Comparative studies of mineralization and detoxification of Mordant Black 17 in aqueous solution by UV light induced \( M^{n+}/H_2O_2 \) and \( M^{n+}/S_2O_8^{2-} \) systems

Mihir Kumar Sahoo, John E. Kumar, Bhauk Sinha, Morten Marbaniang and Rajeshwar N. Sharan

**ABSTRACT**

The present study reports a process for simultaneous mineralization and detoxification of Mordant Black 17 with high electrical energy efficiency. Hydrogen peroxide and ammonium persulphate (APS) were used for the generation of hydroxyl and sulphate radicals using UV light (\( \lambda = 254 \text{ nm} \)) and Fe\(^{2+} \) and Ag\(^+ \) ions as catalysts. The detoxification and energy efficiency of various processes were measured by monitoring growth inhibition of *Escherichia coli* and Electrical Energy per Order (EE/O) applicable for low concentration contaminants respectively. Systems catalyzed by Fe\(^{2+} \) are more energy efficient and possess higher mineralization and detoxification efficiency than that of Ag\(^+ \). The concentration of the catalysts and oxidants were found to strongly influence the EE/O of the systems. The most cost efficient processes for simultaneous mineralization and detoxification are Fe\(^{2+} \)/APS/UV at pH 3.00 and Fe\(^{2+} \)/H\(_2\)O\(_2 \)/UV at pH 3.00 and 5.78. The upper limit concentration of Fe\(^{2+} \) is fixed at 0.01 mM for complete detoxification. The treated solutions start detoxifying at this concentration, above which they remain more toxic than the original dye solution irrespective of the extent of mineralization. On the contrary, no such limit could be established for Ag\(^+ \) systems for complete detoxification even after 91% mineralization.

**Key words** | detoxification, energy efficiency, mineralization, Mordant Black 17, photo-Fenton process

**LIST OF SYMBOLS**

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**INTRODUCTION**

Among various advanced oxidation processes (AOPs), the Fenton reaction (Fe\(^{2+} \)/H\(_2\)O\(_2 \)) is a popular technique among environmental chemists for treatment of wastewater containing organic pollutants. Hydroxyl radicals (HO\(^* \)) are
generated in this process as a result of catalytic decomposition of \( \text{H}_2\text{O}_2 \) by \( \text{Fe}^{2+} \) (Equation (1)) at pH between 2–4 \citep{Xie2016,Ertugay2017}. The other reactions taking place simultaneously in this process are shown in Equations (2)–(4) \citep{Ertugay2017,Liu2018}. It is known that \( \text{Fe} – \text{OOH}^{2+} \) exists in acidic medium and has strong absorption for UV light. \( \text{Co}^{2+} \) is also reported to decompose \( \text{H}_2\text{O}_2 \) in a Fenton-type reaction by providing a continuous source of HO* \citep{Yavuz2009,Ling2010}. However, the Fenton process usually encounters a passivation stage leading to low mineralization \citep{Kwan2007}.

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{HO}^* \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{H}_2\text{O} \\
\text{Fe} – \text{OOH}^{2+} & \rightarrow \text{Fe}^{2+} + \text{HO}^* \\
\text{Fe}^{3+} + \text{HO}_2^- & \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2
\end{align*}
\]

(1)

The other popular AOP involving \( \text{Fe}^{2+} \) for wastewater treatment is the Fenton-like reaction \( \left( \text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-} \right) \) (Equation (5)). Besides \( \text{Fe}^{2+}, \text{Co}^{2+} \) and \( \text{Ag}^+ \) have been used by different researchers for the generation of \( \text{SO}_4^{2-} \) \citep{Gemeay2007,Xu2010,Rasoulifard2012}. These AOPs utilize the oxidizing ability of hydroxyl and sulphate radicals with oxidation potentials between 2.65–2.80 V and 2.5–3.1 V respectively to mineralize the organic contaminants into carbon dioxide, water and inorganic anions \citep{Loaiza-Ambu2014,Monteagudo2015,Shah2015,Kattel2017}.

\[
\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{SO}_4^{2-}
\]

(5)

