

UV-LEDs assisted peroxymonosulfate/ Fe^{2+} for oxidative removal of carmoisine: The effect of chloride ion

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(Received 29 January 2017 • accepted 25 April 2017)

Abstract—The performance of UVA-LEDs assisted peroxymonosulfate (PMS)/ Fe^{2+} system was evaluated on carmoisine (E122) decolorization. Complete color removal was obtained under the conditions of pH=3.0, PMS=1.5 mM, Fe^{2+} =1 mM and 25 min reaction time. UVA-LEDs were preferable compared to conventional UVA lamp in terms of decolorization. The functions of Co^{2+} , Cu^{2+} , Mn^{2+} and Fe^{2+} were compared and their results showed that Co^{2+} and Fe^{2+} had the highest efficiencies. Moreover, the presence of chloride ion showed a double role in different concentrations in which promotional effect was observed in 100 mM Cl^- , while inhibitory effect occurred in 1-10 mM Cl^- . However, the high concentration of chloride had no influence on mineralization of E122. The scavenging results demonstrated that the UV irradiation increased the contribution of HO^\bullet . In addition, in the presence of chloride ion, HOCl along with sulfate and hydroxyl radicals were the major oxidative agents.

Keywords: Food Dye, UVA-LEDs, Sulfate Radical, Peroxymonosulfate, Scavenging Effect

INTRODUCTION

Food additives play a critical role in the food industry. Food dyes have been used for different food products. They are added to replace colors lost during food processing or to make food look more attractive. Food dyes also are extensively used in other industries such as pharmaceutical, cosmetic and medicine [1,2]. Carmoisine (E122) is a common food dye widely used in Swiss rolls, jellies, breadcrumbs, yoghurts, oralene mouthwash, marzipan, and jams. It is classified in azo dye groups, which are suspected to be dangerous to humans. Azo dyes can be reduced in the body's organs to aromatic amine compounds which are often carcinogen. Moreover, carmoisine can affect biochemical markers in the liver and kidney [3]. Today, owing to wide application of azo dyes such as E122 in the world, water resources have been polluted by industrial effluent containing dyes. The presence of dyes in effluents induces the production of colored wastewaters whose biodegradation is difficult due to the toxicity of the dyes for microbes as the main agents of biodegradation [4,5]. In the recent decade, sulfate radical-based advanced oxidation processes (SR-AOPs) have received great attention for the degradation of organic pollutants in contaminated water. Sulfate radical is a strong oxidant ($E^0=2.5\text{--}3.1\text{ V}$) which is generated through the activation of peroxymonosulfate (HSO_5^-) and persulfate ($\text{S}_2\text{O}_8^{2-}$) anions [6,7]. The produced sulfate

radical is able to oxidize organic compounds to smaller compounds and minerals. Compared to HO^\bullet , sulfate radical has more half-life and therefore it has higher chance for reaction with organic compounds [8]. Additionally, the redox potential of sulfate radical is high in a wide range of pH, while the redox potential of HO^\bullet is decreased by increase of pH value ($E^0=2.8\text{ V}$ in pH=1.0 and $E^0=1.9\text{ V}$ in pH=7.0) [9]. Anipsitakis and Dionysiou [10] introduced peroxymonosulfate (PMS) as a new oxidant with high performance for degradation of organic pollutant. PMS is an asymmetrical molecular structure which can be activated by various methods, including transition metals, ultraviolet (UV) irradiation, ultrasound, carbon catalyst, and electrochemical method. PMS is decomposed to sulfate radical in the presence of transition metals based on Eq. (1) [11,12].



Although cobalt has exhibited the highest efficiency for PMS activation compared to other transition metals, its toxicity makes the reduction of cobalt application in PMS activation. Amongst transition metals, iron is a benign element which has no serious threat for human. Moreover, iron is the fourth element of earth's crust in terms of abundance [13,14]. Ferrous ion can catalyze PMS and produce sulfate radical and ferric ion according to Eq. (2). In following reactions, ferric ion can decompose PMS to produce $\text{SO}_5^{\cdot-}$ with less reactivity compared to sulfate radical (Eq. (3)). The regeneration of ferrous ion from ferric ion is slow [15,16].



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To accelerate regeneration of ferrous ion, the use of UV irradiation can be an effective strategy since produced ferric ion can be reduced to ferrous ion and increases the reactions of producing sulfate radical. In addition, during UV irradiation, hydroxyl radical can also be produced based on Eq. (4), enhancing the degradation of organic pollutant [17,18].



Light-emitting diodes (LEDs) have been widely employed for different applications. UV-LEDs produce light with narrow band emission wavelengths within the ultraviolet range. In this manner they are able to produce monochromatic light with narrow emission spectra. Hence, UV-LEDs are more efficient than common UV lamps since they transform less energy into heat and have long lifetime [19,20].

The study on application of UV-LEDs in AOPs has been rarely conducted. Moreover, UV-LEDs assisted PMS/Fe²⁺ system has not been investigated on the degradation of any pollutants so far. In addition, although the effect of chloride ion has been frequently investigated in AOPs, the amount of contributing chlorine species in degradation of pollutants has not been studied by quenching experiments. In this study, Fe²⁺/UV-LEDs/PMS process was used for the degradation of carmoisine in aqueous solutions. The effect of operational parameters was investigated on decolorization of carmoisine. Moreover, the performance of different transition metals was compared with iron. The presence of various concentration of chloride was evaluated on the performance of Fe²⁺/UV-LEDs/PMS process. The function of PMS was compared with that of other oxidants. Toxicity of treated effluents was also investigated. Finally, a scavenging experiment was conducted for the determination of different reactive agents.

