

Photo-electro-oxidation assisted peroxymonosulfate for decolorization of acid brown 14 from aqueous solution

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Abstract—We investigated the simultaneous application of peroxymonosulfate (PMS) and electrogenerated H₂O₂ in presence of ultra violet (UV) to decolorize Acid Brown 14 (AB14). The effects of various operating parameters were evaluated on performance of the hybrid system for decolorization and degradation of AB14. The results showed that the optimal conditions were at UV light intensity of 2.08 mW/cm², pH=4, 200 mA applied current and 3 mM PMS. Moreover, presence of transitional metals (Co²⁺, Fe²⁺ and Cu²⁺) increased decolorization of AB14 significantly. Decolorization was promoted from 80.9% to 97% by addition of Fe²⁺ within 20 min reaction time. First-order model was fitted for this system in absence and presence of Fe²⁺ with rate constants of 1.937×10⁻³ and 3.595×10⁻³ s⁻¹ respectively. Scavenging experiments confirmed that sulfate and hydroxyl radicals were equally effective in degradation of AB14. This hybrid process increased the average oxidation state (AOS) from 0.2 to 2.3.

Keywords: Peroxymonosulfate, Photo-electro-oxidation, Sulfate Radical, Dye, Average Oxidation State

INTRODUCTION

Synthetic dyes are organic compounds that, due to their complex aromatic molecular structure, are resistant to aerobic biodegradation. Dyes are broadly applied in many factories and industries such as dyestuffs, textile, plastic and paper [1,2].

Azo dyes are categorized in a large class of dyes that is characterized by azo functional groups [-N=N-] linking the chromophore and auxochrome to form colored molecules. These dyes are toxic and even carcinogenic provided they are degraded to amines compounds [3,4]. Hence, it is an important environmental challenge to eliminate them from polluted water. Chemical oxidation is effective for degradation and mineralization of azo dyes. In recent decades, the use of advanced oxidation processes (AOPs) has significantly increased. Many AOPs have been used to improve biodegradability of persistent organic pollutants in wastewater treatment [5,6]. These processes are based on production of hydroxyl radical (HO[•]), which is the main agent in pollutant degradation. The hydroxyl radical with E⁰=2.8 (V/NHE) is a powerful, non-selective and highly reactive oxidant that can oxidize organic compounds to mineral matters [7,8]. For the efficient production of HO[•], there are various techniques involving a combination of chemical, electrochemical, photochemical and sonochemical reactions. The use of H₂O₂ as a green chemical agent for HO[•] production is a simple and environmental friendly method that in presence of transitional metals

and ultraviolet (UV) radiation, decomposes to HO[•] (Eq. (1)) [8,9].



As an alternative, hydrogen peroxide (H₂O₂) can be electrochemically produced through continual reduction of oxygen molecule (O₂) (Eq. (2)) at cathode [10]. In-situ electrogeneration of H₂O₂ is safer than using its chemical form. Actually, it is due to the limitations in storage and shipment of concentrated H₂O₂ [11,12]. Moreover, electrogeneration of H₂O₂ brings about better control of hydroxyl radical production especially when UV is used [13].



In recent years, processes based on production of sulfate radical have been widely developed. The sulfate radical (SO₄^{•-}) with high standard redox potential (2.5-3.1 V/NHE) is an alternative oxidizing agent for destruction of organic compounds [14,15]. The sulfate radicals can be produced by decomposition of persulfate or peroxymonosulfate (PMS) in presence of activators such as transitional metals, heat and ultraviolet radiation. Use of ultraviolet radiation for the purpose of peroxide activation is benign and economic. Peroxymonosulfate (HSO₅⁻) is an unsymmetrical peroxide which can be decomposed to SO₄^{•-} and HO[•] under UV radiation based on Eq. (3) [16].



