# EFFICIENT DECOLORIZATION AND DEGRADATION OF AMARANTH AZO DYE VIA PHOTOELECTROCATALYTIC PROCESSES

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## Abstract

This work assesses the electrocatalytic (EC), photocatalytic (PC), and photoelectroncatalytic degradation (PEC) of Amaranth azo dye with ammonium persulfate (APS). The results were observed that the photoelectrocatalytic degradation technique more efficient than other techniques. The effects of operational parameters such as initial pH and APS concentrations on color removal efficiency were investigated. Decolorization and degradation were found to depend strongly on the system parameters. The dye decolorization was enhanced using pH 2.0. The rate of degradation of Amaranth with APS followed pseudo–first order kinetics in the dye concentration. Decolorization efficiency (%) and degradation rates of amaranth were increase with increasing APS concentration.

**Keywords:** Amaranth; Photoelectrocatalytic; Decolorization; Degradation.

## 1. Introduction

Management of water pollution is currently one of the major challenges for environmentalists [1]. Actually, the ensuring of good quality in water reserves represents a basic factor in guaranteeing environmental protection, sustainable development and public health [2].

The dyes and dyestuffs are widely used within the food, pharmaceutical, cosmetic, textile and leather industries. Over 10,000 commercially available dyes exist and more than $7\times10^5$ tons of dyestuffs are produced annually. Among these dyes, azo dyes are the most widely used; these account for over 60% of the total number of dyes structures known to be manufactured [3]. Azo dyes are important colorants and are characterized by the presence of one or more azo groups and constitute the largest class of dyes having extensive applications. These compounds have the azo chromophore (–N=N–) in their structure $R_1$–N=N–$R_2$, where $R_1$ and $R_2$ are aromatic groups [4,5].

The removal of dyes from wastewater is a challenge to the related industries, and is a demanding environmental issue that needs to be addressed [6]. Insufficient treatment of wastes of the dyestuff industries leads to dye contamination of the environment, natural water bodies, and consequently, the soil and groundwater once the dye discharged into the environment as effluent [7]. Dyeing effluents are very

difficult to treat, due to their resistance to biodegradability, stability to light, heat and oxidizing agents [8].

Various methods for removal of synthetic azo dye from wastewaters have been reported in the literature. These include adsorption on inorganic or organic matrices, biological activation, coagulation, chemical oxidation and electrochemical oxidation methods [9,10]. Adsorption and precipitation processes are very time consuming and costly with low efficiency. Chemical degradation by oxidative agents such as chlorine constitutes the most relevant and effective method, but it may produce some very toxic secondary products, such as organochlorine compounds [11]. Lately, Advanced Oxidation Processes (AOPs), such as photochemical processes, Fenton, photo-Fenton, Fenton-like, ozonation and photocatalysis, are being applied to treat textile effluents with encouraging results [12–14].

Among different types and combinations of advanced oxidation processes (AOPs), photochemical processes based on usage of various strong oxidants, such as $H_2O_2$, $O_3$ or $S_2O_8^{2-}$ with UV irradiation, have been shown as suitable for the degradation of colored compounds [15, 16]. More recently, the application of advanced oxidation processes (AOPs) based on sulfate radicals in the field of wastewater treatment have been the subject of interest because sulfate radical anion, $SO_4^{\cdot-}$ ($E^\circ$ = 2.5–3.1V vs. NHE), possesses higher oxidation potential than hydroxyl radical [17, 18]. Several studies have been carried out with sulfate radicals for the degradation of a variety of chemical contaminants [19, 20]. Peroxydisulfate anion, $S_2O_8^{-2}$, by itself, is a strong oxidant and can be used as the source of sulfate radicals, but it slowly reacts with many organics [21]. It can be chemically via transition metals [22], photo-chemically or thermally [23] activated to generate the stronger oxidant sulfate radicals with a kinetically fast reacting tendency.

Electrochemical methods offer many advantages such as low operational cost, be environmentally friendly (its main reagent is an electron), and high mineralization efficiency of various aromatic pollutants, mainly pesticides, dyes, industrial pollutants, and pharmaceuticals [24, 25].