MATERIALS AND METHODS

1. Chemical and Reagents

Carmoisine (E122) (C₂₀H₁₂N₂Na₂O₇S₂) (CAS No. 3567-69-9) was purchased from Alvan Sabet Company with purity of 99%. Oxone salt (KHSO₅·0.5KHSO₄·0.5K₂SO₄) and sodium percarbonate (2NaCO₃·3H₂O₂) were purchased from Sigma-Aldrich. Ferric sulfate (Fe₂(SO₄)₃) (Fisher Scientific Inc.) and ferrous sulfate (Fe₂SO₄)

(Merck Inc.), were used for homogeneous system. Sodium chloride (NaCl), sodium nitrate (NaNO₃), copper sulfate (CuSO₄·5H₂O), and sodium hydrogen phosphate (Na₂HPO₄) were purchased from ChemLab Company. Hydrogen peroxide (30%), sodium hydroxide, cobalt (II) sulfate heptahydrate (CoSO₄·7H₂O), manganese (II) sulfate monohydrate (MnSO₄·H₂O) and sulfuric acid were obtained from Merck Company. Sodium persulfate was purchased from Fluka Company. Sodium percarbonate was provided from Sigma-Aldrich.

2. Experimental Set Up

Photo-oxidation of carmoisine (E122) was in a Pyrex plate as reactor with the height of 3.2 cm and the diameter of 16.2 cm. The 20 mg/L E122 solution with the volume of 400 mL was added in the reactor. The initial concentration of the dye was constant in all experiments. The pH of the dye solution was adjusted by sulfuric and potassium hydroxide (0.02 N) and then a known concentration of Fe²⁺ was introduced to the dye solution; after that a certain amount of PMS was added to the dye solution. The solution was magnetically stirred during the degradation process. The temperature of solution was kept in range of 24-26 °C. 6 UVA-LEDs (1 watt, 300-305 nm) were used for light irradiation in which six UVA-LEDs were placed on the top of the reactor. The diameter of UVA-LED was 0.5 cm. All LEDs were installed on an electronic chip which was operated by a DC power (1,500 mA, 30.0 V). With turning on UVA-LEDs, the photo-oxidation process of E122 was started and sampling was conducted at preselected reaction intervals, and then dye concentration was measured immediately after sampling. The schematic setup of photo-oxidation is presented in Fig. 1. The UV light intensities were monitored with a radiometer (Lux-UV-IR meter, Leybold Didactic GMBH-666-230). The UV light intensities in the center of empty reactor were 2.52 and 2.65 mW/cm² for UVA lamp and UVA-LEDs, respectively.

3. Toxicity Experiment

Toxicity experiments involved measuring dissolved oxygen (DO) during time by a digital DO meter (DO meter, HACH) in activated sludge which came from aeration tank (municipal wastewater plant, Ahvaz) with mixed liquid suspended solids (MLSS) of 3,300 mg/L. For each treated effluent and dye solution, 400 mL of activated sludge was added to beaker (600 mL) and then 100 mL of the effluents within different reaction time was fed to the flask while aeration was conducted by an air pump. A magnetic stirrer was used for agitation of the mixture. OUR (oxygen uptake rate) was calculated by obtained slope from plotting DO versus time. Toxicity percent

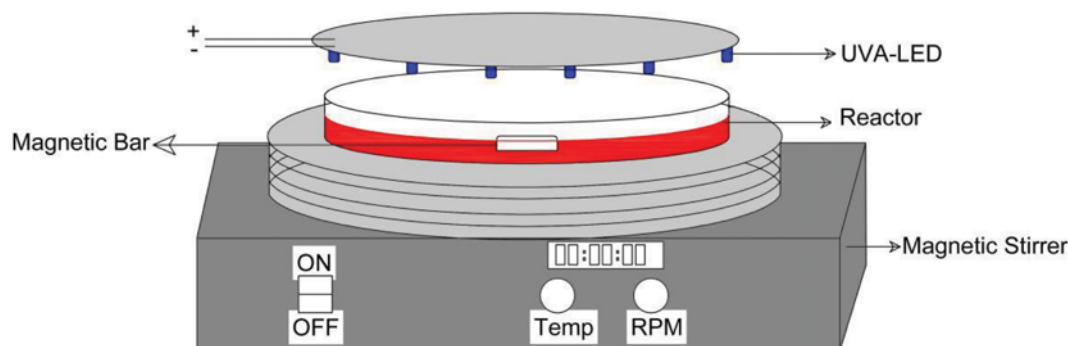


Fig. 1. The schematic set up of UVA-LEDs/Fe²⁺/PMS.

was achieved by comparing OUR values of a high biodegradable compound (acetic acid₁) with acetic acid being fed to a second time to the activated sludge that had been previously contacted with the sample (OUR_{Acetic Acid 2}) (Eq. (5)).

$$\text{Toxicity (\%)} = \frac{(\text{OUR}_{\text{Acetic acid 1}}) - (\text{OUR}_{\text{Acetic acid 2}})}{(\text{OUR}_{\text{Acetic acid 1}})} \times 100 \quad (5)$$

4. Analytical Method

Carmoisine concentration was measured by a spectrophotometer (DR6000, HACH) at the wavelength of 516 nm as absorbance the maximum of carmoisine in visible region. The total organic carbon (TOC) of the solution was measured by TOC ampules in low range (Merck). PMS was measured by iodometric titration method [21].

