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Original article

Experimental evaluation of Reactive Yellow 17 degradation using UV light and iron ions activated peroxydisulfate: Efficiency and kinetic model

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Abstract

In the present study, the degradation of Reactive Yellow 17 (RY17) azo dye in aqueous solution was performed using UV light and iron ions as activators of peroxydisulfate ($S_2O_8^{2-}$ or PDS). The effect of several parameters affecting the degradation process was studied and the optimum conditions are found to be: [RY17] = 10 mg/L, [Fe²⁺] = 0.05 mM, [$S_2O_8^{2-}$] = 1 mM and the pH = 3. The obtained results showed that the removal degrees of RY17 using different processes such as $S_2O_8^{2-}/Fe^{2+}$, $S_2O_8^{2-}/UV$ and $S_2O_8^{2-}/Fe^{2+}/UV$ was 63.3%, 81.0% and 95.4% respectively within 20 min of the degradation. Based on theses removal degrees, the degradation efficiency of the RY17 increases in the order: $S_2O_8^{2-}/Fe^{2+}/UV > S_2O_8^{2-}/Fe^{2+} > UV > S_2O_8^{2-}$. The experimental data were analyzed using the first-order, second-order and Behnajady-Modirshahla-Ghanbery (BMG) kinetic models, and the kinetic data were in good agreement with the BMG model. Under the optimal conditions, the comparative study of the RY17 degradation using two salts Na₂S₂O₈ and K₂S₂O₈ showed a strong similarity. The total mineralization was monitored using COD and TOC techniques. The results showed that the peroxydisulfate activated by UV and Fe²⁺/UV system is efficient for the degradation and mineralization of RY17; it could also be an alternative for the treatment of the real wastewater contaminated by azo dyes. © 2018 Sociedade Portuguesa de Materiais (SPM). Published by Elsevier España, S.L.U. All rights reserved.

Keywords: Degradation; Azo dye; Reactive Yellow 17; Iron ions; Peroxydisulfate; Mineralization

1. Introduction

Wastewaters generated from various industries, and containing dyes represents a threat to aquatic life and environment. Dye effluents may present an ecotoxic risk and have potential dangers of bioaccumulation for humans and other living organisms [1,2]. Synthetic dyes are extensively used in different processing industries such as textile leather, printing, cosmetic, drug and food. Among the synthetic dyes released in effluents from textile industries, azo dyes, which represent almost 50% of about 700 000 tones of dyes produced in the world. Azo dyes are one of the more detrimental classes because it is highly persistent in the aquatic environment, due to its chemical composition, involving aromatic rings, azoic linkages and amino groups [3–5]. Various technologies such as adsorption, ion exchange, reverse osmosis, coagulation flocculation and advanced oxidation processes (AOPs) are used for removing the dyes from wastewater; theses later have received great attention for the oxidative destruction of refractory compounds. In addition, they have the potential to completely oxidize organic contaminants to CO_2 , H_2O and mineral salts. Their advantages for the treatment of dye wastewater include fast reaction, complete treatment and being pollution-free [6–8].

Recently, Peroxydisulfate Oxidation (PDSO) was proved to be a novel and promising technique for the treatment of wastewaters, especially for the removal of organic pollutants. The peroxydisulfate is a strong oxidant (redox potential equal to 2.01 V) and kinetically slows when reacting with a large numbers of organic compounds. However, it was found that the peroxydisulfate anion can be thermo-chemically activated by transition metal ions, such as Fe²⁺, which leads to the generation of sulfate radicals (SO₄•⁻) oxidant (redox potential is E_o \approx 2.6 V) [9,10]. The reduction of peroxydisulfate anion leads to the production of sulfate anions [11].

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 $S_2 O_8^{2-} + e^- \to S O_4^{2-} + S O_4^{\bullet-}$ (1)

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Fig. 1. UV-vis spectra with main characteristics of RY17 dye.