In this study, the degradation of Amaranth using oxidation by ammonium persulfate (APS) was investigated. Important parameters, such as the effect of photocatalytic, electrocatalytic, photoelectrocatalytic, pH, and $S_2O_8^{2-}$ concentrations were investigated to examine their effects on the decolorization efficiency and degradation rate of Amaranth dye.

## 2. Material and methods

### 2.1. Materials

All reagents used in the present study were of analytical reagent grade and used without any further purification. Amaranth, Molecular Formula = $C_{20}H_{11}N_2Na_3O_{10}S_3$, Molecular Weight = 604.47, $\lambda_{max}$ = 520 ±2 nm, Class = Azo Dye, C.I. number 16185, C.I. name Food Red 9, Acid Red 27. It is a dark red to purple azo dye once used as a food dye and to color cosmetics and having structure (Scheme 1) was purchased from  Aldrich. Sulfuric acid (96%), and sodium hydroxide were obtained from El-Gomhuryia Company for Chemical Industries, Cairo, Egypt.

### 2.2. Experimental procedures

Three techniques were used to catalyze the reaction between Amaranth dye and ammonium persulfate (APS) as an oxidant. First technique is the electrocalalytic degradation (EC) between two graphite electrodes at 20 mA. Each electrode has surface area 0.5 cm$^2$. Second technique is the photocalalytic degradation (PC) by using UV lamp. Third, it is the mixture between above two techniques, photoelectrocatalytic degradation (PEC).

Artificial light source of 6W medium pressure mercury vapor lamp 256 nm is used. Pyrex glass reactor of surface area is 82.8 cm$^2$ is directly exposed to the light source in open-air conditions. The entire photo reactor system is maintained at 25 °C using a thermostat. The pH variation of the solution is adjusted either by adding dilute NaOH or dilute $H_2SO_4$. In a typical experiment, 200 ml of 0.1 mM dye solution was used with 2.0 mM of APS. The reaction mixture is stirred at 450 rpm. The light is focused on the solution was placed horizontally at a distance of 15 cm. The change in pH of the reaction solution was measured using PHYWE digital pH meter 13702-93.

### 2.3. Analytical method

Progress of oxidation (decolorization/degradation) of Amaranth azo-dye was monitored in the present study by UV–visible absorption measurements. The solution is taken out from the reactor at desired time intervals, and it was analyzed by UV–vis spectroscopy using Schimadzu UVmini-1240 UV–vis spectrophotometer with a spectrometric quartz cell (1 cm path length). Quantitative analysis of Amaranth dye in aqueous solution was monitored spectrophotometrically by measuring its absorbance at $\lambda_{max.}$=520 nm at different time intervals. The zero time

reading was obtained from blank solution kept in the dark but other wise treated similarly to the irradiated solution.

The better experiment's technique is conducted kinetically using the following different reaction conditions (i) variation of pH from 0.5 to 3.0, (ii) variation of oxidant concentration at constant pH value. These experiments were planned in order to determine an optimum condition for the dye degradation.
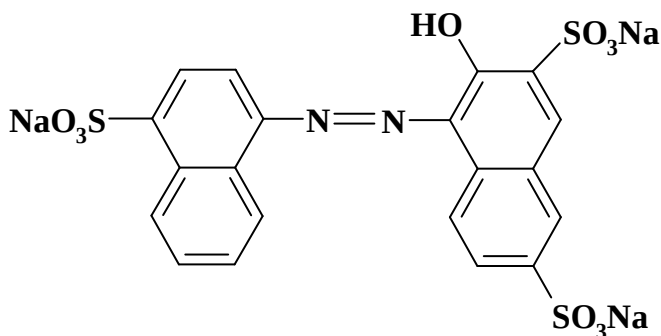