It is a known fact that the efficiency of the Fenton and Fenton-like processes can be significantly increased in the presence of UV light (photo-Fenton, \( \left( \text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV} \right) \) and photo-Fenton-like, \( \left( \text{Fe}^{2+}/\text{S}_2\text{O}_8^{2-}/\text{UV} \right) \) processes) \citep{Tamimi2008,Monteagudo2015,Kattel2017}. In the later process, the \( \text{Fe}^{3+} \) ion formed during the Fenton reaction (Equation (1)) is photo-reduced to \( \text{Fe}^{2+} \) (Equation (6)) and generates hydroxyl radicals \citep{Zepp1992}. The regenerated \( \text{Fe}^{2+} \) further participates in the Fenton reaction (Equation (1)) and completes a redox. Besides this, additional hydroxyl radicals are also generated from the photolysis of iron aquocomplex \( \text{Fe} – \text{OOH}^{2+} \) (Equation (7)) \citep{Brand1998} and the photolytic decomposition of \( \text{H}_2\text{O}_2 \) (Equation (8)) \citep{Baxendale1956}. Additional generation of sulphate radicals in the later process takes place by the photolysis of \( \text{S}_2\text{O}_8^{2-} \) (Equation (9)) \citep{Criquet2009}.

\[
\begin{align*}
\text{Fe}^{3+} + \text{H}_2\text{O} + \text{UV} & \rightarrow \text{Fe}^{2+} + \text{HO}^* + \text{H}^+ \\
\text{Fe} – \text{OOH}^{2+} + \text{UV} & \rightarrow \text{Fe}^{2+} + \text{HO}^* \\
\text{H}_2\text{O}_2 & \rightarrow 2\text{HO}^* \\
\text{S}_2\text{O}_8^{2-} + \text{UV}(<270 \text{ nm}) & \rightarrow 2\text{SO}_4^{2-}
\end{align*}
\]

(6) (7) (8) (9)

A study on the oxidation of carbamazepine by sulphate radicals shows that the generation of toxic intermediates was avoided by achieving 90% mineralization in 90 min \citep{Monteagudo2015}. The successful degradation of ace-sulfame in ultrapure water, groundwater, and secondary effluent by UV/\( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) and UV/\( \text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+} \) processes has demonstrated the possibility of using these methods as promising alternatives for wastewater treatment \citep{Kattel2017}. The efficiency of the photo-Fenton process in the removal of ibuprofen from water was reported recently by achieving 96% TOC removal in 8 hours \citep{Loaiza-Ambu2014}. The presence of peroxide or persulphate is reported to have an accelerating effect on the degradation of endosulfan by UV/\( \text{Fe}^{2+} \) process \citep{Shah2015}. Recently we have reported UV (\( \lambda = 254 \text{ nm} \)) mediated mineralization of Mordant Black 17 (MB 17), an azo dye, in the presence of \( \text{H}_2\text{O}_2 \) and APS as oxidants \citep{Shah2012}. Upon UV irradiation, these oxidants generate hydroxyl and sulphate radicals respectively, which act on the MB 17 molecules causing their mineralization. Mineralization was found to be highest at pH 1.00, yielding 87.0% and 92.6% mineralization for UV/\( \text{H}_2\text{O}_2 \) and UV/APS systems, respectively, at 120 min. Further, on increasing the UV intensity, more than 95% mineralization was achieved in the same time period. However, in spite of high mineralization, the treated solutions were toxic to the microorganism, \textit{Escherichia coli} \citep{Sahoo2012}. Similar results were also reported for mineralization of two other azo dyes, namely Ponceau S (3-hydroxy-4-(2-sulfo-4-[4-sulfophenylazo]-phenylazo)-2,7-naphthalenedisulfonic acid sodium salt) and Acid blue 29 \citep{Sahoo2012,Sahoo2013}. In all those studies, we have shown that the toxicity of the treated solutions was due to their high acidity. This toxicity in all those cases was eliminated by adjusting the pH of the mineralized solution to 7.00.

With an aim of finding a better process for the mineralization of MB 17, we have adopted another approach of AOP, which involves \( \text{H}_2\text{O}_2 \) and APS as oxidants and transition metal ions such as \( \text{Fe}^{2+}, \text{Ag}^+ \) and \( \text{Co}^{2+} \) as catalysts \citep{Sahoo2012}.
processes. All the processes yield maximum mineralization at pH 1.00 except Fenton’s (Fe²⁺/H₂O₂), where maximum mineralization was at pH 3.00. However, the treated solutions remained toxic, which inhibited E. coli growth even after adjusting the pH to 7.00. We believe that the sustained toxicity of the mineralized solution could be due to the presence of metal ions, as reported earlier (Sahoo et al. 2012c).

This led us to conclude that metal ion catalyzed AOPs are not environment friendly under the present experimental conditions. Thus, further research on simultaneous mineralization and detoxification of the treated solutions in the presence of metal ions posed a challenge before us.

