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ORIGINAL ARTICLE

Degradation of acid red 17 dye with ammonium persulphate in acidic solution using photoelectrocatalytic methods

M. Thabet, A.A. El-Zomrawy *

Department of Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt

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KEYWORDS

Acid red 17;
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Abstract Advanced oxidation processes (AOPs) have proved very effective in the treatment of the various hazardous organic pollutants in water. The photoelectrocatalytic degradation of azo dye acid red 17 (AR-17) with ammonium persulphate (APS) was studied. Various operational parameters effect on the photoelectrocatalytic degradation rate, such as pH and the amount of APS oxidant, were investigated. The rate of degradation of dye with these composites followed pseudo-first order kinetics in the dye concentration. The results were observed and it was found that the dye decolorization was enhanced using pH 2.0. Also, the degradation rates were found to be strongly influenced by the increasing of the APS oxidant. The addition of $(NH_4)_2S_2O_8$ considerably increased the removal effectiveness due to the generation $SO_4^{\bullet -}$ radicals.

1. Introduction

The introduction of waste products in the environment is a world wide problem that has been highlighted by various environmentalist groups. Dyes are widely used in industries such as textiles, rubber, paper, plastics, cosmetics, foods, etc., to color their products. The dyes are invariably left as the major waste in these industries. Due to their chemical structures, dyes are resistant to fading on exposure to light, water and many chemicals and, therefore, are difficult to be decolorized once released into the aquatic environment (Sharma and Janveja, 2008). Many of the organic dyes are hazardous and may affect aquatic life and even the food chain (Sheikh and Rana, 2009). Release of these dyes in water stream is esthetically undesirable and has serious environmental impact. Due to intense color they reduce sunlight transmission into water hence affecting aquatic plants, which ultimately disturb aquatic ecosystem; in addition they are toxic to humans also.

The release and accumulation of dyes in suspension solution from tanneries, textile, paper and other industries formed in inland waters produce tremendous chemico-azo stress on aquatic organism including fishes and some time results in their mass mortality. The removal of dyes from industrial waste before they are discharged into the water bodies is therefore very important from health and hygiene point of view and for environmental protection.

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* Corresponding author. Tel.: +20 106416041.
E-mail address: azomrawy@yahoo.com (A.A. El-Zomrawy).

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Methods for treating dye wastewaters consist of various chemical, physical and biological processes. These include: adsorption (Bilal, 2004), nanofiltration (Chakraborty et al., 2003; Capara et al., 2007), colloidal gas aphrons (Roy et al., 1992), electro coagulation (Alinsafi et al., 2004), coagulation and precipitation (Liu et al., 2003), advanced chemical oxidation (Arslan et al., 2000), electrochemical oxidation (Riera-Torres and Gutiérrez, 2010), photo-oxidation (Patricia et al., 2003), predispersed solvent extraction (Mahmoud et al., 2007), ozonation, supported liquid membrane (Mahmoud et al., 2007) and liquid–liquid extraction (Venkateswaran and Palanivelu, 2005). The reaction rate of azo dyes depends on the basic structure of the molecule and on the nature of auxiliary groups attached to the aromatic nuclei of dyes.

The persulphate also could be a good candidate for the photochemical oxidation technique. Persulphate ($S_2O_8^{2-}$) is a strong oxidant ($E_0 = 2.05$ V) which has been used widely in the petroleum industry for the treatment of hydraulic fluids or as a reaction initiator in the petrochemical industry (Daneshvar et al., 2007). The persulphate is normally available as a salt associated with ammonium, sodium, or potassium. It has also been reported to be effective for degrading organics in hazardous wastewaters in acidic or basic media through direct chemical oxidation (DCO), where persulphate is used as a sacrificial reagent (McCallum et al., 2000; Lau et al., 2007). The thermal or photochemical activated decomposition of $S_2O_8^{2-}$ ion to $SO_4^{\cdot-}$ radical has been proposed as a method to accelerate the process because the reactions of persulphate are generally slow at normal temperature (Lau et al., 2007). Photolysis of $S_2O_8^{2-}$ produces sulphate radical anions $SO_4^{\cdot-}$ with 100% photochemical efficiency, yielding $SO_4^{\cdot-}$ as summarized in the following reactions (Yu et al., 2004):

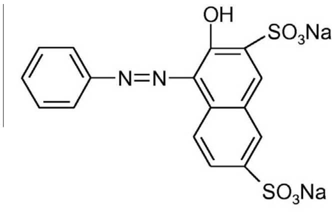
$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{-} \quad (SO_4^{-}, E_o = 2.60\ \text{V})$$

Similar to hydroxyl radicals, sulphate radicals may react with organics by electron transfer, hydrogen abstraction, or addition mechanisms (Anipsitakis et al., 2006).