**Scheme 1**  Structure of Amaranth dye

## 3. Results and Discussion

### 3.1. UV–visible absorption spectral measurements

The reactions of dyes with $S_2O_8^{-2}$ are very slow at room temperature, thus the different techniques (EC, PC, and PEC) have been proposed to activate or accelerate organic molecule decomposition. Fig. 1, shows the absorption spectra of Amaranth azo dye with the APS aqueous solution at pH 1.0 of various techniques displayed a main band in a visible region with a maximum absorption ($\lambda_{max}$) at 520 nm. The band in visible region accounts for color of the azo-dye was attributed to the absorption of the $n \rightarrow \pi^*$ transition related to the –N=N– group [26]. The results were observed that, photoelectrocatalytic degradation technique (PEC) is been found to be better for the degradation of Amaranth dye, where the Amaranth removal efficiency was 34.0 % after 30 minutes, (Fig. 1). The extent of color removal of the investigated solution can be expressed as:

$$\text{Decolorization \%} = [1 - (A_t / A_o)] \times 100$$

where $A_o$ is the initial absorbance of the wastewater sample and $A_t$ the absorbance at time t.
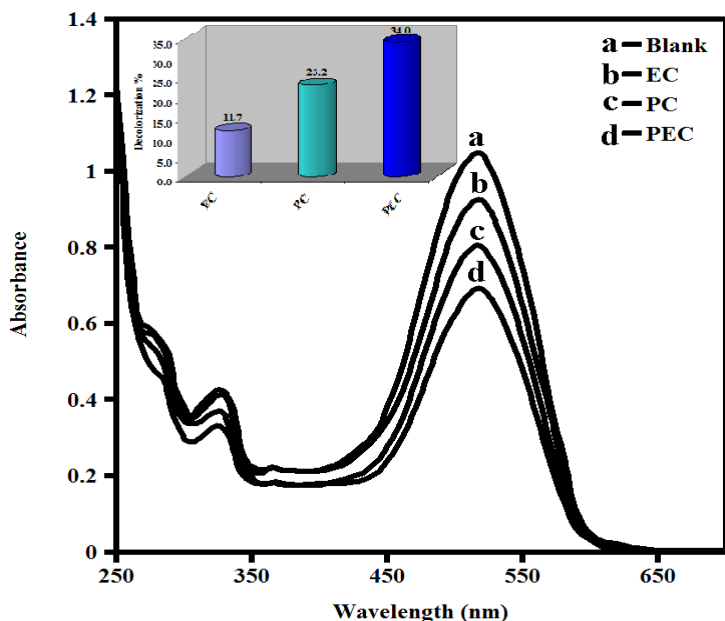
**Fig. 1** UV–visible absorption spectra of decolorization of Amaranth with APS by different techniques at pH 1.0 and 30 min. The inset shows decolorization efficiency of Amaranth with APS by different techniques.
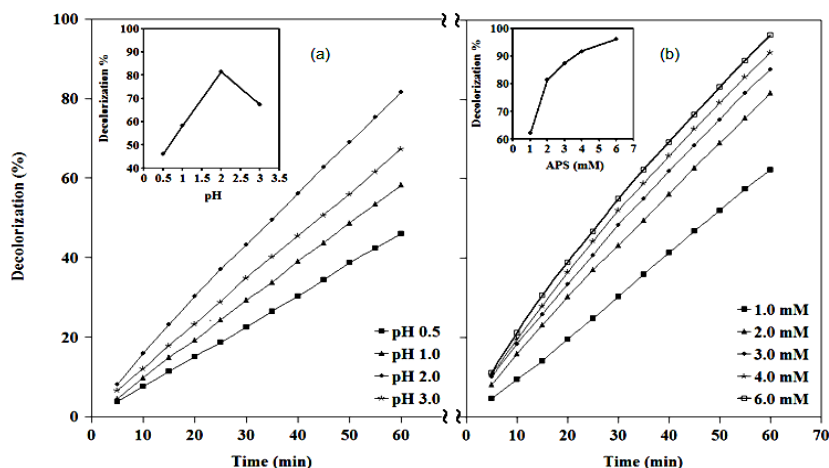
### 3.2. Decolorization efficiency with time

PEC technique can be used to determine the role of pH and APS concentration in the decolorization process at time intervals. The experiments were performed at pH 0.5 – pH 3.0 of 0.1 mM of Amaranth with 2.0 mM of APS. Fig. 2 shows the effect of pH on the decolorization efficiency. The results showed that the decolorization efficiency of the Amaranth solution increased from pH 0.5 to 2.0. After that, the efficiency decreased slightly with the pH increased.