Several investigations have been carried out on dye removal based on photo-electrogenerated H₂O₂ [17,18] and UV/PMS [15,19] separately; whereas the combination of photo-electrogenerated H₂O₂

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and UV/PMS has not been studied for degradation of organic pollutants. So, simultaneous application of H_2O_2 and PMS for production of hydroxyl and sulfate radicals has not been considered in hybrid processes for the destruction and mineralization of organic compounds. We studied activation of H_2O_2 (electrogenerated) and PMS photolysis to decolorize Acid Brown 14 (AB 14) as a sample of azo dye. The effects of various parameters (light intensity, pH, applied current, electrolyte concentration and PMS concentration) were evaluated. The effect of transitional metals in this hybrid system was also assessed. The reactive species of radicals were also determined in the presence of various alcohols as scavenger. Finally, the mineralization of AB 14 was investigated by chemical oxygen demand (COD), total organic carbon (TOC) and average oxidation state (AOS) indices.

MATERIALS AND METHODS

1. Materials

Acid Brown 14 (AB14), which was used as the target pollutant, was purchased from Alvan-Sabet Inc. Some characteristics of AB14 are given in Table 1. Sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2 , 30%), methanol, ethanol and sulfuric acid (H_2SO_4 , 98%) were obtained from Merck. Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), as source of peroxymonosulfate (PMS), and *tert*-butanol (*tert*-butyl alcohol) were purchased from Sigma and Alfa Aesar Inc., respectively. All reagents used for COD test were supplied from Sigma-Aldrich Inc. All solutions were prepared with double-distilled water. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$), cobalt sulfate ($CoSO_4 \cdot 7H_2O$) and copper sulfate ($CuSO_4 \cdot 5H_2O$) were provided by Sigma-Aldrich.

2. Experimental

The experiments were conducted at room temperature (26–28 °C) in an undivided cell equipped with two electrodes and filled with 300 mL solution. The cell used was a cylindrical quartz container (6 cm diameter × 16 cm height). Tri-dimensional graphite electrodes (1 cm × 1 cm × 14 cm) were used as anode and cathode and the space between them was 20 mm. The surface area of electrodes immersed in electrolyte was 88 cm². The experiments were carried out at constant current using a DC power supply (TNU 3A-30V). Prior to the electrolysis, compressed air (2 L/min) was bubbled for 10 min throughout the solution to saturate the aqueous solution for electrogeneration of hydrogen peroxide. In all experiments, synthetic dye of Acid Brown 14 (50 mg/L) was prepared and Na_2SO_4 (0.01

M) was used as the supporting electrolyte. The source of UV light used in this study was two types of UVC lamps (4 and 6 W, Philips) with maximum emission at 254 nm wavelength. In this way, four emission conditions including 4, 6, 10 and 12 W were evaluated corresponding to light intensities of 0.96, 1.15, 2.08 and 2.32 mW/cm², respectively. The UVC light intensity was measured with a radiometer (Lux-UV-IR meter, Leybold Didactic GMBH-666-230) to ensure the constancy of UVC lamp irradiation. The distance of lamps to quartz cell was 2.5 cm. The maximum temperature reached in this study was 33 °C.

The solution pH values were adjusted with NaOH or H_2SO_4 using pH meter (Eutech-CyberScan pH 1500). Turning the DC power supply and UV lamp on, the photo-electrochemical process was started for decolorization of AB14. Before beginning the electrolysis and the photolysis, a certain amount of PMS was added to the solution to form sulfate and hydroxyl radicals.

3. Analytical Procedure

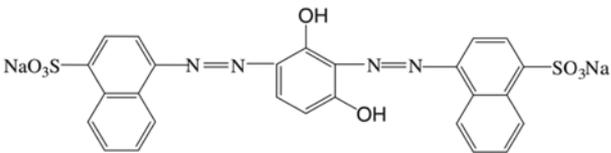
Dye concentrations were determined by a UV-Vis spectrophotometer (Hach-DR5000) at 462 nm. Note that λ_{max} is dependent on solution pH. COD of solution was measured by colorimetric procedure at wavelength of 420 nm using a UV-Vis spectrophotometer (Hach-DR 5000) based on the Standard Methods [20]. The accuracy of COD value was evaluated by potassium hydrogen phthalate (KHP). TOC values were determined by TOC analyzer (Shimadzu-V_{CHS}, Japan). The cumulative concentration of oxidants (H_2O_2 , PMS) was analyzed by iodometric method [21].