RESULTS AND DISCUSSION

1. The Effect of Solution pH, Ferrous and PMS Dosage

In chemical oxidation, especially in homogeneous systems, solu-

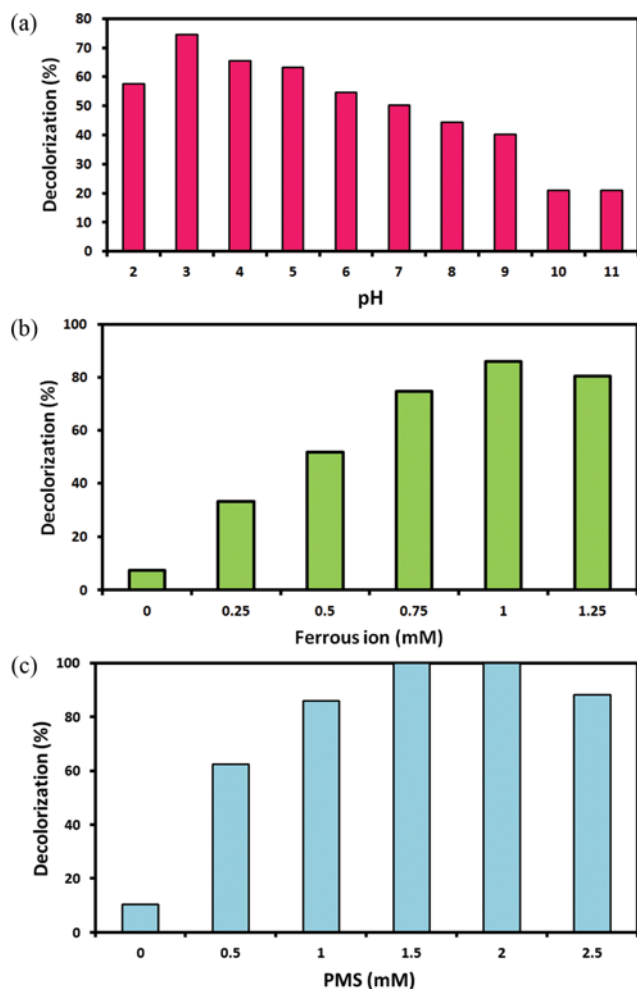


Fig. 2. (a) the effect of pH on decolorization of E122 (PMS=1 mM, Fe²⁺=0.75 mM, time=25 min) (b) the effect of Fe²⁺ dosage on decolorization of E122 (PMS=1 mM, pH=3.0, time=25 min) (c) the effect of PMS dosage on decolorization of E122 (Fe²⁺=1 mM, pH=3.0, time=25 min).

tion pH plays a vital role in the determining species of transition metals. In this way, the effect of pH was evaluated in the range of 2-11 under the condition of PMS=1.0 mM and ferrous ion of 0.75 mM, and their results are presented in Fig. 2(a). With the increase of pH, decolorization was significantly reduced. This phenomenon is related to two reasons. First, iron complexes were produced in pH value more than 4.0 in which the catalytic activity of iron was reduced in forms of oxyhydroxide [16]. Second, PMS is decomposed to SO₅²⁻ in pH>9.0 in which its pK_{a2} is equal to 9.4 [22]. Indeed, the non-radical decomposition of PMS reduced decolorization efficiency. Although UV regenerates ferrous ion and increases the generation of hydroxyl radical, PMS decomposition in non-radical pathway at alkaline condition was the dominant phenomenon, which reduced efficiency. One can see that a pH of 3.0 was the best condition for the decolorization of E122 with 74.6% efficiency. At strong acidic condition (pH=2.0), a slight reduction was observed. This reduction can be interpreted as the iron species of (Fe(II)(H₂O)₆) produced at acidic pH had less tendency to the reaction with PMS [23]. Moreover, excessive protons could consequently scavenge sulfate radical (Eq. (6)) and reduce decolorization efficiency [6,24]. To adjust pH in large scale, mixing acidic waste with colored wastewater is a low cost method for operation of the process in acidic condition. However, the application of heterogeneous catalysts improves the system for operating the system at near neutral conditions.



The effect of ferrous ion dosage in the range of 0-1.25 mM was investigated under the condition of pH=3.0 and PMS of 1 mM. Fig. 2(b) depicts the decolorization of E122 in different Fe²⁺ concentration. With the addition of only 0.25 mM ferrous ion, decolorization was boosted from 7.5 to 33.2%. With increase in ferrous ion dosage enhanced removal efficiency significantly and reached 85.9% at 1 mM Fe²⁺ concentration. It is clear that the higher the ferrous ion is, the more sulfate radical can be produced based on Eq. (2). Hence, high decolorization was obtained in higher ferrous ion concentration. However, a reduction in efficiency was seen in the higher concentration of 1 mM in which decolorization declined to 80.3%. Scavenging effect has been reported in the literature for excess Fe²⁺ in which it can reduce the amount of sulfate radical based on Eq. (7) [25,26]. This behavior has been often observed in Fenton-based process [27].