Since the Fenton process shows some practical disadvantages, efforts are now focused on finding new practically-acceptable and economically-viable Fenton catalysts to generate HO• from H₂O₂ (Bokare & Choi 2014). For an efficient electron transfer to H₂O₂, the ideal Fenton catalyst should exhibit multiple oxidation states, as the catalytically-active species with a given oxidation state can be regenerated through a simple redox cycle from an inactive form. Although iron-catalyzed Fenton and Fenton-like reactions have been studied in detail, those catalyzed by Ag⁺ are scarcely found in literature, even though it has been suggested that it can activate H₂O₂ and APS to generate hydroxyl and sulphate radicals (Equations (10) and (11)) (Walling & Camaioni 1978; Anipsitakis & Dionysiou 2004a, 2004b; Rasoulifard et al. 2012).

\[
\text{Ag}^+ + \text{H}_2\text{O} \rightarrow \text{Ag}^{2+} + \text{HO}^* + \text{HO}^- \quad (10)
\]

\[
\text{Ag}^+ + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Ag}^{2+} + \text{SO}_4^{2-} + \text{SO}_4^{2-} \quad (11)
\]

The present work relates to the treatment of MB 17 aqueous solution by other AOPs employing metal ion catalysts, i.e. photo-Fenton (Fe²⁺/H₂O₂/UV) and photo-Fenton-like (Mⁿ⁺/oxidant/UV) processes, for generation of eco-friendly effluent having no adverse impact on the aquatic organisms. We have employed H₂O₂ and APS as oxidants, Fe²⁺ and Ag⁺ as metal ion catalysts, and UV light (λ = 254 nm) in this study. In other words, the present study aims to investigate the effect of UV light on the Fenton and Fenton-like processes. Instead of focusing on finding a new optimization of the reaction parameters now that UV is added, to start with we have taken the already optimized parameters (MB 17) = 0.05 mM; [oxidant] = 0.55 mM; [Mⁿ⁺] = 0.05 mM) from the previous research on Fenton and Fenton-like processes (Sahoo et al. 2012c) and investigate the effect of exposing UV to the mix. This is to enable us to find the extent of mineralization and toxicity in the treated solutions, so as to evolve a better comparison between these processes. Although the process involving Ag⁺ may well be considered for the goal of expanding the knowledge, it has some disadvantages associated with its cost and toxicity, which should be addressed by further research in the topic.

**MATERIALS AND METHODS**

**Reagents**

The azo dye, MB 17 (Synonyms: Eriochrome Blue Black R, Palantine Chrome Black 6BN; IUPAC name: 1-(2-Hydroxy-1-naphthylazo)-2-naphthol-4-sulfonic acid sodium salt; C. 1. Number: 15,705; molecular formula: C₂₀H₁₃N₂NaO₅S; Molecular weight: 416.38 (g mol⁻¹), used in this work was purchased from Sigma Aldrich (Germany). Its molecular structure is shown in Figure 1. Ferrous sulphate heptahydrate (FeSO₄.7H₂O, GR), silver nitrate (AgNO₃, GR), hydrogen peroxide (H₂O₂, 30% w/w, purified), sulphuric acid (H₂SO₄, GR), sodium hydroxide (NaOH, GR), and ammonium persulphate ((NH₄)₂S₂O₈, extra pure) were acquired from Merck (India). Luria Bertoni (LB) agar, LB broth and ampicillin used in the detoxification experiment were acquired from HiMedia (India). All the reagents were used without further purification.

**The photoreactor**

The experiments were performed in a multi lamp photoreactor (Haber Scientific, Chennai, India; Model: HML-Compact-LP-MP-812). 12 + 12 numbers of 8 W Mercury UV lamps of 254 nm and 365 nm wavelengths are permanently fixed inside the reaction chamber, which has a built-in, highly polished anodized aluminium reflector, so that the UV rays are focused at the centre where the samples are irradiated (Figure S1 in Supplementary Information, available with the online version of this paper). There is provision for using 2, 4, 6, 8, or 12 numbers of lamps, which can be employed in a combination of any two (Figure 2). A summary of the experimental conditions is given in Table 1. A fixed concentration of 0.05 mM MB 17 was used in all the experiments. The experiments were performed at an initial pH of 7.00. The samples were irradiated with UV light (λ = 254 nm) for a period of 180 min. The treated solutions, so as to evolve a better comparison between these processes. Although the process involving Ag⁺ may well be considered for the goal of expanding the knowledge, it has some disadvantages associated with its cost and toxicity, which should be addressed by further research in the topic.