RESULTS AND DISCUSSIONS

1. The Effect of UV Light Intensity

Light intensity is a major parameter in all photolysis-based processes. The influence of UV-light intensity on the decolorization of AB14 dye was evaluated under various conditions and the results are displayed in Fig. 1. In absence of UV source (in dark), decolorization is merely related to electrogeneration of H_2O_2 and PMS that are not effectively able to oxidize dye. With increase of light intensity, decolorization increased, which was attributed to greater excitation of PMS and electrogenerated H_2O_2 , resulting in higher concentrations of hydroxyl and sulfate radicals, leading to degradation enhancement [13]. With increase of light intensity from 2.08 mW/cm² to 2.32 mW/cm², insignificant change was observed in decolorization trend of AB14. Therefore, light intensity of 2.08 mW/cm²

Table 1. Characteristics of Acid Brown 14

Dye	Acid Brown 14
Structure	
Chemical formula	$C_{26}H_{16}N_4Na_2O_8S_2$
Color index no.	20195
Molecular weight (g/mol)	622.2
CAS No.	5850-16-8

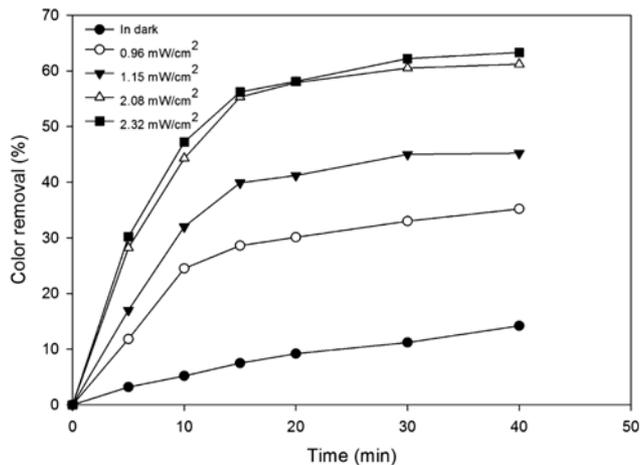


Fig. 1. The effect of UV light intensity on color removal (150 mA applied current, pH=3, 2 mM PMS).

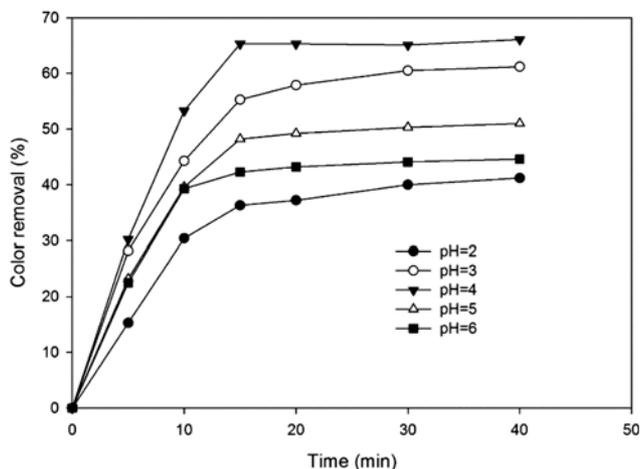


Fig. 2. The effect of pH on color removal (150 mA applied current, 2.08 mW/cm² light intensity, 2 mM PMS).

(10 W) is economically preferable in comparison to light intensity of 2.32 mW/cm² (12 W). Thus, subsequent experiments were done in light intensity of 2.08 mW/cm².