The generated radical (SO₄ \bullet^-) is a stronger oxidant with a kinetically fast reacting tendency. The peroxydisulfate chemistry can be summarized in the following equations [12,13]:

$$S_2 O_8^{2-} \rightarrow hv \ 2SO_4^{\bullet-} \tag{2}$$

At all pH
$$SO_4^{\bullet-} + H_2O \rightarrow HSO_4^- + HO^{\bullet}$$
 (3)

Mostly in alkaline pH $SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + HO^{\bullet}$ (4)

This oxidant has been used for the treatment of organic contaminants such as Orange G [14], Coprofloxacin, Sulfamethoxazole [15], Dithyl Phthalate [16] and Catechol [17]. Compared to the other oxidants, Peroxydisulfate is a solid chemical sufficiently stable below ambient temperature ($25 \,^{\circ}$ C), very soluble in water, and it's easy for transport and storage [18]. However, at ambient temperature, peroxydisulfate is slowly reacting with contaminants in water, its activation is therefore necessary for accelerating the degradation process. Peroxydisulfate can be activated using Fe²⁺ ions because they are nontoxic, cheap and effective.

The activation of peroxydisulfate by using Fe^{2+} ions has been previously introduced into wastewater treatment; this process has many similarities to the Fenton systems which can help us to better understand the degradation mechanism [19]. Once the sulfate radicals $SO_4^{\bullet-}$ is generated, a series of reactions are propagated involving the formation of other active species, in particular the hydroxyl radical (HO[•]). The mechanism describing the Fe²⁺ activated peroxydisulfate process includes primarily the following reactions [15]:

$$S_2 O_8^{2-} + Fe^{2+} \to Fe^{3+} + SO_4^{\bullet-} + SO_4^{2-}$$
 (5)

$$SO_4^{\bullet-} + SO_4^{\bullet-} \to S_2O_8^{2-}$$
 (6)

$$SO_4^{\bullet-} + Fe^{2+} \to SO_4^{2-} + Fe^{3+}$$
 (7)

$$SO_4^{\bullet-} + S_2O_8^{2-} \to SO_4^{2-} + S_2O_8^{\bullet-}$$
 (8)

$$HO^{\bullet} + HO^{\bullet} \to H_2O_2 \tag{9}$$

$$HO^{\bullet} + SO_4^{\bullet-} \to HSO_4^- + \frac{1}{2}O_2 \tag{10}$$

$$HO^{\bullet} + S_2 O_8^{2-} \to OH^- + S_2 O_8^{\bullet-}$$
 (11)

The aim of the present work is to remove RY17 dyes from aqueous solution using the process of peroxydisulfate activated with ferrous ion. During this study, several parameters affecting the degradation process were studied, such as: The evaluation of the pH effect on the $S_2O_8^{2-}/Fe^{2+}$ and $S_2O_8^{2-}/UV$ processes, the determination of $Na_2S_2O_8$ concentration effect and Fe^{2+} dosage on the degradation efficiency. The investigation of the discoloration kinetics by $Fe^{2+}/S_2O_8^{2-}$ at optimal conditions, and the comparative study of RY17 oxidation using two salts $Na_2S_2O_8$ and $K_2S_2O_8$ were also studied. The TOC and COD analysis were done in order to prove the complete RY17 mineralization. To the best of our knowledge, no studies have been carried out on the application of the peroxydisulfate process activated with ferrous ion for the degradation of the selected dye RY17.

2. Materials and methods

2.1. Materials

All chemicals used are reagent grade: RY17 of 99.9% purity. They are kindly supplied by the National Research Center in Egypt. Sodium peroxydisulfate (Na₂S₂O₈, \geq 99%) is reagent grade and Sulfuric acid (H₂SO₄, 98%), Sodium hydroxide, Iron (II) sulfate heptahydrate (FeSO₄.7H₂O, \geq 98%), ethanol (EtOH, 99.8%) and potassium Sodium peroxydisulfate (K₂S₂O₈, \geq 99%) are of analytical grade bought from Sigma–Aldrich and Merck products. Aqueous solutions are prepared by using distilled water. The UV–vis spectra with main characteristics are provided in Fig. 1.