**Figure 1** | Structure of Mordant Black 17.
lamps of either 254 or 365 nm at a time to vary the intensity of UV light. Four cooling fans are mounted at the bottom of the reaction chamber to minimize the heat generated inside it. The outer cover of the system has a specially designed vent for air circulation inside the system. The intensity of the UV light was measured with a UV light meter (Lutron, Taiwan; Model: UVC-254).

**Procedure**

Millipore water (Millipore India, Bangalore; Model: Elix3 Century) was used for preparing the solutions. Equal volumes of 0.05 mM dye solutions of the desired pH in different quartz reaction vessels were put in the multi lamp photoreactor. The initial pH of the solution was adjusted to the desired value with H₂SO₄ (0.05–0.2 N) or NaOH (0.025–0.1 N) using a digital pH meter (Chemiline; Model: CL 110). To the dye solution, 0.5 mL each of the metal ion and oxidant solutions of the desired concentration were added in sequence, keeping the total volume of the mixture in all cases constant at 100 mL. In this way, different concentrations of metal ions (0.05, 0.04, 0.03, 0.02, 0.01 and 0.005 mM) and oxidants (0.35, 0.70 and 1.40 mM) in the solution were obtained. All solutions used in this work were freshly prepared except the dye solution, which was stored at 4 °C and used for up to three days. The photoreactor, with the desired UV lamp intensity, was switched on for a predetermined time period immediately after the addition of the oxidants. Neither the pH nor temperature was controlled during the course of the experiments. The air stream was purged through the solution during addition of the reagents and the irradiation process using an air pump (Taiyo, India; Model: TI-5000; Air flow rate: 2.5 l min⁻¹). Samples from each reaction vessel, having one parameter different from each other, were analyzed for decolorization and total organic carbon (TOC).

Decolorization was monitored by recording the decrease in absorbance with time at 513 nm with the help of a UV-vis spectrophotometer (Perkin Elmer; Model: Lambda 25). Mineralization was monitored by measuring the TOC of the samples using a TOC analyzer (Elementar Analysensysteme GmbH, Model: Liqui TOC II). Analyses were done immediately after the reaction and the reproducibility in TOC measurement was checked by frequent measurement of the standards (1:1 solution of potassium phthalate and sodium carbonate as TOC and total inorganic carbon standard, respectively) as suggested by the manufacturer. The reported data are the average of three measurements and the error were always found to be within ±5%. The data presented in the text and figures were analyzed by standard deviation using ‘Origin 7’ (Microcal Inc.) and has been rounded up to significant values.

The cost effectiveness of a UV based AOP with low contaminant concentration is expressed as EE/O, which is defined as the electrical energy in kilowatt hours (kWh) required to remove a target constituent (TOC in this particular case) by an order of magnitude (or 90%) in 1 m³ of contaminated water (Bolton & Cater 1994; Bolton et al. 2001). Mathematically, it may be expressed as:

\[
\text{UV dose} = \text{EE/O log} \frac{\text{TOC}_0}{\text{TOC}_t}
\]

where the UV dose gives a measure of the total lamp electrical energy applied to a fixed volume of water. It is expressed as:

\[
\text{UV dose} = \frac{1000 \times \text{lamp power (kW)} \times \text{time (h)}}{\text{treated volume (L)}}
\]

The operating cost of TOC removal by one order in 1 m³ of effluent is given by:

\[
\text{Electrical cost} = \frac{\text{EE/O} \times \text{cost of 1 kWh}}{}
\]

Toxicity of the treated solutions was assessed by the method adopted by us and reported earlier (Sahoo et al. 2012a, 2012b, 2012c, 2013). Briefly, 40 g of LB agar dissolved in 1,000 mL of water was autoclaved for 30 min. Upon cooling down to about 40 °C, ampicillin (1 μL mL⁻¹ of LB agar solution) was added, mixed, and aliquots of approximately 10 mL of the medium was poured into sterile Petri plates to prepare LB agar plates. LB broth (25 g) was separately dissolved in 1,000 mL of water, aliquoted (9 mL) in 100 mL conical flasks and sterilized by autoclaving for 30 min. To the sterilized LB broth, 10 μL of ampicillin, 100 μL of the E. coli culture inocula and 1 mL of the dye or other test solutions were added, and the cultures were grown at 37 °C overnight in a rotary shaker. The following day, the mid-log phase culture was diluted 10,000 times and 10 μL of the diluted culture was spread over the LB agar plates prepared earlier. The plates were incubated for 24 h in a 37 °C incubator and the number of CFUs formed in each plate was counted. All the experiments were performed under sterile conditions.
RESULTS AND DISCUSSION