2. The Effect of Initial pH

The solution pH is a crucial factor in chemical and electrochemical processes. Due to instability of H₂O₂ in alkaline media and needing proton for electrogeneration of H₂O₂, the effect of pH on decolorization of AB14 was evaluated in range of 2.0 to 6.0 under the following conditions: 150 mA electrical current, 2 mM PMS and 2.08 mW/cm² light intensity. Fig. 2 shows decolorization of AB14 in various pH values. At low and high pH values, a reduction in decolorization is observed. In all pH values, major color removals occurred within the first 15 min reaction time, while afterwards decolorization rates were not significantly changed. At pH of 2.0, color removal decreased significantly. The low pH may affect both sulfate radical and hydroxyl radical, in a way that exceeding hydrogen ions react with radicals acting as scavenging agent (Eqs. (4) and (5)) [22].

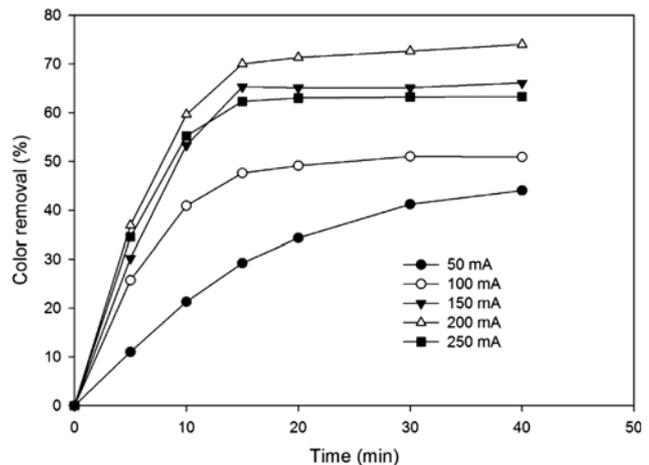


Fig. 3. The effect of applied current on color removal (pH=4, 2.08 mW/cm² light intensity, 2 mM PMS).



In addition, excessive H⁺ can also directly react with H₂O₂ and consequently decreases electrogenerated H₂O₂ (Eq. (6)).



Regarding the results, at the first 15 min, the best initial pH value was 4.0 in photo-electro-oxidation assisted PMS system, attaining a maximum decolorization of 65.3%.

3. The Effect of Electrical Current

The electrical current is a paramount factor in all electrochemical processes frequently used to produce a chemical agent for the treatment of polluted water. The effect of the electrical current in the range of 50-250 mA upon the oxidation of 50 mg/L AB14 by photo-electro-oxidation assisted PMS was evaluated at initial pH of 4.0 and 2 mM PMS. Fig. 3 shows decolorization of AB14 in several applied currents during electrolysis. The color removal percentages in 15 min electrolysis time were 29.2%, 47.6%, 65.3%, 70.0% and 62.3% for applied currents of 50, 100, 150, 200 and 250 mA, respectively. Color removal behavior in 50 mA is different from the others, which can be due to low electrogeneration of hydrogen peroxide. Decolorization was enhanced with increasing applied current when applied current was less than 250 mA. Increase of applied current develops generation of H₂O₂, which induces more production of hydroxyl radicals. For applied current of more than 200 mA, removal efficiency decreased, so that its presumed reason is decomposition of hydrogen peroxide at the anode based on Eqs. (7) and (8) [23,24]:



Apart from that, at high levels of applied current, four-electron reduction of O₂ occurs at the cathode that leads to formation of H₂O (Eq. (9)), which competes with electrogeneration of H₂O₂ [23]. Hence, applied current plays an important role in this hybrid pro-