2.2. Experimental procedure

As shown in Fig. 2, all experiments were carried out in a cylindrical Pyrex reactor with an internal diameter of 80 mm and a height of 120 mm. A high-pressure mercury lamp (125 W, Philips HPK) emitting 365.5 nm UV light with protection against quartz tubes was placed in the center of the closed reactor. In a typical reaction experiment, a 500 mL of the RY17 solution



Fig. 2. Experimental installation of photochemical reactor.

(10 mg/L) was added to the reactor. The reaction temperature was maintained at 23 °C using a cooling water jacket around the reactor. Desirable solution pH was adjusted by sulfuric acid H_2SO_4 or sodium hydroxide NaOH using a pH meter (HANNA Instrument Ph209, HI 1332). The appropriate amounts ferric salt (catalyst) and Sodium Peroxydisulfate are introduced entirely into the photoreactor just before starting the UV lamp. At each designated sampling time, 3 mL of the sample was collected from the reactor periodically using a syringe and the reaction was stopped by adding a drop of ethanol, a well-known radical quenching agent, subsequently filtered immediately through 0.45 mm nylon filter (Millipore) membrane before the analysis.

2.3. Analytical methods

The UV–VIS spectra of the dye were recorded from 200 to 800 nm using a UV–VIS spectroscopy (JASCO V-630 Spectrophotometer). The maximum absorbance wavelength (λ_{max}) of RY17 is 402 nm. Therefore, the concentration of azo dyes in water was determined by the absorption intensity at λ_{max} . Chemical oxidation demand (COD) was tested by using colorimetric method, as described in the Standard Methods for the Examination of Water and Wastewater (5220-D; colorimetric) [20]. The total organic carbon (TOC) was also measured using a TOC analyzer (Shimadzu, model TOC-L CPH). The dye decolorization (degradation efficiency DE) used is calculated as follows:

$$\% DE = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{12}$$

where the C_0 and C_t were the concentrations of dye solution at time 0 and *t*.

3. Results and discussion

3.1. Effect of operational parameters

3.1.1. Effect of pH

The pH of aqueous solution has a significant influence on the $S_2O_8^{2-}/Fe^{2+}$ and $S_2O_8^{2-}/UV$ processes via changing the ionization degree of the organic pollutants, the surface charac-

teristics, as well as the degree of activity and solubility reaction agents [21]. Fig. 3(a) shows the influence of initial pH on the RY17 degradation using $S_2O_8^{2-}/UV$ process. As can be seen in the figure, the acid pH favored the withdrawal of dye. For the value of pH = 3, the degradation efficiency of RY17 reaches to more than 60% after 60 min of the degradation, for pH=5and pH = 10 the degradation efficiency decreases and we note a low efficiency for pH = 10. The degradation efficiency of RY17 after 60 min increases in the following order : pH 3 > pH 5 >pH 10. It is also interesting to note that RY17 is most rapidly degraded at pH = 3. In the $S_2O_8^{2-}/UV$ process, the total radical's concentration can depend heavily on pH. On the other side, in addition to sulfate radicals, high pH may produce hydroxyl radicals through sulfate radical transformation by Eq. (4). According to Fig. $3(a_1)$, the degradation rate coefficient (k) with Na₂S₂O₈ dose of 0.1 mM for the pH values of 3, 5, and 10 were 0.0162, 0.0134, and 0.0042 min^{-1} , respectively. These results show that the k value at pH 3 was 4 times higher than at pH 10. Under acidic conditions, and according to Eqs. (13) and (14), $SO_4 \bullet^-$ can be generated from acid-catalyzation [22], and react with RY17 to enhance the degradation efficiency of RY17.

$$S_2 O_8^{2-} + H^+ \to H S_2 O_8^-$$
 (13)

$$HS_2O_8^- \to SO_4^{\bullet-} + SO_4^{2-} + H^+$$
 (14)