Effect of pH of the medium in different $\text{Mn}^{3+}$/oxidant/UV systems

It is well established that the generation of hydroxyl as well as sulphate radicals from $\text{H}_2\text{O}_2$ and APS respectively is influenced by the pH of the medium (Modirshahla et al. 2007; Hou et al. 2012). As described earlier, mineralization of MB 17 proceeds well at pH 1.00 in UV/oxidant systems and at pH 3.00 and 1.00 in Fenton and Fenton-like processes, respectively (Sahoo et al. 2012a, 2012b, 2012c, 2013). Since the present treatment protocol (photo-Fenton and photo-Fenton-like processes) is based on the combination of both the systems, i.e., UV/oxidant and Fenton/Fenton-like processes, the reactions were carried out at pH 3.00 by irradiating it with UV irradiation of intensity of 213 $\mu$W cm$^{-2}$. Treatment at pH 1.00 was ruled out as it does not provide a realistic option for large scale operations.

As treatment in the pH range of near neutral to alkaline media is a favorable option for wastewater treatment, pH 5.78 (the natural pH of the dye), was selected as the other pH for the treatment process. Experiments at higher pHs were ruled out as both processes, i.e. UV/oxidant and Fenton/Fenton-like processes ($\text{Mn}^{3+}$/oxidant) yielded low mineralization. The mineralization dependency on pH for all the systems at 240 min was found to be in the order: pH 3.00 > pH 5.78 and at both pH, the mineralization efficiency was in the order: Fe$^{2+}/\text{H}_2\text{O}_2$/UV > Fe$^{2+}$/APS/UV > Ag$^{+}$/APS/UV > Ag$^{+}$/H$\text{O}_2$/UV. The corresponding data given are presented in Figure 2. As more than 90% mineralization was achieved with Fe$^{2+}$ catalyzed systems, it is concluded that Fe$^{2+}$ is a better catalyst than Ag$^{+}$ for the activation of both $\text{H}_2\text{O}_2$ and APS under UV irradiation (Figure 2).

In addition, during this period complete decolorization was achieved at pH 3.00, and 5.78, in systems catalyzed by Fe$^{2+}$, and only at pH 3.00 when catalyzed by Ag$^{+}$ in the

Figure 2 | Effect of pH on the mineralization of MB 17: [MB 17] = 0.05 mM; [M$^{3+}$] = 0.05 mM; [oxidant] = 0.35 mM; UV intensity = 213 $\mu$W cm$^{-2}$. 

Downloaded from http://iwaponline.com/wst/article-pdf/77/12/2917/371913/wst077122917.pdf by guest
presence of APS. On the other hand, only nearly 60% decolorization is achieved when catalyzed by Ag⁺ at pH 5.78. It may be mentioned that the dye solution used in the present study is prepared from Millipore water. Textile industries use many alkaline substances (Khatmode & Thakare 2015) during the processing. It is, therefore, expected that the realistic pH of the textile effluent is more than the natural pH of the dye solution (pH = 5.78) used in the present study.

**Optimization of UV intensity for different Mⁿ⁺/oxidant/UV systems**

In the previous section, we have mentioned that more than 90% mineralization was achieved in 240 min in Fe²⁺/H₂O₂/UV and Fe²⁺/APS/UV systems with a UV light intensity of 213 μW cm⁻² (Figure 2). Hence, the intensity of UV light was varied with an aim of achieving maximum mineralization in the shortest treatment period. Our strategy was to increase the intensity of UV light and decrease the exposure period in such a way that ≥90% mineralization is achieved in the shortest treatment period and then to identify the intensity and exposure period for the lowest EE/O. As higher EE/O indicates that more energy is required to remove an order of magnitude of the target contaminant (in this case TOC) (Equation (14)), it is possible to identify the parameters with the highest electrical energy efficiency. The dependence of mineralization and EE/O in Fe²⁺ catalyzed systems on UV intensity and exposure period is presented in Table 1. It may be noted that irradiation for 120 and 150 min with a UV intensity of 453 μW cm⁻² yielded >90% mineralization (Table 1). Since irradiation lower than 120 min yields <90% mineralization, we have not shown the values in the table. As per our strategy, we reduced the irradiation period as we increased the intensity of UV light, while keeping in mind that mineralization is ≥90%. Thus, irradiation time for a particular dose may not be found at other doses. Consider the irradiation of a Fe²⁺/H₂O₂ system with UV light intensity of 1,755 μW cm⁻². Irradiation for 50 min gives 87% mineralization. To increase the mineralization, we did not irradiate for 60 min as 96.8% mineralization is already achieved in 60 min with a lower intensity of 1,417 μW cm⁻². We would like to emphasize here that Table 1 does not give a comparison among the systems. Rather, it is used to find the irradiation period and UV intensity for which EE/O is the lowest. It is also possible to identify the system having the lowest EE/O. A thorough study of the table reveals that treatment with UV intensity of 1,417 μW cm⁻² at pH 3.00 for both Fe²⁺/H₂O₂ and Fe²⁺/APS systems yielded comparable mineralization with the lowest EE/O – the values at 30 min and 60 min being ≈92% and ≈96%, respectively.