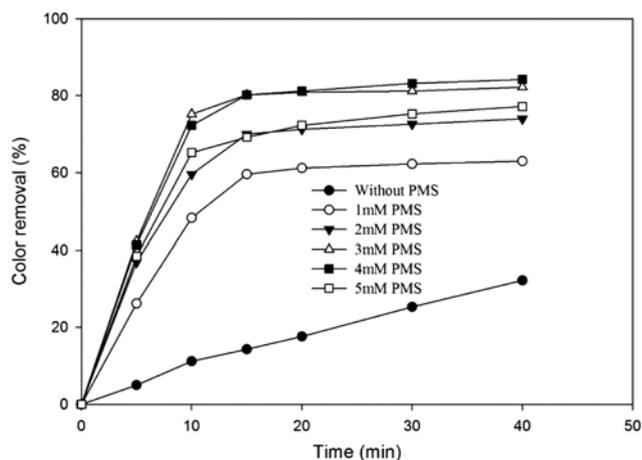


Fig. 4. The effect of PMS concentration on color removal (pH=4, 2.08 mW/cm² light intensity, 200 mA applied current).

cess. And applied current has a bilateral influence on O₂ according to Eqs. (8) and (9).



4. The Effect of PMS Concentration

In the chemical oxidation process, the optimization of chemical oxidant concentration is the most important stage that reduces cost of chemicals. To evaluate the effect of PMS dosage, several experiments were carried out in optimized conditions of the previous experiments (pH=4.0, 200 mA applied current and 2.08 mW/cm² light intensity). Fig. 4 shows the findings of these experiments. In the presence of PMS, color removal revealed similar trends and reached to plateaus after 20 min reaction time. It seems that after 20 min, sulfate and hydroxyl radicals are depleted and are no longer capable of degradation of residual dyes. Apart from this, increasing the PMS dosage increases production of sulfate and hydroxyl radicals, and consequently enhances decolorization of AB14. The decolorization of AB14 was rapidly enhanced when the PMS dosage was increased from 0 to 3 mM. As can be seen, decolorization trends using 3 and 4 mM PMS are similar and decolorization percentage in these two conditions is 80.2% within 15 min reaction time. But with increasing PMS concentration to 5 mM, decolorization trend drops in comparison with the PMS dosages of 3 and 4 mM. This behavior can be explained by the scavenging effect of exceeding concentration of PMS, which has been reported by many researchers. Herein, exceeding PMS scavenges hydroxyl and sulfate radicals and peroxysulfate radical (SO₅⁻) is formed as the radical product that is a weaker oxidant in comparison with sulfate and hydroxyl radicals (Eqs. (10) and (11)) [25,26].



5. The Effect of Concentration of Supporting Electrolyte

The effect of electrolyte concentration was evaluated under the following conditions: 200 mA applied current, pH=4.0, 3 mM PMS and light intensity of 2.08 mW/cm² and the results are illustrated

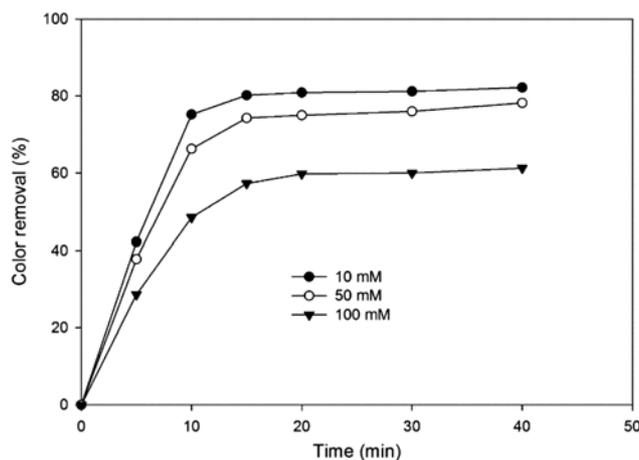


Fig. 5. The effect of concentration of supporting electrolyte (Na₂SO₄) on color removal (3 mM PMS, pH=4, 2.08 mW/cm² light intensity, 200 mA applied current).

in Fig. 5. As shown, increase of electrolyte concentration from 10 mM to 100 mM decreases decolorization percentage from 81% to 60% at 20 min reaction time. Lin et al. also observed behavior, which is attributed to high concentration of sulfate ion that inhibits reactivity of sulfate radical [27]. These results show that electrolyte concentration can affect the of the process.