Liang and Su [23] studied the inter-conversion from sulfate radical to hydroxyl radical by the reaction Eq. (4), and found that $SO_4^{-\bullet}$ gradually prevails at pH < 7. Both of $SO_4^{-\bullet}$ and OH are present at pH = 9 with a dominance of \bullet OH at pH = 12. Accordingly, the concentration of $SO_4^{-\bullet}$ reacting with RY17 may be lower at pH more than 5, which could be explain the slower degradation efficiency of RY17 at pH = 10. At pH = 5, the three reactions compete with each other: Eqs. (10), (15) and (16) and their simultaneous occurrence may decrease the degradation of RY 17, that is why at pH = 3 achieved a higher degradation than at pH = 5.

$$RH + SO_4^{\bullet -} \to RH^{\bullet +} + SO_4^{\bullet 2-} \ (R = RY17) \tag{15}$$

$$RH + HO^{\bullet} \to (OH) RH \tag{16}$$

Degradation experiments were also studied at pH ranged from 3 to 10 to assessing the degradation efficiency of RY 17 with the $S_2O_8^{2-}/Fe^{2+}$ process. The results are given in Fig. 3(b). The degradation of RY17 decreases for the pH value more than 3, because of different reasons : iron precipitation (Eq. (17)) and decrease in the production of free radicals derived from the electrostatic repulsion forces between oxidant and catalyst with negative surface charges and peroxydisulfate molecules of SO_5^{2-} and HSO_5^{-} [24,25]. Furthermore, the previous studies reported on peroxydisulfate process showed that the used catalyst was $FeSO_4$ [26,27]. In this sense, the best results were obtained when the initial solution pH = 3.

$$Fe^{3+} + RH \to Fe^{2+} + R^{\bullet} + H^+ \ (R = RY17)$$
 (17)

3.1.2. Influence of catalyst concentration

The rate of disappearance of RY17 is given by Eq. (18). The integration of this differential equation gives Eq. (19) consid-

(a)

pH=3

pH=5

100

90

70

80 😴



Fig. 3. Effect of initial pH on the degradation of RY17 by: (a) $S_2O_8^{2-}/UV$, (a₁) kinetics of degradation of RY17 and (b) $S_2O_8^{2-}/Fe^{2+}$. [RY17] = 10 mg/L; $[S_2O_8^{2-}] = 0.1 \text{ mM}; [Fe^{2+}] = 0.01 \text{ mM}.$

Table 1 Influence of the Fe²⁺ concentration on the degradation of RY17 using the $S_2O_8^{2-}/Fe^{2+}$ process, $[S_2O_8^{2-}] = 0.1$ mM.

(a1)

[Fe ²⁺] (mM)	[S ₂ O ₈ ²⁻]/[Fe ²⁺]	<i>R</i> ²	k _{app}	% DE
0.005	20	0.9995	0.0293	13.64
0.01	10	0.9996	0.0865	35.12
0.05	2	0.9997	0.1507	52.94
0.1	1	0.9993	0.1248	39.68
0.2	0.5	0.9994	0.0892	35.98

ering a quasi-stationary state for the concentration of radicals $SO_4^{-\bullet}$, that is, their non-accumulation in the solution. The kinetic law can be written:

$$V = {}^{-d[RY\,17]} {}^{\prime}_{dt} = k_{app} [RY\,17] = k \left[OH^{\bullet} \right] [RY\,17]$$
(18)

The integration of Eq. (18) gives:

$$\ln^{[RY\,17]} \varphi_{[RY\,17]_t} = k_{app} \,.t \tag{19}$$

The determination of apparent constant of the RY17 degradation is calculated from the slope of the curve $\ln[RY17]_0/[RY17] = f(t)$ (Fig. 4(a)).