The effect of PMS concentrations in the range of 0-2.5 mM was assessed in optimized previous condition (pH=3.0 and Fe²⁺=1 mM), and the results are shown in Fig. 2(c). In the absence of PMS as oxidant, decolorization was negligible while with increase of PMS dosage, decolorization was considerably enhanced in a way that complete decolorization was obtained in 1.5 mM PMS. It is clear that PMS is the main agent of generating the free radicals; therefore, the increase of PMS dosage resulted in more production of free radicals. The decolorization efficiencies were 100 and 88.1% in 2 and 2.5 mM PMS. In 2 mM PMS, decolorization efficiency was not changed compared to 1.5 mM PMS while decolorization was retarded in 2.5 mM PMS, indicating that PMS had a negative

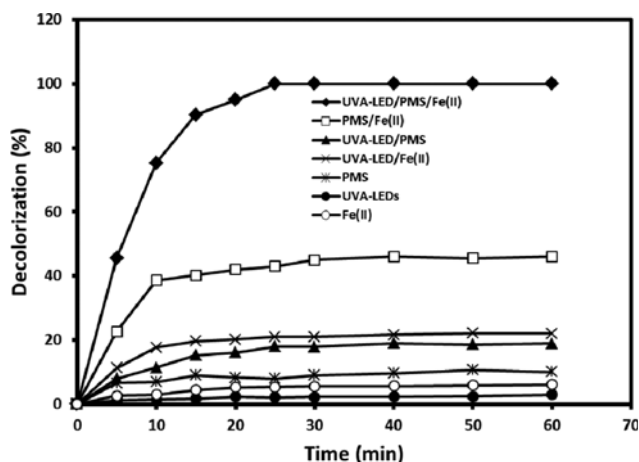


Fig. 3. The comparison of different processes for decolorization of E122 (PMS=1.5 mM, pH=3.0 and Fe²⁺=1 mM).

impact in excess concentration. In this way, unreacted PMS can play in a scavenger role to quench sulfate radical according to Eq. (8). Hence, decolorization reduced since peroxymonosulfate radical (SO₅^{•−}) produced was not able to oxidize organic compounds due to lower redox potential (E⁰=1.1 V) [28,29]. Moreover, PMS may react with ferric ion to regenerate ferrous ion based on Eq. (3) and produce SO₅^{•−}. In case of large scale, open channel UV systems (unpressured) and pressurized reactors are applied for actual wastewater in which UV lamps are submerged in the wastewater to provide enough UV intensity for regeneration of Fe²⁺.



2. Comparative Studies

The performance of different processes in decolorization of E122 was compared to illustrate effective combination of Fe²⁺, UV-LEDs and PMS (Fig. 3). One can see that the sole applications of PMS, UV-LEDs and Fe²⁺ was not effective in the decolorization of E122 since each one cannot produce free radical alone. On the other hand, binary systems of UVA-LEDs/PMS and UVA-LEDs/Fe²⁺ showed a slight decolorization, showing that PMS was not activated in the presence of UVA-LEDs, which these results were in agreement with other studies. PMS/Fe²⁺ system decolorized 45% of E122 during 30 min reaction time. In this system, decolorization rate was fast in first 10 min, which was related to the rapid reaction of PMS with ferrous ion; after that the decolorization rate was gradually increased up to 30 min, and after that reached steady state. The slow regeneration of ferrous ion and low availability of ferrous ion can be the rational reasons for this behavior of the PMS/Fe²⁺ system. Whereas, UVA-LEDs/PMS/Fe²⁺ displayed high efficiency in the degradation of E122. The synergistic effects of the simultaneous presence of UVA-LED, Fe²⁺ and PMS were obvious in which complete decolorization was achieved in only 25 min reaction time. Hence, the obtained optimum conditions were pH=3.0, Fe²⁺=1 mM and PMS=1.5 mM and 25 min reaction time which under this condition complete decolorization took place. Although hybrid processes increase operating cost, high efficiency and synergistic effect justify the application of such process for degradation of organic pollution at short reaction time.

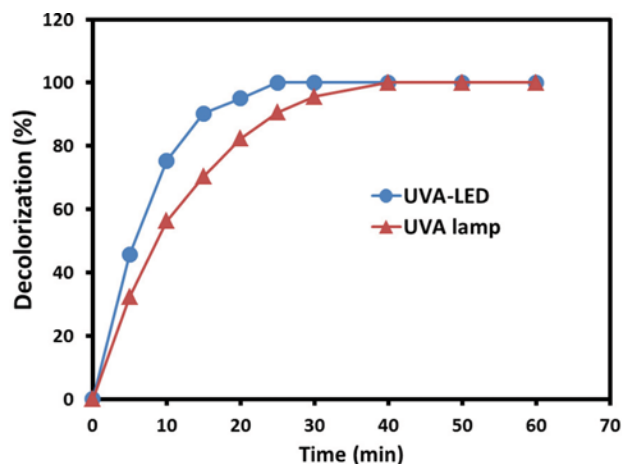


Fig. 4. Comparative performance of UVA-LEDs and UVA in presence of PMS/Fe²⁺ (PMS=1.5 mM, pH=3.0 and Fe²⁺=1 mM).