However, on the basis of EE/O, it is established that treating for 30 min is about 1.5 times more cost effective in terms of electrical energy consumption than treating for 60 min. Thus, Fe²⁺/H₂O₂ and Fe²⁺/APS systems are equally energy consuming with respect to mineralization if
UV light intensity of 1, 417 μW cm⁻² is exposed for 30 min at pH 3.00. On the other hand, treatment at pH 5.78 is preferable in the Fe²⁺/H₂O₂ system than in the Fe²⁺/APS system in terms of EE/O and treatment period. This is evident from the fact that the Fe²⁺/H₂O₂ system was about 1.9 times more cost effective than the Fe²⁺/APS system when UV light of 1, 064 μW cm⁻² intensity was used for 60 min in the former system and 1, 417 μW cm⁻² for 90 min in the latter system. Nevertheless, treatment at pH 5.00 proved to be less energy consuming than treatment at pH 5.78 in both the systems. This result was expected even without this analysis. The oxidation potential of HO⁺, which causes degradation of the dye, decreases with increasing pH. While this value is 2.80 V at pH 3.00, it becomes 1.90 V at pH 7.00 (Buxton et al. 1988). Thus, treatment at pH 3.00 is kinetically faster and therefore should be less energy consuming than treatment at pH 5.78.

As with Fe²⁺ systems, Ag⁺ catalyzed systems at pH 3.00, where they exhibit modest mineralization (Figure 2), were irradiated with UV light with different intensities for various durations. Although it was observed that >90% mineralization was achieved with all the intensities except 213 μW cm⁻², the lowest EE/O values were obtained when irradiated with 1, 755 μW cm⁻² light for 60 min irrespective of the nature of the oxidant. Nevertheless, Ag⁺ catalyzed processes were more than 5 times more electrical energy consuming processes than the most economical Fe²⁺ catalyzed processes. Apart from this aspect, being cheaper and more abundantly available than Ag⁺, Fe²⁺ is the preferred catalyst for the present study.

Effect of simultaneous variation of oxidant and metal ion concentration on mineralization, EE/O and toxicity of the treated solutions

Fe²⁺/oxidant/UV system

Since the toxicity of the treated solutions, as reported earlier, in Fenton and Fenton-like processes might be due to the presence of metal ions (Sahoo et al. 2012), further experiments were carried out at pH 3.00 and 5.78 for 60 min with reduced concentrations of Fe²⁺ (0.05 to 0.005 mM) and increased concentrations of H₂O₂ (0.35 to 1.4 mM) while keeping other parameters constant. It was ensured that mineralization remained ≥90% without adversely affecting the electrical energy efficiency, i.e., EE/O. The generation of hydroxyl radicals is expected to decrease at lower concentration of Fe²⁺ (Equation (1)) and increase at higher concentration of H₂O₂ (Equation (8)). Thus, at certain concentrations of both, there should be no impact on the generation of hydroxyl radicals and hence mineralization. We have not considered treatment for 30 min even though it showed the lowest EE/O value (Table 1), as less than 90% mineralization was achieved when the concentration of Fe²⁺ was below 0.04 mM (data not shown). UV light intensities corresponding to the treatment period, which gives lowest EE/O values at pH 3.00 (1, 417 μW cm⁻²) and 5.78 (1, 064 μW cm⁻²), as described in the previous section, were used in this part of the experiment. A similar procedure was adopted for the Fe²⁺/APS system, with the exception that light intensity of 1, 417 μW cm⁻² was used for 30 min and 90 min, respectively, at pH 3.00 and 5.78. This is in accordance with the lowest EE/O values obtained in the Fe²⁺/APS system as described in the previous section (Table 1). The results of mineralization and the corresponding EE/O values under these specific conditions are given in Figures 2 and 3. It may be noted that the mineralization pattern is as per our expectation, i.e., directly proportional to the concentration of Fe²⁺ and the oxidants (H₂O₂ and APS) (Figure 3).