Fig. 4 (a) shows that the degradation kinetics of RY17 follows a pseudo-first order. This is in agreement with the values of the obtained correlation coefficients. It can be also seen that the values of the apparent constants (k_{app}) increase significantly when Fe²⁺ concentration increases, until the concentration of 0,05 mM, then it decreases until the concentration of 0.2 mM as shown in Table 1.

Table 1 summarizes for different concentrations of Fe²⁺, apparent kinetic constants and degradation efficiencies during 5 min of treatment. The best obtained result is found for $[Fe^{2+}] = 0.05$ mM corresponding to the ratio 2. This ratio gives a better kinetic constant (0.15 min^{-1}) and a better degradation performance (52.9%).

Iron concentration is also an important parameter in the $S_2O_8^{2-}/Fe^{2+}$ process because it directly affects the performance of sulfate radical SO_4^{\bullet} , by catalytically decomposing $S_2O_8^{2-}$

as shown in Eq. (5), but it can also act as a scavenger of sulfate radicals [28,29], while also acting as scavengers of radicals SO4^{-•} if it is in excess.

(b)

- pH=5

pH=10

pH=3

Fig. 4 (b) shows the degradation efficiency and the evolution of the apparent kinetic constant of the degradation of RY17 by the radicals $SO_4^{-\bullet}$ depending on the initial iron concentration. The effect of different iron concentrations ranging from 0.005 to 0.2 mM on the elimination efficiency of RY17 using the $S_2O_8^{2-}/Fe^{2+}$ process was studied at an optimal pH of 3 and 0.1 mM of $S_2O_8^{2-}$. Indeed, increasing the concentration of Fe²⁺ ions between 0.005 and 0.05 mM leads to a significant increase in the discolouration from 13.6 to 52.9% compared to 7% without addition of catalyst. Thus, the value of the apparent kinetic constant is in the range of 0.15 min^{-1} . Therefore, the optimal catalyst concentration (Fe²⁺) is 0.05 mM. This value is the most appropriate for subsequent experiments, since the significant change was not observed by a further increase in the quantity of catalyst. This phenomenon could possibly be explained by the fact that the decomposition rate of $S_2O_8^{2-}$ increases substantially due to the presence of additional redox-active centers (ions Fe^{2+} [30]. However, the use of an additional concentration of 0.05 to 0.2 of Fe^{2+} ions reduced the degradation efficiency of RY17 from 53 to 39% after 5 min of treatment, which may be due to the trapping effect of $SO_4^{\bullet-}$ in the iron species (Eq. (7)).

The high concentration of catalyst Fe²⁺ in the solution is not in favor of a better degradation rate, as activators of persulfate, the ultimate oxidizing power is limited by: (a) an excessive amount of Fe²⁺ can act as a scavenger of $SO_4^{\bullet-}$ (Eq. (7)), which explains the decrease in the degradation rate of RY17 in the $S_2O_8^{2-}/Fe^{2+}$ process. (b) A high concentration of Fe²⁺ also promotes the parasitic reaction between ferric ions and sulfate radicals formed to the detriment of the reaction $S_2O_8^{2-}/Fe^{2+}$ in the medium. (c) The rapid conversion of Fe^{2+} to Fe^{3+} limits the ultimate capacity for oxidation of ferrous-peroxydisulfate process [31]. (d) The generation of excess radicals $SO_4^{\bullet-}$ followed by the disappearance of the $SO_4^{\bullet-}$ species without decomposition of the pollutant due to the combination of the species of $SO_4^{\bullet-}$ (Eq. (6)).

120

110

90

\$ 100

0.9

0.5



Fig. 4. (a) Determination of order and apparent constant degradation of RY 17 by the $S_2O_8^{2-}$ /Fe²⁺ process, (b) Evolution of apparent kinetic constant and Efficiency degradation of RY 17 as a function of Fe²⁺ concentration. [$S_2O_8^{2-}$] = 0.1 mM, [RY17] = 10 mg/L, pH = 3.0.