3. Comparison to Conventional UVA Lamp

To compare the performance of conventional UVA lamp with UVA-LEDs, a series experiment was conducted by a UVA lamp (6 watt) as UVA/PMS/Fe²⁺ under similar conditions. Fig. 4 shows that a shorter time is needed for the complete decolorization of E122 in UVA-LEDs/PMS/Fe²⁺ compared to UVA/PMS/Fe²⁺ system. Indeed, UVA/PMS/Fe²⁺ process provided complete decolorization in 40 min reaction compared to 25 min reaction time for UVA-LEDs/PMS/Fe²⁺. First-order kinetics was fitted for both systems based on Eq. (9).

$$-\ln \frac{C}{C_0} = kt \quad (9)$$

where C is dye concentration in reaction time (mg/L), C₀ is initial dye concentration (mg/L), k is rate constant (min^{−1}) and t is reaction time (min). According to the obtained results from Eq. (9), the rate constants were 0.1553 and 0.0928 min^{−1} for UVA-LEDs/PMS/Fe²⁺ and UVA/PMS/Fe²⁺ systems, respectively. In fact, the rate constant of UVA-LEDs/PMS/Fe²⁺ was 1.7-times more than that of UVA/PMS/Fe²⁺. This result illustrates that UVA-LEDs accelerated the regeneration of ferrous ion compared to UVA lamp. In addition, the energy consumption for complete decolorization of E122 was 6.25 and 10.0 Wh/L for UVA-LEDs/PMS/Fe²⁺ and UVA/PMS/Fe²⁺ systems, respectively. These results show that UVA-LEDs are also cost beneficial compared to conventional UVA.

4. Compare to Other Transition Metals

The performance of other transition metals (Co²⁺, Cu²⁺ and Mn²⁺) was compared with ferrous ions. Fig. 5 displays the decolorization of E122 in various conditions. Fe²⁺ and Co²⁺ had a similar trend for the decolorization of E122. In case of Cu²⁺, decolorization was lower than Co²⁺ and Fe²⁺ system; this behavior can be due to slow regeneration of Cu²⁺/Cu⁺ since the standard reduction potentials of Cu²⁺/Cu⁺ is 0.16 V, which is unfavorable compared to Fe³⁺/Fe²⁺ (0.77 V) and Co³⁺/Co²⁺ (1.82 V) [30]. On the other hand, the efficiency of Mn²⁺/PMS/UVA-LEDs system was lower than other ones. Mn²⁺ may react with PMS and produce permanganate ion (MnO₄[−]). In fact, non-radical pathway may be preferable to sulfate radical production (Eq. (10)). In addition, the produced Mn³⁺ from the main

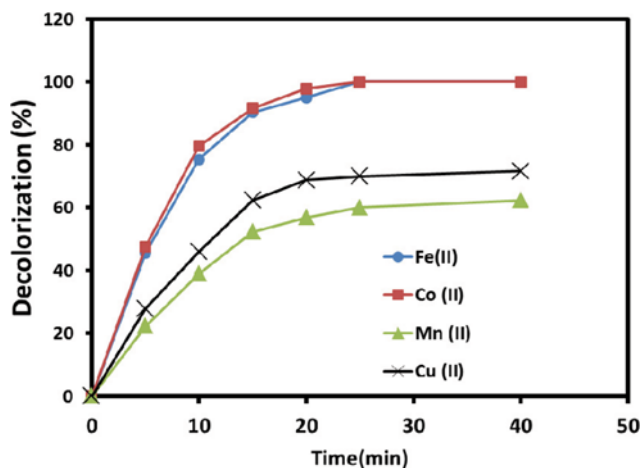
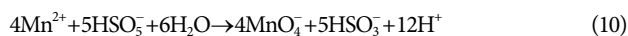


Fig. 5. The effect of various transition metals on decolorization of E122 (PMS=1.5 mM, pH=3.0 and transition metal=1 mM).

reaction with PMS (Eq. (1)) can precipitate in the form of oxide (MnO_2) and it consequently reduced catalytic activity (Eq. (11)) [11].



The performance of transition metals was in order $\text{Co}^{2+} > \text{Fe}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+}$. As above-mentioned, ferrous ion is superior compared to Co^{2+} thanks to the non-toxic character. In homogeneous systems, catalysts remain in the solution in forms of solids (sludge) and are soluble. To solve this problem, two strategies can be considered. First, the recycling of the sludge to the reactor for reuse of the catalyst [31,32]; second, the immobilizing of transition metals on various supports [6].

5. Comparison of Various Oxidants

The performance of persulfate (PS) and H_2O_2 in UVA-LEDs/ Fe^{2+} system was compared to PMS. Fig. 6 shows the decolorization of E122 in three systems at the same conditions. As illustrated in Fig. 6, PS behavior for the decolorization of E122 was similar to PMS. Both oxidants can provide complete decolorization within 25 min

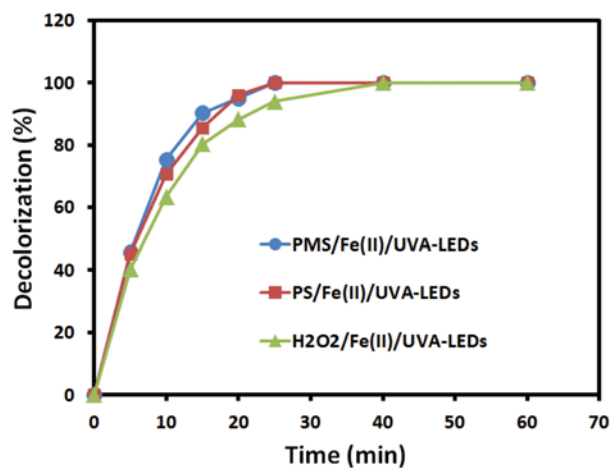


Fig. 6. The comparison of various oxidants in UVA-LEDs/ Fe^{2+} system (PMS=1.5 mM, pH=3.0 and transition metal=1 mM).

reaction, while in case of H_2O_2 , 40 min reaction time was required for 100% decolorization. The successful functions of sulfate-based oxidant (PMS and PS) compared to H_2O_2 can be attributed to the performance of produced sulfate radical from PS and PMS compared to hydroxyl radical produced from H_2O_2 . The rate constants of H_2O_2 /UVA-LEDs/ Fe^{2+} , PS/UVA-LEDs/ Fe^{2+} and PMS/UVA-LEDs/ Fe^{2+} systems were 0.1117, 0.1542, 0.1554 min^{-1} , respectively. In this way, sulfate radical is more selective than hydroxyl radical in attack on organic compounds [33,34]. There is a hypothesis that the tendency of E122 is high for the reaction with sulfate radical compared to hydroxyl radical. On the other hand, as previously mentioned, the redox potential of sulfate radical was more than that of hydroxyl radical.

