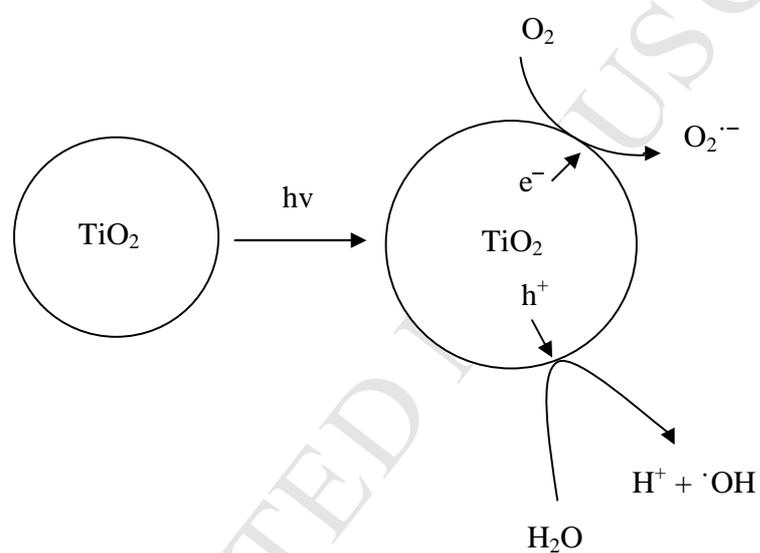


Fig. 5. Schematic presentation of mechanism of oxidative species production

(Stylidi et al., 2003)

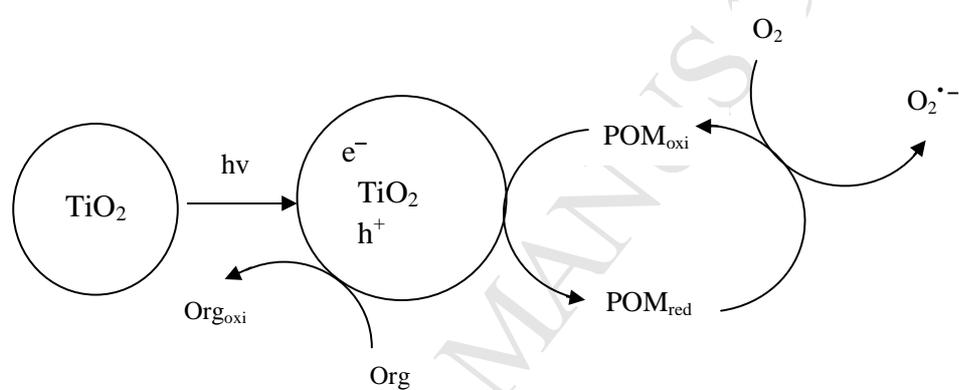


Fig. 6. Electron transfer in presence of POM