The results indicate that the catalytic activity of the ferrous ion allows it to be an effective agent in the degradation of RY17 using sodium peroxydisulfate. concentration of $S_2O_8^{2-}$, an adequate number of $SO_4^{-\bullet}$ radicals cannot be produced, which contributes to low oxidation rate, and reduction of removal efficiency.

3.1.3. Effect of $S_2O_8^{2-}$ concentration

Initial $S_2O_8^{2-}$ concentration can play an important role as an oxidizing agent in the $S_2O_8^{2-}/UV$ and $S_2O_8^{2-}/Fe^{2+}$ process due to the production of a broad number of $SO_4^{-\bullet}$. Fig. 5 shows the effect of $S_2O_8^{2-}$ concentration on the RY17 removal. At any particular peroxydisulfate concentration, the degradation of the RY17 is presented in the form: BMG kinetics by $S_2O_8^{2-}/Fe^{2+}$ and $S_2O_8^{2-}/UV$ process. The parameters of kinetic model at different peroxydisulfate concentrations are summarized in Table 2. The effect of different concentrations of $S_2O_8^{2-}$ on the RY17 degradation efficiency is investigated in the range of 0.1-2 mM peroxydisulfate using $S_2O_8^{2-}/UV$ and $S_2O_8^{2-}/Fe^{2+}$ processes for 10 mg/L of RY17 solution with the optimum value of pH fixed at 3.0, and the iron concentration of 0.05 mM. According to the Fig. 5 and Table 2, the degradation of RY17 increases significantly with increasing the peroxydisulfate concentration from 0.1 to 2 mM. This phenomenon can be explained by the fact that more reactive radicals are generated for the degradation of RY 17 at higher S₂O₈²⁻ concentrations. Herein, by increasing the concentration of $S_2O_8^{2-}$, more $S_2O_8^{2-}$ molecules could reach the surface of dye and subsequently react with Fe²⁺, which improves the degradation of RY17. But, further increase in $S_2O_8^{2-}$ concentration to 1.0 mM decreased slightly the elimination of RY17. The higher peroxydisulfate concentration provides more sulfate radicals which act in favor of target contaminants degradation [32,33]. Therefore, 1.0 mM is considered as an optimum dose of $S_2O_8^{2-}$ and applied for next experiments. The experiments with the catalyst were done for 3 times and the reproducibility was about 2.8%.

So, it was noticed that any enhancement in the concentrations of applied $S_2O_8^{2-}$ did not increase continuously the elimination of the contaminant due to the possibility of reaction of sulfate and hydroxyl radicals (Eq. (10)), the recombination of both sulfate and hydroxyl radicals (Eqs. (6) and (9)) and peroxydisulfate scavenging reactions (Eqs. (8) and (11)) [34]. However, at low

3.2. Kinetic study at optimum condition

In the kinetic study, first and second order reaction kinetics are used to study the degradation kinetic of the RY 17 by the $S_2O_8^{2-}/Fe^{2+}$ process. The obtained kinetic parameters are illustrated in Fig. 6(a)–(c). As can be seen in the figure, the BMG kinetics model shows a higher correlation coefficient (0.99) compared to that based on the first-order (0.83) and the second-order (0.96). The results indicate that the BMG kinetics is the best model to describe the degradation of RY17 by the $S_2O_8^{2-}/Fe^{2+}$ process. The linear forms equations of first-order, second-order and BMG models are given in Table 3. The BMG mathematical model to simulate the reaction kinetics has proposed by Behnajady, Modirshahla and Ghanbery [35]. Previous studies reported that these results are consistent with the results of the decolonization of other contaminants in aqueous solution by Fenton process [36,37].

Where k_1 and k_2 represent the apparent kinetic rate constant of pseudo first and second-order kinetic model, respectively; (*t*) is the reaction time, [RY17] is the concentration of RY17 at time *t*, [RY17]₀ is the initial concentration of RY17 at time t = 0, (*m*) and (*b*) are two constants characteristic relating to the reaction kinetics and oxidation capacity, and (*k*) is the observed degradation rate coefficient (Table 4).