6. The Effect of Chloride Ion

The chloride ion is one of the most dominant components of ground waters and surface waters. It can be stated that chloride exists in all natural waters. Moreover, chloride ion can affect chemical oxidation processes. The effect of chloride ion concentration was investigated in the range of 1-500 mM. Chloride ion is known as a common scavenger of free radicals. Fig. 7(a) presents the effect of various chloride ions concentration on the decolorization of E122. As illustrated, an inhibitory effect was observed in

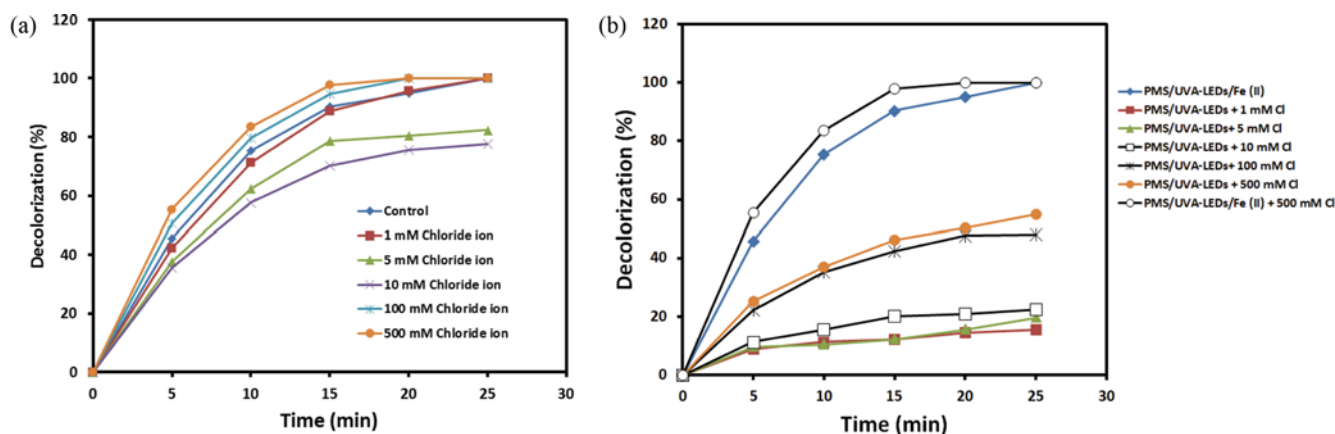
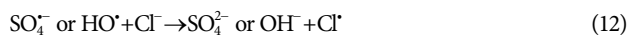
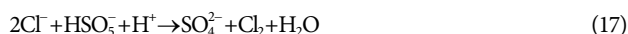
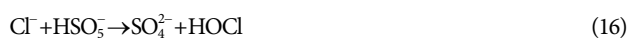


Fig. 7. (a) The effect of chloride ion in PMS/UVA-LEDs/ Fe^{2+} (b) the effect of chloride ion in PMS/UVA-LEDs.

the presence of chloride ion in concentrations of 1-10 mM in a way that with increase of Cl⁻, inhibitory effect was increased, which in turn decolorization rate subsequently reduced. This reduction can be attributed to the scavenging effect of chloride ion for sulfate or hydroxyl radicals based on the following equations. In this way, Cl₂ produced has low reactivity ($E^0=1.36$ V) compared to free radicals [35-37].



Moreover, chloride ion can directly react with PMS and prevent the production of sulfate radical [22].



However, with increase of chloride ion to 100 mM, decolorization was slightly enhanced compared to when no chloride was added. Moreover, higher chloride ion increased decolorization rate significantly. Two reasons can describe this phenomenon: first, degradation of E122 by the high concentration of HOCl which was reported by Lou et al. [38]. Second, hydroxyl radical can be produced via the reaction of HOCl with ferrous ion based on Eq. (18) [39,40]. As a remarkable result, chloride ion had a bilateral role in sulfate radical-based oxidation in which inhibitory and promotional effects occurred in the low (<100 mM) and high concentration (>100 mM) of chloride, respectively.



To confirm this issue, a series experiments were conducted without ferrous ion and the results are presented in Fig. 7(b). In the presence of 1-10 mM chloride ion in PMS/UVA-LEDs system, a slight decolorization (22%) occurred during 25 min reaction time. This result indicated that the amount of chlorine species was insufficient for the destruction of E122. On the other hand, in the condition of 100 and 500 mM chloride, decolorization was dramatically enhanced to 48 and 55%, respectively, indicating that high concentration chloride produced HOCl as oxidative agent. With addition of ferrous ion (PMS/UVA-LEDs/Fe²⁺+500 mM Cl⁻), as previously mentioned, decolorization was significantly increased. These results showed that generation of free radical depended on ferrous ion for the catalyzing of PMS or HOCl.