One important observation that comes out here is that the EE/O values increased with decrease in Fe²⁺ concentration at a given concentration of oxidant and decreased with oxidant concentration at a given concentration of Fe²⁺, and the lowest EE/O values are obtained at the oxidant concentration of 1.4 mM (Figure 4). Thus, it may be concluded that the concentrations of Fe²⁺ and oxidant influence the electrical energy efficiency of the process. The resulting efficiency of various systems based on the EE/O values is in the order: Fe²⁺/APS/UV (pH 3.00) >Fe²⁺/H₂O₂/UV (pH 5.78) >Fe²⁺/H₂O₂/UV (pH 3.00) >Fe²⁺/APS/UV (pH 5.78). As shown above, higher concentration of Fe²⁺ helps to reduce the EE/O of the process, so it is worth trying at higher concentrations as it is possible to remove any precipitation downstream easily and cheaply. However, this was not investigated in our research. Nevertheless, the toxicity aspect of the treatment process should be considered while dealing with higher concentrations of Fe²⁺.

In order to evaluate the practical application of the processes, we also tested the toxicity of the products generated at pH 3.00 and 5.78 with various concentration of Fe²⁺ and oxidants by observing their influences on the viability and growth of E. coli. At both pH, the highest growth of E. coli is found at [Fe²⁺] = 0.005 mM and [oxidant] = 1.4 mM (Figure 5). However, the solutions still remained more toxic than the original dye solution, i.e. the number of CFU in the treated solutions were less than that in the untreated dye and control (the CFU for untreated dye solution and control were 172 and 217, respectively).
As reported earlier, this enhanced toxicity might be due to the presence of Fe$^{2+}$ in the treated solutions, which are acidic in nature (Sahoo et al. 2015). It may be noted that the pH of the solutions remained unaffected after treatment at either pH 3.00 or 5.78. In our effort to detoxify the treated solutions, we have again *E. coli* to grow after adjusting the pH to 7.00. The results were quite encouraging and we noticed that there was an increase in the number of CFU with a decrease in Fe$^{2+}$ concentration and increase in oxidant concentration. Further, at each of the oxidant concentrations, a sudden jump in CFU was observed when the concentration of Fe$^{2+}$ was lowered from 0.02 mM to 0.01 mM. At this stage, the CFU exceeded that of the untreated dye at [Fe$^{2+}$] = 0.01 mM and the data are represented graphically in Figure 5. Thus, the treated solution started to lose its toxicity when the Fe$^{2+}$ concentration reached 0.01 mM and complete detoxification was achieved at [Fe$^{2+}$] = 0.005 mM and [oxidant] = 1.4 mM (CFU becomes almost equal to that of the control). Therefore, the maximum concentration of Fe$^{2+}$ that can be used in photo-Fenton and photo-Fenton-like processes for simultaneous mineralization and detoxification of MB 17 solution is 0.01 mM. At higher concentrations, the solutions remained toxic even when the mineralization was above 96%. Thus, photo-Fenton and photo-Fenton-like processes catalyzed by Fe$^{2+}$ could be made environment friendly or environmentally benign by controlling the concentrations of Fe$^{2+}$ and oxidants. A comparison of the data presented in Figure 5 confirms that the most suitable process capable of simultaneous mineralization and detoxification with highest electrical energy efficiency is Fe$^{2+}$/APS/UV at pH 3.00.

![Figure 3](http://iwaponline.com/wst/article-pdf/77/12/2917/371913/wst077122917.pdf)

**Figure 3** | Effect of Fe$^{2+}$ and oxidant concentration on the mineralization of MB 17 by Fe$^{2+}$/oxidant/UV systems: [MB 17] = 0.05 mM; oxidant concentration: - , 0.35 mM; - , 0.70 mM; - , 1.4 mM. A: UV intensity = 1, 417 μW cm$^{-2}$, treatment period = 60 min; B: UV intensity = 1, 064 μW cm$^{-2}$, treatment period = 60 min; C: UV intensity = 1, 417 μW cm$^{-2}$, treatment period = 30 min; D: UV intensity = 1, 417 μW cm$^{-2}$, treatment period = 90 min.
Ag⁺/oxidant/UV system