In this work, the decoloration of acid red 17 by $S_2O_8^{2-}$ photochemically assisted and photoelectrochemically assisted in the work in different pH values has been studied. The study is based on monitoring reduction in the solution absorbance at the wavelength that corresponds to the maximum absorbance of the dye sample.

2. Materials and experimental methods

Bordeaux R, molecular formula = $C_{20}H_{12}N_2Na_2O_7S_2$, molecular weight = 502.42, λ_{max} = 511 ± 2 nm, class = azo dye, C.I. number 16180, C.I. name acid red 17, and having structure:



Chemical structure of acid red 17

Discoloration efficiency of AR-17 was measured by electrocatalytic, photocatalytic, and photoelectrocatalytic methods at pH 1.0 and 20 mA between two graphite electrodes. Initial concentrations of acid red, AR-17, and ammonium persulphate, APS, were 0.1 and 2.0 mM, respectively. Samples were withdrawn from a sample point at certain time intervals and analyzed for decoloration of acid red 17 dye. Thus, an optimum pH for maximum degradation of the aqueous AR-17 dye solutions by PECO method was studied. The reactions were carried out at different pH values in the range of 0.5–3.0 by adding H_2SO_4 or NaOH to adjust the pH value. PCO and PECO experiments of acid red dye (100 ml, 0.1 mmol) were carried out using UV Lamp (256 nm) of intensity 6 W.

Discoloration of dye solutions was checked and controlled by measuring the absorbance of dye at different intervals using UVmini-1240 SHMADZU, UV–vis spectrophotometer. The variation of pH of the sample before and after the irradiation was measured with a digital pH-meter, PHYWE 13702-93.

The degree of decoloration, i.e. the removal degree of color at the λ_{max} of the sample (511 nm) was calculated with the relation

$$\% = [(A_0 - A_t)/A_0] \times 100$$

where A_0 is the initial absorbance of the wastewater sample and A_t is the absorbance at the time t of the photodegradation.

Kinetic experiments were conducted by using PECO method. Kinetic decoloration behavior of AR-17 was investigated at different pH's. The effects of initial pH value on the degradation process were conducted by preparing 200 mL solutions containing 0.1, 2.0 mM of AR-17 and APS, respectively. On the other hand; the effects of initial APS concentrations were investigated at pH 2.0 and 0.1 mM of dye. All the samples at different time intervals (0–60 min) were taken.

3. Results and discussion

3.1. Decolorization efficiency

The results of decolorization of AR-17 dye with APS were obtained by the various methods; electrocatalytic oxidation (ECO), photocatalytic oxidation (PCO) and combination with each other, photoelectrocatalytic oxidation (PECO) in acidic medium. By using (PCO) the dyes molecules absorb photon, the UV energy will be transferred to the dyes molecules and the electronic structures of the dyes are excited. Thus, molecules excited states are unstable and short lived and will dispense their excitation energy in some physical way or undergo chemical reactions and form new species. The combination photoelectrocatalytic oxidation (PECO) was more effective in the decoloration of dye at pH 2.0 than (ECO) and (PCO) alone, where the AR-17 dye removal efficiency was 24.7% after 30 min, Fig. 1a and b.

The dye is attacked by UV photon and by hydroxyl and sulphate radicals, which are powerful oxidants generated from the electro and the photolysis of H_2O and ammonium persulphate by UV light, making possible the degradation of the dyes. The destruction of azo bond –N=N– in the chromophore of azo dyes led to the decoloration of the dye solutions.

The effects of PECO method on the decoloration efficiency of AR-17 at various pH (0.5, 1.0, 2.0, 3.0) and in presence of 2.0 mM of APS were investigated. Discoloration of AR-17 dye at pH 2.0 was more efficient than other pH values under this study, Fig. 2, suggesting that the pH value would affect the amount of $OH^{\cdot}$ and $SO_4^{\cdot}$ generation, and the preferable condition for $OH^{\cdot}$ and $SO_4^{\cdot}$ generation was under acidic conditions.