7. Mineralization Degree and Toxicity Evaluation

The mineralization of E122 was evaluated by TOC removal efficiency in three processes under the same conditions (pH=3.0, PMS=1.5 mM, Fe²⁺=1 mM and 60 min reaction time), and the results are indicated in Fig. 8(a). In the absence of UV irradiation (PMS/Fe²⁺), TOC removal was 30.8% while 58.9 and 57.3% of TOC were removed in PMS/UVA-LEDs/Fe²⁺ and PMS/UVA-LEDs/Fe²⁺/500 mM Cl⁻ systems, respectively. Regarding the results, the presence of high concentration of chloride ion had a negligible effect on mineralization. Although the high concentration of chloride improved decolorization efficiency, no change was observed

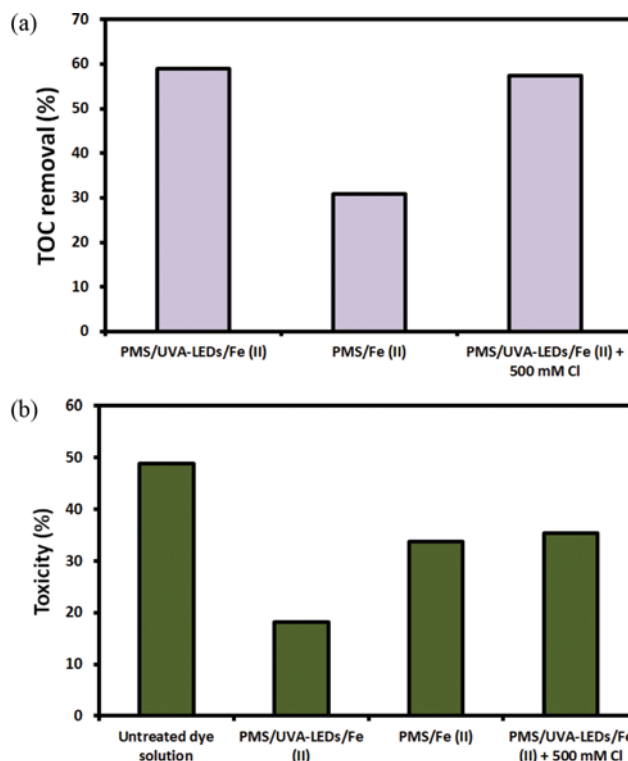


Fig. 8. (a) Mineralization degree in different processes (b) toxicity in different effluents (pH=3.0, PMS=1.5 mM, Fe²⁺=1 mM and 60 min reaction time).

in mineralization degree. In AOPs, the possible of production of halogenated organic compounds increased in the presence of active chlorine species, which may be more dangerous and toxic than mother molecule. Hence the application of this system in water containing chloride ion faces scientists with a great challenge, generating chlorinated organic compounds [41,42].

In this way, toxicity of the dye solution and different treated effluents was evaluated by respirometry experiments and their results are presented in Fig. 8(b). As can be seen, toxicity was significantly decreased after treatment by PMS/UVA-LEDs/Fe²⁺ while PMS/Fe²⁺ could not effectively detoxify dye solution. On the other hand, although PMS/UVA-LEDs/Fe²⁺/500 mM Cl⁻ was effective in the removals of dye and TOC, it was unsuccessful in detoxification of dye solution. These results indicate that chlorinated organic compounds might be formed during the oxidation of dye in the presence of chloride in which these compounds were more toxic compared to non-chlorine aromatic compounds.



8. Scavenging Test

A chemical probe was used to identify the oxidative agent of organic compounds in AOPs. Accordingly, three processes were evaluated by different chemical probes. In this way, benzoic acid (BA) is a strong scavenger for hydroxyl radical ($k=4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and sulfate radical ($k=1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). On the other hand, *tert*-butyl alcohol (TBA) is a particular scavenger for HO[·] ($k=3.8-7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), while its rate constant for reaction with SO₄^{·-} ($k=4-9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$)