In line with Fe²⁺, we have also tested Ag⁺ with H₂O₂ and APS, for their mineralization and detoxification efficiency. It is described under ‘Optimization of UV intensity for different Mn⁺/oxidant/UV systems’ that Ag⁺/H₂O₂/UV and Ag⁺/APS/UV systems are more energy consuming processes due to low mineralization in comparison to Fe²⁺ catalyzed processes under similar operational conditions. The concentration of Ag⁺ as well as those of H₂O₂ and APS were varied in line with Fe²⁺ catalyzed processes as discussed earlier in this section. Irradiation was done for 60 min with UV light intensity of 1, 755 μW cm⁻². It was observed that the number of CFU after treating the solutions with any concentration of Ag⁺, irrespective of the nature of the oxidant (maximum of 88 for both Ag⁺/H₂O₂ and Ag⁺/APS systems corresponding to Ag⁺ concentration of 0.005 mM and oxidant (H₂O₂ or APS) concentration of 1.4 mM), lies below that of the control (CFU at control being 217), i.e., the treated solutions remained more toxic than the pure dye solution. Further, to test the toxicity of the solutions, *E. coli* was grown after adjusting the pH to 7.00. We observed that the resulting number of CFU could not reach the level of the control even when the concentration of Ag⁺ and oxidants was 0.005 and 1.4 mM, respectively (Figure 6). Thus, Ag⁺ catalyzed processes with low energy efficiency are not suitable for treatment due to their inability to remove the toxic effect of the treated solutions. The standard reduction potential of reduction half cell (Fe³⁺|Fe²⁺), i.e. $E^\circ(\text{Fe}^3+/\text{Fe}^2+)$, is 0.771 V and that of (Ag²⁺|Ag⁺), i.e. $E^\circ(\text{Ag}^2+/\text{Ag}^+) = 1.980$ V. Thus, the oxidation of Fe²⁺ is easier than that of Ag⁺ and, therefore, it is expected that Fe²⁺-catalyzed photochemical oxidation will outperform Ag⁺-catalyzed photochemical oxidation both in terms of
kinetics and toxicity. Thus, our result is in line with the standard reduction potential of respective reduction half cells.

CONCLUSION

The present study was undertaken with an aim of making metal ion catalyzed AOPs eco-friendly with potential industrial application. For this purpose, we have selected photo-Fenton and photo-Fenton-like processes for mineralization of MB 17. One of the main objectives was to find suitable operational parameters to make the processes environmentally benign with high energy efficiency. It is established that the concentration of Fe$^{2+}$ is the key parameter for making the process environment friendly. The maximum concentration of Fe$^{2+}$ that is recommended for use in photo-Fenton and photo-Fenton-like processes for simultaneous mineralization and detoxification of MB 17 is 0.01 mM, above which the solution remains toxic even when the mineralization is near completion. Further, it is established that the electrical energy efficiency of the process varies directly as the concentrations of Fe$^{2+}$ and oxidants. Complete detoxification is possible when the concentration of Fe$^{2+}$ is maintained at 0.005 mM in the presence of 1.4 mM of either of the oxidants. Hence, it is of practical importance to fix the concentrations of Fe$^{2+}$ and oxidants to make the process environmentally benign and electrical energy efficient. The most suitable Fe$^{2+}$ catalyzed process capable of simultaneous mineralization and detoxification with the highest electrical energy efficiency is Fe$^{2+}$/APS/UV at pH 3.00. On the other hand, Ag$^+$ catalyzed processes are not suitable for treatment due to their low electrical

Figure 5 | Effect of Fe$^{2+}$ concentration on E. coli growth in MB 17 solution after treatment with Fe$^{2+}$/oxidant/UV system: [MB 17] = 0.05 mM; pH for E. coli growth = 7. Oxidant concentration: 0.35 mM, 0.70 mM, 1.4 mM. A: UV intensity = 1, 417 μW cm$^{-2}$, treatment period = 60 min; B: UV intensity = 1, 064 μW cm$^{-2}$, treatment period = 60 min; C: UV intensity = 1, 417 μW cm$^{-2}$, treatment period = 30 min; D: UV intensity = 1, 417 μW cm$^{-2}$, treatment period = 90 min.
energy efficiency and their inability to remove toxicity even when the mineralization is greater than 91% at the lowest concentration of Ag⁺, i.e. 0.005 mM. Another significant finding of this study is that the second most electrical energy efficient system, i.e. Fe²⁺/H₂O₂ at pH 5.78, can simultaneously mineralize and completely detoxify MB 17 solution. Treatment at the natural pH of the dye, i.e. pH 5.78, would further reduce the cost of treatment as no external chemical is required to adjust the pH before treatment.

The research was conducted to investigate the effect of UV on a system studied in multiple prior studies in greater detail. This research was, therefore, not focused on making the treatment process cost effective or to address toxicity considerations related to the use of Ag. While our intention is to keep the electrical energy usage under control, this parameter alone does not confer on the process the category of 'cost effective', where multiple other considerations are needed.

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