Fig. 6(d) presents the operational experiments realized for RY 17 degradation using different processes: $S_2O_8^{2-}$, UV, $S_2O_8^{2-}/UV$, $S_2O_8^{2-}/Fe^{2+}$ and $S_2O_8^{2-}/Fe^{2+}/UV$. The optimum conditions for the experimental results are : pH=3, the iron concentration is 0.05 mM, the $S_2O_8^{2-}$ concentration is 1 mM and the RY17 concentration is 10 mg/L (see Fig. 6). Note that the degradation efficiencies of the individual processes (UV, $S_2O_8^{2-}$) are lower than those of the simultaneous processes, that can be associated with the lower oxidation potential of UV and peroxydisulfate and the lack of effectiveness of these to remove contaminants [25].



Fig. 5. Degradation of RY17 by: (a) $S_2O_8^{2-}/UV$ and (b) $S_2O_8^{2-}/Fe^{2+}$ at different $S_2O_8^{2-}$ concentrations. [RY17] = 10 mg/L; $Fe^{2+} = 0.05$ Mm.

Table 2 The parameter of BMG kinetic model of the degradation of RY 17at different $S_2O_8^{2-}$ concentrations by: (a) $S_2O_8^{2-}/UV$ and (b) $S_2O_8^{2-}/Fe^{2+}$.

[S ₂ O ₈ ²⁻] (mM)				BMG kir	netic model			
	S ₂ O ₈ ²⁻ /UV			S ₂ O ₈ ²⁻ /Fe ²⁺				
	$\overline{Y=ax+b}$	1/m	1/b	R^2	Y = ax + b	1/m	1/b	R^2
0.1	0.146x + 2.903	0.344	6.849	0.8257	0.201x + 0.183	5.464	4.975	0.9993
0.2	0.111x + 1.554	0.643	9.01	0.9054	0.171x + 0.219	4.566	5.847	0.9989
0.5	0.118x + 0.945	1.058	8.474	0.9656	0.143x +0.357	2.801	6.993	0.9939
1	0.101x + 0.586	1.706	9.901	0.9764	0.150x + 0.494	2.024	6.666	0.9958
2	0.103x + 0.494	2.024	9.708	0.9836	0.143x + 0.194	5.144	6.993	0.9979

Table 3

Linear forms equations of the first-order, second-order and BMG reaction kinetics.

Reaction order	First order reaction kinetics	Second reaction kinetics	BMG kinetics
Differential rate equation	$\frac{-d[RY17]}{dt} = K_1 [RY17]$	$\frac{-d[RY17]}{dt} = K_2 [RY17] [SO_4^{-}]$	$\frac{[RY17]}{[RY17]} = 1 - \frac{t}{m} + b$
Integrated Rate equation	$[RY17] = [RY17]_0 e^{-K_1 t}$	$[RY17] = \frac{[RY17]_0}{1+K_2t[RY17]}$	[KI17]0 m
Characteristic Kinetic Plot	$ln(\frac{[RY17]_0}{[RY17]}) = f(t)$	$\frac{1}{[RY17]} = f(t)$	$\frac{t}{1 - \frac{[RY17]}{[RY17]_{\circ}}} = f(t)$
Units of Rate constant	Min^{-1}	$L. mol^{-1}. min^{-1}$	Min

Table 4

The parameters of kinetic models for degradation of RY17.