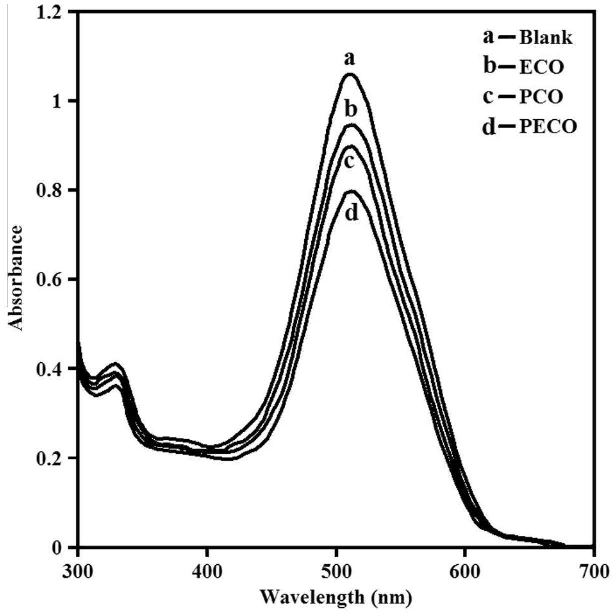


Figure 1a UV–vis spectral of AR-17 dye degradation by various methods at pH 1.0 and 30 min.

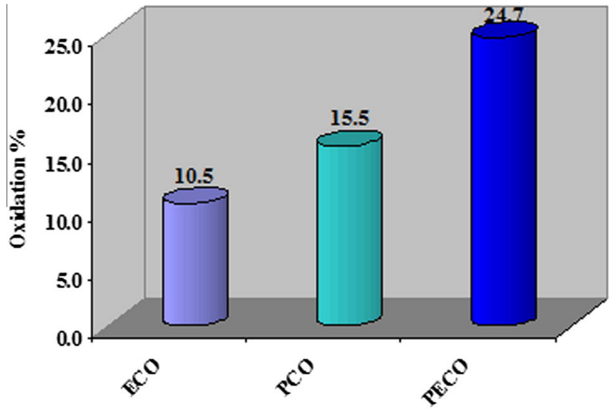


Figure 1b Degradation efficiency of AR-17 by various methods at pH 1.0 and 30 min.

3.2. Kinetic studies

The kinetic parameter, which is helpful for the prediction of degradation rate, gives important information for designing and modeling the processes. Thus, the effects of initial concentration, contact time, and pH were analyzed from the kinetic point of view. The kinetics of the adsorption data was analyzed using different kinetic models such as pseudo-first order and pseudo-second order models:Pseudo-first-order kinetic model

$$\ln A_t = -k_1 t + \ln A_0$$

Pseudo-second order kinetic model

$$1/A_t = k_2 t + 1/A_0$$

The calculated slopes and intercepts from the plots were used to determine the rate constants (k_1, k_2) and initial absorbance (A_0). The values of k_1, k_2, A_0 and regression co-efficient are provided in Table 1.

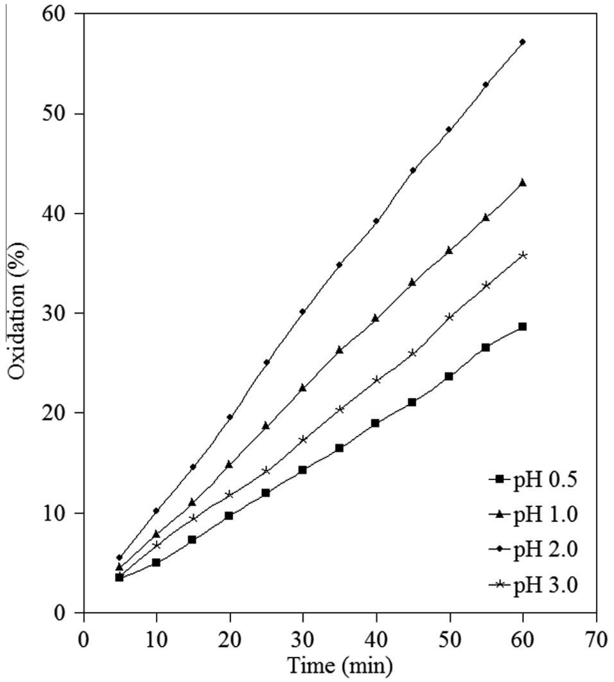


Figure 2 Degradation efficiency vs. time of AR-17 at different pH values.