6. The Effect of Transitional Metals

The oxidants, PMS and hydrogen peroxide, can be activated by transitional metals (M) such as Fe²⁺, Cu²⁺, and Co²⁺ leading to the formation of hydroxyl radical and sulfate radical, respectively (Eqs. (12) and (13)) [7,28]. In this study, several experiments were conducted in the presence of these metals.

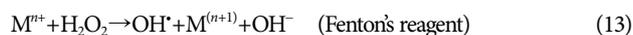


Fig. 6(a) illustrates the effect of the presence of transitional metals (Fe²⁺, Cu²⁺ and Co²⁺) on decolorization of AB14. As shown in Fig. 6(a), in presence of transitional metals, decolorization rate accelerates, which is attributed to more generation of sulfate and hydroxyl radicals in less reaction time. The decolorization was rapid in the initial stages during the first 15 min in all conditions.

Fig. 6(b) displays the calculations of apparent first-order model of the AB14 removal in various conditions for the first 15 min of electrolysis time using linear regression. These results showed that rate constant (k) in the absence of the transitional metal; in the presence of Cu²⁺, Co²⁺ and Fe²⁺ were 1.937×10⁻³, 2.238×10⁻³, 2.453×10⁻³ and 3.595×10⁻³ s⁻¹, respectively. Regarding these rate constants, ferrous ion can significantly enhance reaction rate in comparison with the other metal ions. In this way, for ferrous ion, 97% decolorization occurred within 20 min reaction time. It is worth emphasizing that the produced ferric ion (Fe³⁺) in Eqs. (12) and (13) can be reduced to ferrous ion at the cathode that propagates reaction chains of radical production [11]. From Fenton chemistry perspective, solution pH must be in range of 2-4 as this study was conducted at pH of 4 (optimum condition). Therefore, the combination of Fenton reagent with this hybrid system can be justified.

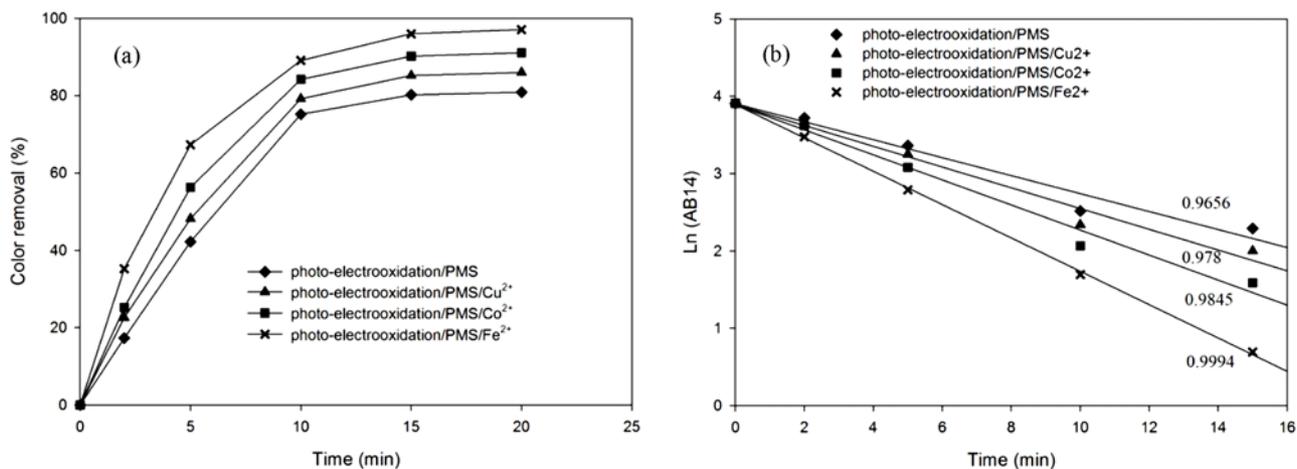


Fig. 6. The effect of transitional metal on color removal in condition of Cu^{2+} , Co^{2+} and $\text{Fe}^{2+}=2 \text{ mM}$, 200 mA , $\text{pH}=4$, 2.08 mW/cm^2 light intensity and 3 mM PMS ((a) color removal (%), (b) AB14 removal kinetic).