The influence of APS concentration (1.0 – 6.0 mM) on the Amaranth dye removal efficiency using PEC technique at pH 2.0 is shown in Fig. 2. The results show that the removal efficiency of Amaranth increased ascending with time, and decolorization was continuously increased in the presence of increasing concentration of APS.

### 3.3. Kinetic studies

The parameter of kinetic, which is helpful for the prediction of degradation rate, gives important information for designing and modeling the processes. Thus, the effects of initial concentration, and pH were analyzed from the kinetic point of view.

**Figure 2.** Decolorization efficiency of Amaranth vs time at various initial pH values (a), and APS concentrations (b).

The kinetics of disappearance of Amaranth dye for the PEC processes were summarized and presented in Figs. 3-6. All kinetic curves in the first period of the reaction could be fitted reasonably well by an exponential decay curve suggesting the pseudo-first and pseudo-second kinetics orders. First and second orders kinetic models were utilized as follows [27]:

*Pseudo-first order kinetic model*

$$ln\ A_t = -k_1 t + ln\ A_o$$

*Pseudo-second order kinetic model*

$$1/A_t = k_2 t + 1/A_o$$

The calculated slopes and intercepts from the plots were used to determine the rate constants ($k_1$, $k_2$) and initial absorbance ($A_o$). The values of $k_1$, $k_2$, $A_o$ and $r^2$ are summarized in Table 1. Considering the results in Table 1 which reveals that the decolorization of Amaranth dye followed the first order kinetic model, because it has the highest correlation coefficient ($r^2$) values, the practical initial absorbance ($A_{o(Exp.)}$) correspods to which calculated from the intercepts ($A_{o(Cal.)}$), and it is in good agreement with the experimental results.
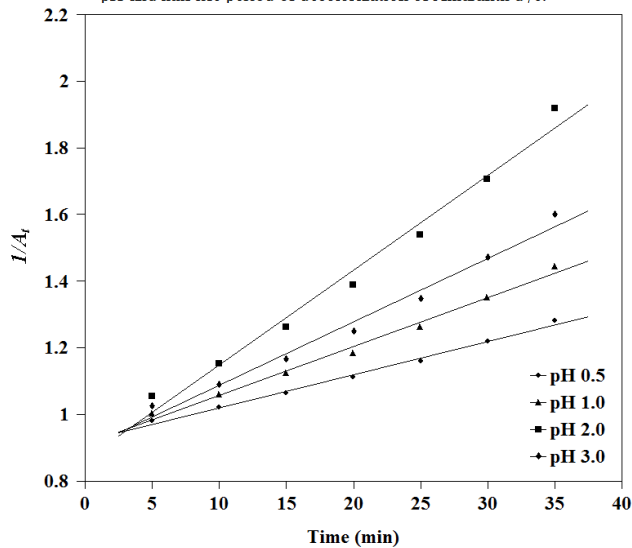
### 3.3.1. Effect of the initial pH

It has been established that pH is an important parameter influencing the performance of the PEC process. Therefore, the degradation of dye was studied at different pH range from 0.5 to 3.0 in the presence of 2.0 mM of Amaranth and APS respectively. The kinetic of decolorization of Amaranth is strongly affected by the pH. Figs. 3 and 4 illustrates the effect of pH on the rate of decolorization of the