3.2.1. *Effect of pH*

The first order and second order plots of dye degradation with time under PECO process at different pH values are shown in Figs. 3 and 4. Results proved that the pseudo-first order kinetic model has the highest correlation coefficient (r^2) values, measured initial absorbance ($A_{0(\mathrm{Exp.})}$) corresponds to which calculated from the intercepts ($A_{0(\mathrm{Cal.})}$), and it is in good agreement with the experimental data. The results show that high degradation rate constant values are observed at pH 2.0 for azo dye. Similar results have already been reported for azo dyes (Galindo et al., 2001; Galino and Kalt, 1998). The high rate constant value observed at pH 2.0 can be explained by the change in the molecule structure. The presence of labile H atom makes the molecule of dye especially vulnerable toward attack of $OH^{\cdot}$ radicals (Galino and Kalt, 1998).

3.2.2. *Effect of APS oxidant concentration*

In optimum condition of pH, the effect of persulphate concentrations was investigated. The results showed that efficiency of AR-17 dye removal was induced by increasing of APS concentration from 1.0 up to 5.0 mmol/L, Figs. 5 and 6. Rate constant values were found to increase with increasing the amount of persulphate ions (electron scavenger). Table 1, reveals that, the increase in rate constant values may be due to the formation of SO_4^{2-}.

The sulphate radical anion ($SO_4^{\cdot -}$) thus formed is a sufficiently strong oxidant ($E_0 = 2.6$ V) and may act in the following three possible ways with organic compounds (i) by abstracting a hydrogen atom from saturated carbon, (ii) by adding to unsaturated or aromatic carbon and (iii) by removing one electron from the carboxylate anions and from certain neutral molecules (Vinodogopal et al., 1996, 1997).

In addition, it can trap the photogenerated electron and/or generate hydroxyl radicals (Neppolian et al., 2002; Vinodgopal et al., 1997).

Table 1 Kinetic parameters of decoloration of AR-17.

		$A_{0(\text{Exp.})}$	Pseudo-first order			Pseudo-second order		
			$A_{0(\text{cal.})}$	r^2	k_1	$A_{0(\text{cal.})}$	r^2	k_2
pH	0.5	1.16	1.17	0.995	0.006	1.18	0.987	0.006
	1.0	1.16	1.19	0.997	0.009	1.24	0.984	0.011
	2.0	1.17	1.23	0.992	0.014	1.41	0.963	0.019
	3.0	1.16	1.18	0.990	0.007	1.21	0.977	0.008
APS (mM)	1.0	1.16	1.19	0.994	0.008	1.24	0.980	0.010
	2.0	1.17	1.23	0.992	0.014	1.41	0.963	0.019
	3.0	1.14	1.22	0.990	0.016	1.48	0.949	0.024
	4.0	1.16	1.24	0.981	0.019	1.67	0.921	0.029
	5.0	1.17	1.27	0.989	0.021	1.97	0.927	0.037

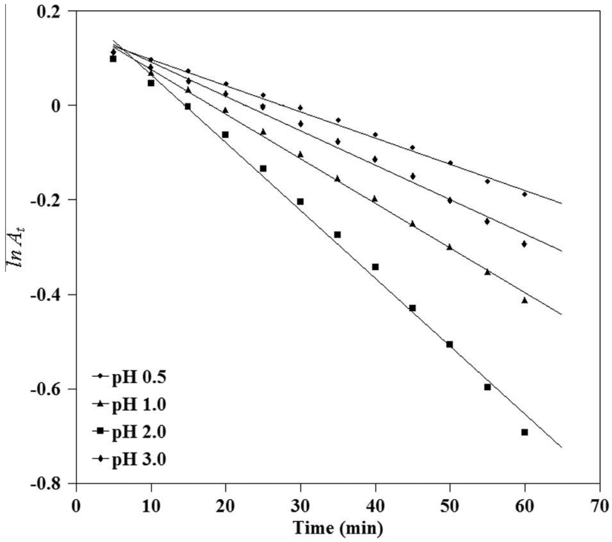


Figure 3 First order plot of dye photoelectrochemical degradation at various pH values.

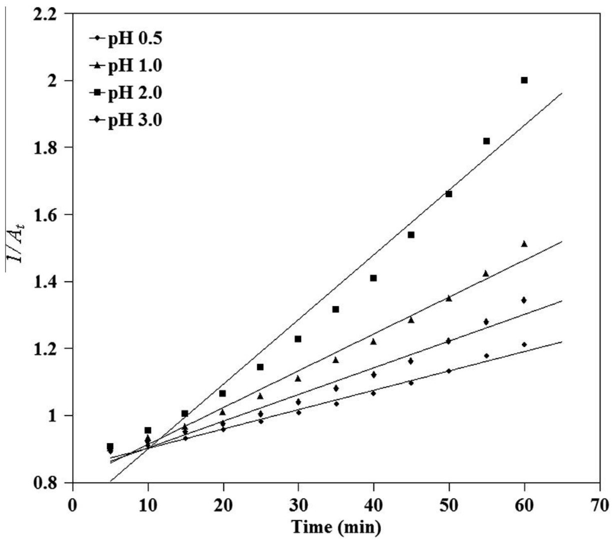


Figure 4 Second order plot of dye photo-electrochemical degradation at various pH values.