7. Determination of Reactive Species and Mechanism

Alcohols have been widely used as radical scavengers to determine the formation of radicals in advanced oxidation processes. Amongst alcohols, methanol, ethanol and *tert*-butanol have frequently been used for quenching the hydroxyl and sulfate radicals. Ethanol and methanol with α -hydrogen can scavenge sulfate and hydroxyl radicals, whereas *tert*-butanol without α -hydrogen is an efficient agent for scavenging the hydroxyl radical, while its reactivity with sulfate radical is 1,000 times less than that of hydroxyl radical (rate constant of 3.8×10^8 vs $4 \times 10^5 \text{ mol L}^{-1} \text{ s}^{-1}$) [14,29]. Note that SO_5^- and HO_2^{\cdot} can also be produced during the process, but due to their low redox potentials, these radicals have not adequate ability for degradation of AB14.

With this description, we carried out quenching experiments with these three alcohols at concentration of 0.1 M and results obtained are shown in Fig. 7. As shown, in the blank condition (no addition of scavenger), decolorization percentage was 80.2% in 15

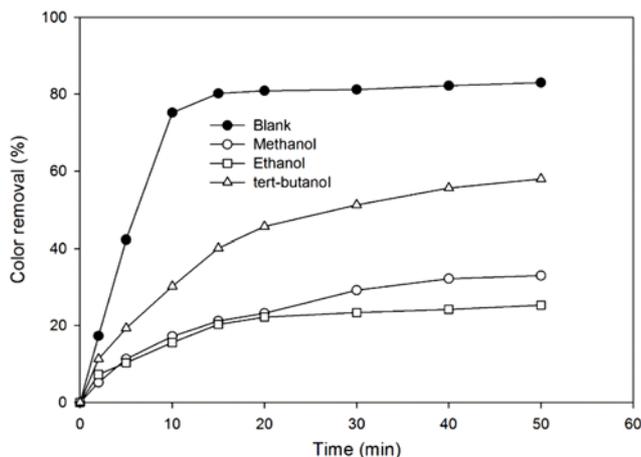


Fig. 7. The effect of scavenging agents on the efficiency of photo-electro-oxidation assisted peroxymonosulfate process in condition of, 200 mA , 2.08 mW/cm^2 light intensity, $\text{pH}=4$ and 3 mM PMS .

min reaction time, while in the presence of methanol, ethanol and *tert*-butanol, color removal was 21.2%, 20.3% and 40.1%, respectively. In general, in presence of scavengers, decolorization decreased considerably. For methanol and ethanol, decolorization decreased remarkably within the first 15 min which in comparison with the blank condition, decolorization dropped by about 60% (from 80% to 20.3%). This reduction indicates that the active radicals of sulfate and hydroxyl have been quenched by scavengers. While in presence of *tert*-butanol, decolorization dropped to around 40% (from 80% to 40.1%), demonstrating sulfate radical had also a key role in decolorization of AB14. Regarding these results, we can conclude that both sulfate and hydroxyl radicals are equally effective in degradation of AB14.

8. Mineralization of AB14

It is crucial to determine the mineralization of dyes in AOPs since some of intermediates could be more hazardous as compared to the parent molecule. TOC, COD and average oxidation state (AOS) parameters were considered for mineralization of AB14. AOS was calculated based on Eq. (14) [26,30].