examined dye. It was found that the decolorization rate reaches a maximum as the pH increases from 0.5–2.0 in the first period of PEC process, to be followed by a significant decrease at the pH above 2.0 and highest degradation rate was observed at pH 2.0. Furthermore, Fig. 3 reflects that the lower half life degradation period ($t_{1/2}$) at the same pH value.
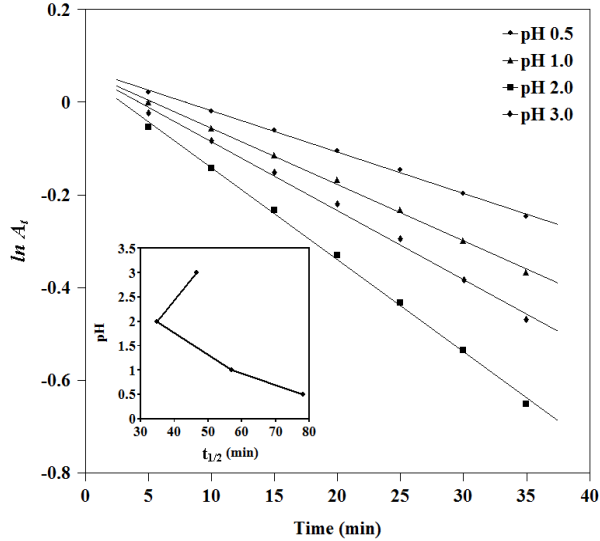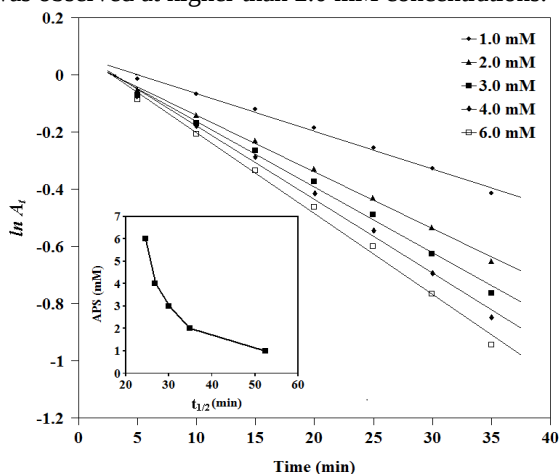


**Figure 3.** First order kinetic model of the decolorization of Amaranth at various initial pH values. The inset shows the relation between pH and half life period of decolorization of Amaranth dye.
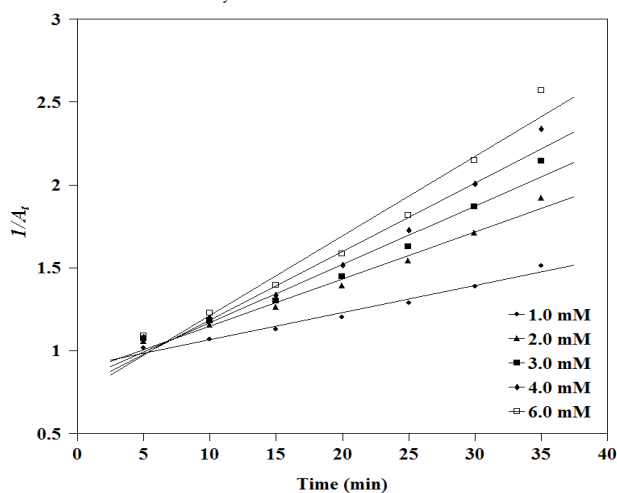


**Figure 4.** Second order kinetic model of the decolorization of Amaranth at various initial pH values.

### 3.3.2. Effect of initial concentration of APS

Persulfate anion is the most powerful oxidant of the peroxygen family of compounds and one of the strongest oxidants used in remediation [28]. The concentration of $S_2O_8^{2-}$ was found to be an important parameter for the degradation of Amaranth dye in PEC technique. Fig. 5 shows the decolorization of Amaranth at different initial concentrations of APS at pH 2.0. The photoelectrocatalytic degradation rate of dye increased with an increase in the APS concentration from 1.0 to 6.0 mM. On the other hand, it is interesting to note that half life degradation period ($t_{1/2}$) decrease with the increase in APS concentration from 1.0 to 2.0 mM and slight decrease was observed at higher than 2.0 mM concentrations.



**Figure 5.** First order kinetic model of the decolorization of Amaranth at various concentrations of APS. The inset shows the relation between APS concentration and half life period of decolorization of Amaranth dye.