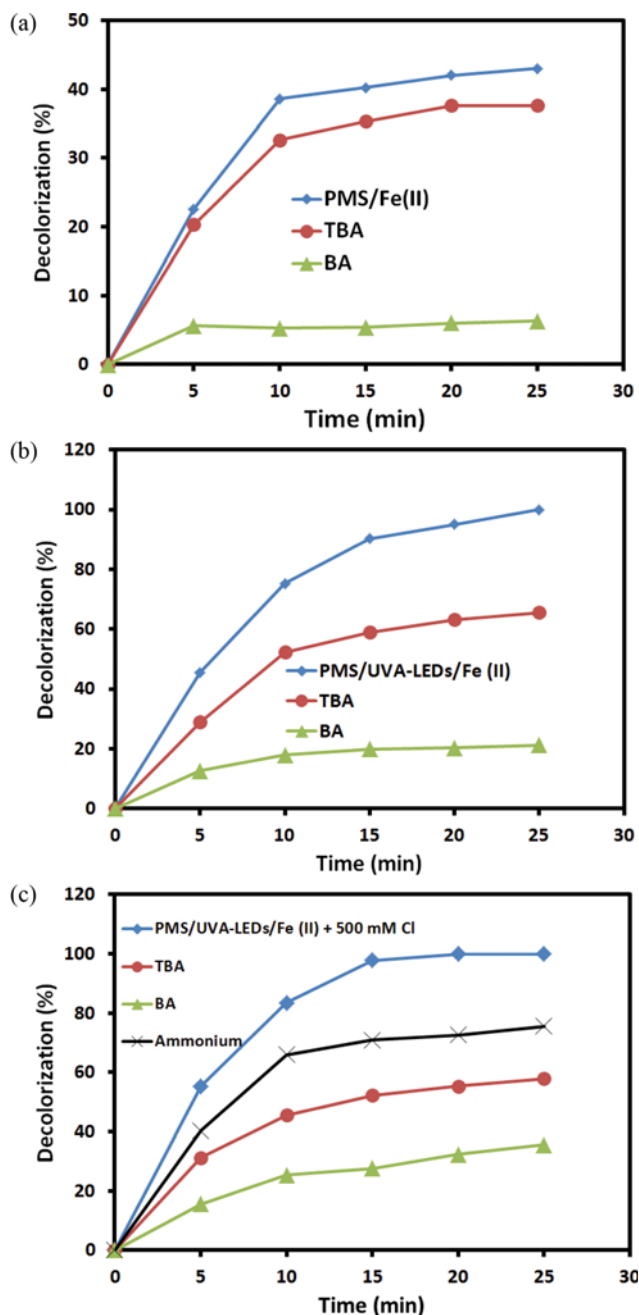


Fig. 9. The effect of chemical probes (TBA=BA=NH₄⁺=30 mM) (a) PMS/Fe²⁺ system (b) PMS/UVA-LEDs/Fe²⁺ system (c) PMS/UVA-LEDs/Fe²⁺/500 mM Cl⁻ (condition: pH=3.0, PMS=1.5 mM, Fe²⁺=1 mM).

is 1,000-2,000 times lower compared to hydroxyl radical [6,43,44]. Based on this theory, two scavengers (BA (7:1 in ethanol) and TBA with concentration of 30 mM) were added to the solution in PMS/Fe²⁺ and PMS/UVA-LEDs/Fe²⁺ systems, and their results are presented in Figs. 9(a) and 9(b), respectively. As shown in Fig. 9(a), in the presence of BA in PMS/Fe²⁺ system, decolorization was significantly reduced, indicating that free radicals were mainly responsible for E122 degradation. However, TBA had a slight effect on decolorization of E122 in which 37% and 43% decolorization was

obtained in the presence and absence of TBA, respectively. These outcomes confirmed that sulfate radical was the major agent of oxidative removal of E122.

As illustrated in Fig. 9(b), similar to PMS/Fe²⁺ system, BA had a strong inhibitory effect on decolorization efficiency in PMS/UVA-LEDs/Fe²⁺ system. However, in the presence of TBA decolorization was reduced to 65.6% compared to 100% decolorization in control condition. Indeed, TBA showed more inhibitory effect in PMS/UVA-LEDs/Fe²⁺ system in comparison with PMS/Fe²⁺ system. This result implies that HO• also contributed to E122 decolorization. In fact, UV irradiation generated hydroxyl radical through Eq. (4). Moreover, sulfate radical can be converted to hydroxyl radical in water solution according to Eq. (20) [45]. Hence, both hydroxyl and sulfate radicals were mainly responsible in the degradation of E122.



In case of PMS/UVA-LEDs/Fe²⁺/Cl⁻ system (Fig. 9(c)), a different trend was observed, which was related to the high inhibitory of TBA, indicating that there was more production of hydroxyl radical. This behavior might be due to the generation of hydroxyl radical based on Eq. (18). In other words, the presence of chloride ion boosted HO• contribution in the degradation of organic pollutant. To identify contribution of HOCl in E122 degradation, 30 mM NH₄⁺ was added to the solution to quench HOCl and the formation of chloramine with low reactivity. As can be seen, ammonium decreased decolorization efficiency indicating that HOCl was also one of the oxidative agents of E122 decolorization. Since, in the presence of BA, decolorization was considerably decreased, it can be stated that sulfate and hydroxyl radicals contributed in degradation mechanism. Actually, E122 degradation corresponded to three oxidative agents of HOCl, SO₄^{•-} and HO• in PMS/UVA-LEDs/Fe²⁺/Cl⁻ system. Moreover, it can be concluded that the presence of UV and chloride increased generating hydroxyl radical in of PMS/Fe²⁺ system.

CONCLUSION

UVA-LEDs assisted PMS/Fe(II) was used for the decolorization of a food dye (E122). PMS/UVA-LEDs/Fe²⁺ system showed that acidic condition (pH=3.0) could provide the best condition for decolorization. Moreover, the higher dosages of PMS and ferrous ion showed a scavenging effect. Compared to H₂O₂, PMS and PS demonstrated better functions, which was attributed to the production of sulfate radical in sulfate-based oxidants. To compare with copper and manganese, Co²⁺ and Fe²⁺ showed higher performance in the decolorization of E122. Chloride ion showed a mutual role in PMS/UVA-LEDs/Fe²⁺ system in which its low and high concentration had inhibitory and promotional effects on E122 decolorization. Scavenging experiments showed that UV irradiation increased hydroxyl radical contribution in the degradation of E122. In the presence of chloride in PMS/UVA-LEDs/Fe²⁺ system, HOCl and free radicals (sulfate and hydroxyl radicals) were the oxidative agents in E122 degradation. Finally, photo-oxidation process indicated which can be an efficient and promising technology to treat colored wastewater.

ACKNOWLEDGEMENT

This research was financially supported by the Student Research Committee, Ahvaz Jundishapur University of Medical Sciences under grant No. 95s.81.

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