$$\text{AOS} = \frac{4(\text{TOC} - \text{COD})}{\text{TOC}} \quad (14)$$

where, TOC and COD are in molar units (C/L and O_2/L , respectively) and AOS is in the range of +4 for CO_2 (the most oxidized state) and -4 for CH_4 (the most reduced state) [31]. Variations in AOS are also brought in Fig. 8(a). The rapid reduction of COD and TOC indicates that photo-electro-oxidation is efficient for degradation of organic matter. In confirmation of this fact, AOS value is considerably raised from 0.22 to 2.3 in 30 min. As Sirtori et al. [32] have stated, AOS increases with reaction time until reaching a constant value, which ascertains the formation of more oxidized organic intermediates during the process, demonstrating the biodegradability improvement. Fig. 8(b) shows TOC and COD removal percentages in absence and presence of transitional metals. As can be seen in Fig. 8(b), the presence of transitional metals increased COD and TOC removals. The maximum efficiency was observed in presence of Fe^{2+} in terms of TOC and COD removals.

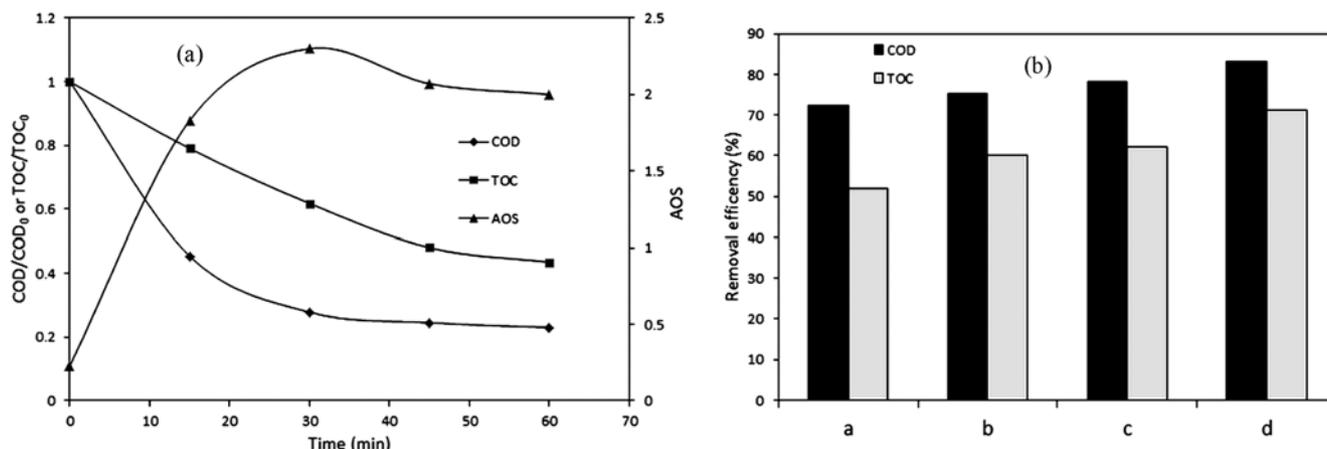


Fig. 8. (a) Mineralization of AB 14 at pH=4, applied current=200 mA, light intensity=2.08 mW/cm² and 3 mM PMS. (b) in absence of transitional metal (a) 2 mM Cu²⁺ (b) 2 mM Co²⁺ (c) 2 mM Fe²⁺ (d).

CONCLUSION

We investigated the combination of electrogenerated H₂O₂ and PMS in presence of UV radiation to produce hydroxyl and sulfate radicals for decolorization of AB14. Important factors affecting the decolorization and mineralization of AB14 were assessed. This study showed that simultaneous application of HO[•] and SO₄⁻ can significantly enhance dye decolorization. The best decolorization rate was achieved under the following conditions: pH=4.0, applied current of 200 mA, 3 mM PMS and light intensity of 2.08 mW/cm². The presence of transitional metals increased the removal efficiency, especially in case of ferrous ion by which 97% decolorization was obtained during 20 min reaction time. The scavenging tests by alcohols showed that both HO[•] and SO₄⁻ were effective in this system. AOS value was markedly increased from 0.2 to 2.3 during 30 min. Finally, the combination of photo-electro-oxidation with PMS is a promising hybrid process for degradation of organic compounds.

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