**Figure 6.** Second order kinetic model of the decolorization of Amaranth at various initial concentrations of APS.

**Table 1. Kinetic parameters for first order and second order models of Amaranth dye decolorization.**

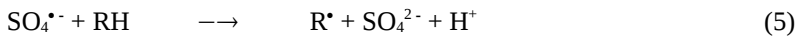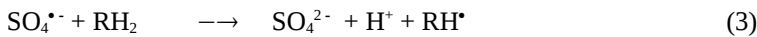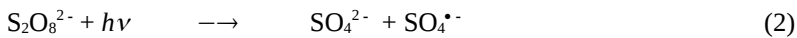|  |  | $A_{o\,(Exp.)}$ | Pseudo-first order | | | Pseudo-second order | | |
|---|---|---|---|---|---|---|---|---|
|  |  |  | $A_{o\,(cal.)}$ | $r^2$ | $k_1$ | $A_{o\,(cal.)}$ | $r^2$ | $k_2$ |
| pH | 0.5 | 1.06 | 1.07 | 0.998 | 0.009 | 1.09 | 0.992 | 0.010 |
|  | 1.0 | 1.05 | 1.07 | 0.998 | 0.012 | 1.10 | 0.991 | 0.015 |
|  | 2.0 | 1.03 | 1.06 | 0.998 | 0.020 | 1.16 | 0.983 | 0.028 |
|  | 3.0 | 1.05 | 1.07 | 0.995 | 0.015 | 1.12 | 0.983 | 0.019 |
| APS (mM) | 1.0 | 1.03 | 1.07 | 0.993 | 0.013 | 1.11 | 0.980 | 0.016 |
|  | 2.0 | 1.03 | 1.06 | 0.998 | 0.020 | 1.16 | 0.983 | 0.028 |
|  | 3.0 | 1.04 | 1.07 | 0.994 | 0.023 | 1.22 | 0.970 | 0.035 |
|  | 4.0 | 1.04 | 1.08 | 0.995 | 0.026 | 1.29 | 0.967 | 0.041 |
|  | 6.0 | 1.03 | 1.08 | 0.994 | 0.028 | 1.36 | 0.961 | 0.048 |

*3.4. Photoelectrocatalytic decolorization mechanism*

The increased rate of decolorization of Amaranth with the addition of persulfate may be explained as follows: the persulfate can trap the photogenerated conduction band electrons, and generate strong oxidizing $SO_4^{2-}$ according to the following reaction [29, 30]:
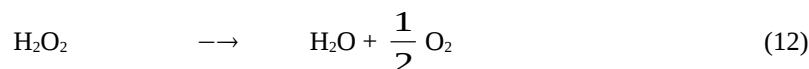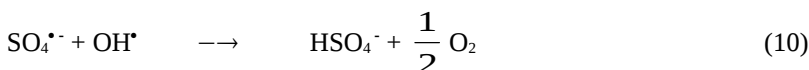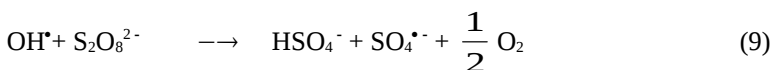
$$S_2O_8^{2-} + e_{CB}^- \quad \longrightarrow \quad SO_4^{2-} + SO_4^{\bullet-} \tag{1}$$
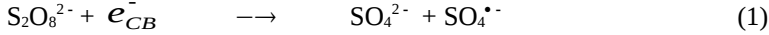
Sulfate radical anion ($SO_4^{\bullet-}$) is a very strong oxidant and engages in at least three reaction modes with organic compounds: by abstracting a hydrogen atom from saturated hydrocarbon, by adding to unsaturated or aromatic hydrocarbon and by removing one electron from carboxylate anions and from certain neutral molecules [31].