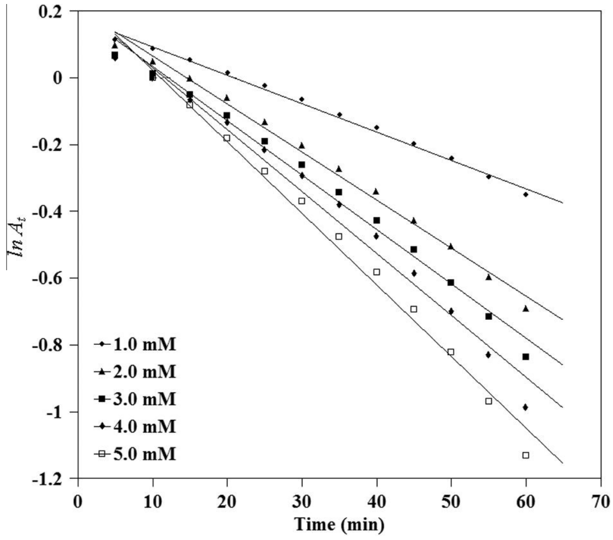


Figure 5 First order plot of dye photoelectrochemical degradation at pH 2.0 and different concentration of APS.

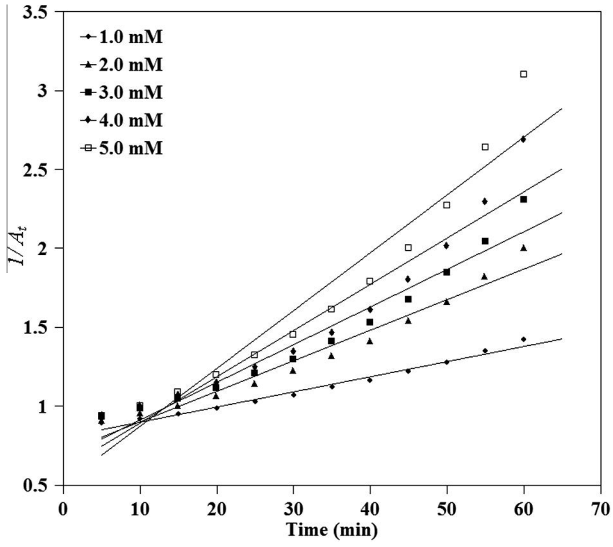


Figure 6 Second order plot of dye photoelectrochemical degradation at pH 2.0 and different concentration of APS.

$$SO_4^{\cdot-} + e_{cb}^- \rightarrow SO_4^{2-}$$

$$SO_4^{\cdot-} + H_2O \rightarrow OH^{\cdot} + SO_4^{2-} + H^+$$

The hydroxyl radical and sulphate radical anion being powerful oxidants degrade the dye molecule at a faster rate. Hydroxyl radicals may attack organic molecules by abstracting a hydrogen atom from the molecule that can oxidize organic compounds (RH) producing organic radicals ($R^{\cdot}$), which are highly reactive and can be further oxidized (Georgiou et al., 2002; Azbar et al., 2004).

The $SO_4^{\cdot-}$ has the unique nature of attacking the dye molecule at various positions and hence the fragmentation of the dye molecules is rapid (Saver et al., 2002).

$$SO_4^{\cdot-} + \mathrm{Dye} \rightarrow SO_4^{2-} + \mathrm{Dye}^{\cdot}(\mathrm{intermediate})$$

$$SO_4^{\cdot-} + \mathrm{Dye}^{\cdot}(\mathrm{intermediate}) \rightarrow SO_4^{2-} + CO_2 + NO_2 + \text{other inorganics}$$

4. Conclusion

This work has shown that the photoelectrochemical degradation (PECO) in the presence of persulphate ion is a good method for color removal of AR-17 in synthetic textile wastewater. The decolorization is enhanced by the presence of UV irradiation and $(NH_4)_2S_2O_8$, APS, due to the sulphate radical anions and hydroxyl radicals generated during the photochemical reactions.

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