Sulfate radical anion is also generated thermally or photolytically ($\lambda \leq 270$ nm) and can participate in reactions with the solvent, according to the following scheme [32-34]:

$$S_2O_8^{2-} + h\nu \quad \longrightarrow \quad SO_4^{2-} + SO_4^{\bullet-} \tag{2}$$

$$SO_4^{\bullet-} + RH_2 \quad \longrightarrow \quad SO_4^{2-} + H^+ + RH^{\bullet} \tag{3}$$

$$RH^{\bullet} + S_2O_8^{2-} \quad \longrightarrow \quad R + SO_4^{2-} + H^+ + SO_4^{\bullet-} \tag{4}$$

$$SO_4^{\bullet-} + RH \quad \longrightarrow \quad R^{\bullet} + SO_4^{2-} + H^+ \tag{5}$$

$$2R^{\bullet} \quad \longrightarrow \quad RR \text{ (dimmer)} \tag{6}$$

(R is an organic material)

Furthermore, the available oxidants in the solution and its related intermediates were indicated in the following reactions:

$$SO_4^{\bullet-} + H_2O \quad \longrightarrow \quad HSO_4^- + OH^\bullet \tag{7}$$

$$HSO_4^- \quad \longrightarrow \quad H^+ + SO_4^{2-} \tag{8}$$

$$OH^\bullet + S_2O_8^{2-} \quad \longrightarrow \quad HSO_4^- + SO_4^{\bullet-} + \frac{1}{2}O_2 \tag{9}$$

$$SO_4^{\bullet-} + OH^\bullet \quad \longrightarrow \quad HSO_4^- + \frac{1}{2}O_2 \tag{10}$$

$$2OH^\bullet \quad \longrightarrow \quad H_2O_2 \tag{11}$$

$$H_2O_2 \quad \longrightarrow \quad H_2O + \frac{1}{2}O_2 \tag{12}$$

$$S_2O_8^{2-} + H_2O_2 \quad \longrightarrow \quad 2H^+ + 2SO_4^{2-} + O_2 \tag{13}$$
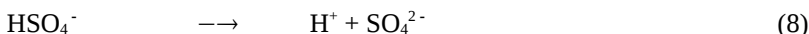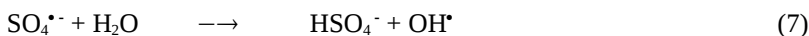
On the other hand, the current density also affects the persulfate. As shown in half reaction below, the product of persulfate reduction is sulfate ion ($SO_4^{2-}$), which is a relatively benign species.

$$S_2O_8^{2-} + 2e^- \quad \longrightarrow \quad 2SO_4^{2-} \qquad E^\circ = 2.01 \text{ V} \tag{14}$$

It is believed that persulfate reacts with organic compounds primarily by the sulfate radical ($SO_4^{\bullet-}$), which can be generated in solution by several mechanisms. The oxidation process begins with the formation of sulfate and hydroxyl radicals, which can transform organic matter (R) into more or less toxic byproducts or into $CO_2$ and $H_2O$. The sulfate ion generated as final product is virtually inert and it is not considered a pollutant, unlike $H_2O_2$, which must be removed after its application. For this reason, the $SO_4^{\bullet-}$ radical has been increasingly used for pollutant degradation over the past few years. The USEPA has listed it under the secondary drinking water standards with a maximum concentration of 250 mg/l, based on aesthetic reasons [35, 36].

The rate increment of Amaranth photoelectrooxidative decolorization is slightly slowed down at higher $S_2O_8^{2-}$ dosages. Therefore, $SO_4^{2-}$ concentration increases in solution which leads less dye degradation [37]. However, such a recombination effect of the radical is likely not very effective due to the low steady-state concentrations of the radicals; higher decay rates of Amaranth dye at higher $S_2O_8^{2-}$ dosages are still expected.

## 4. Conclusion

Discoloration of Amaranth with ammonium persulfate (APS) was catalyzed by three techniques. Photoelectrocatalytic technique (PEC) is better than the two other techniques for the decolorization of Amaranth dye. Effect of pH variation and APS concentration on the decolorization of dye was studied kinetically at 25 °C. The decolorization of dye was tested for both pseudo–first order and second order kinetics; it was observed that the interactions could be better explained based on first order kinetic. The results were observed that, highest decolorization rate was found at pH 2.0, and the degradation efficiency of Amaranth increase with APS concentration increased.

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