Kinetic models	First order		Second order		BMG		
Parameters	$k_1(\min^{-1})$ 0.019	R^2 0.825	$k_2 \text{ (min}^{-1}\text{)}$ 0.007	<i>R</i> ² 0.961	1/m 2.024	1/b 6.666	<i>R</i> ² 0.994

The obtained degradation efficiencies of RY17 by $S_2O_8^{2-}$, UV, $Fe^{2+}/S_2O_8^{2-}$, $S_2O_8^{2-}$ /UV and $Fe^{2+}/S_2O_8^{2-}$ /UV processes are, respectively, 6.2%, 9.6%, 63.3%, 81.0% and 95.4%, during 20 min of reaction. On the other hand, the better performance of the simultaneous processes can be attributed to the formation of reactive oxidizing specie radical $SO_4^{\bullet-}$ playing an important role in the oxidative catalysis of RY17. These results indicate that the peroxydisulfate molecules decomposed effectively in the presence of UV light rather than Fe^{2+} . Furthermore, when iron ions, UV light and peroxydisulfate are

utilized together, we can reach the highest degradation efficiency of RY17 (95.4%). This increase might be due to the presence of both activators (Fe²⁺ and UV) resulting in efficient decomposition of $S_2O_8^{2-}$ and also to the presence of radical $SO_4^{\bullet-}$ in the solution [30]. In $S_2O_8^{2-}/UV$ and $S_2O_8^{2-}/Fe^{2+}/UV$ process, both Fe²⁺ and UV and only UV light plays a significant role in the $S_2O_8^{2-}$ decomposition to produce the free radical $SO_4^{\bullet-}$. The results confirm that UV and Fe²⁺/UV have high potential in activation of peroxydisulfate molecules and have therefore an effective in the catalytic oxidation of azo dye



Fig. 6. (a) First-order reaction kinetics, (b) second order reaction kinetics, (c) BMG kinetics, for degradation of RY17 by $S_2O_8^{2-}/Fe^{2+}$ process, and (d) Kinetics comparison between applied processes for RY17 removals from aqueous solution. [$S_2O_8^{2-}$] = 1 mM, [Fe^{2+}] = 0.05 mM, [RY17] = 10 mg/L, pH = 3.

via generation of reactive species. According to these results, the degradation efficiency of RY17 dye increases in the following order: $S_2O_8^{2-}/Fe^{2+}/UV > S_2O_8^{2-}/UV > S_2O_8^{2-}/Fe^{2+} > UV > S_2O_8^{2-}$.

3.3. The mineralization study

The mineralization assessment was studied through COD and TOC analysis during the degradation process of RY17 in aqueous solution. In order to confirm the mineralization of RY17 using $S_2O_8^{2-}/Fe^{2+}/UV$ process, Table 6 present the results of COD and TOC analysis as a function of degradation time in optimum experimental conditions (0.05 mM iron dosage, 1 mM PDS dose, pH 3 and T=25 °C). As listed in Table 5, around 100% of RY17 was degraded within 60 min. Using $S_2O_8^{2-}/Fe^{2+}/UV$ process, the mineralization percentage was 68.2 and 49.4% respectively for COD and TOC analysis and these percentages increase with degradation time. These results are probably caused by the specific oxidation pathway of the dye. Additionally, ecological toxicity of intermediate products could be avoided when the contact time was enough to mineralize the tar-

Table 5			
Mineralization	ı of	RY	17

Time (min)	COD (%)	TOC (%)
30	30.7	18.2
60	68.2	49.4
90	90.4	62.5
120	96.1	74.3
180	100	80.2

get pollutants into non-toxic CO₂ and H₂O by $S_2O_8^{2-}/Fe^{2+}/UV$ process.

3.4. Comparative study of the degradation and mineralization of RY17 between two salts $Na_2S_2O_8$ and $K_2S_2O_8$

The peroxydisulfate is normally available as a salt associated with ammonium, sodium, or potassium. Salari et al. [13] reported that potassium peroxydisulfate (K_2S_2O8) gives a better result in photo-oxidative removal of some organic materials than (NH₄)₂S₂O₈ showing instability due to the oxidation of the ammonium and ammonia by peroxydisulfate [38].

lable 6	
Comparison of the degradation efficiency (%) of RY17 between $Na_2S_2O_8$ and $K_2S_3O_8$	S_2O_8 .

Oxidative treatment Time	SPDS /UV	SPDS /Fe ²⁺	SPDS /Fe ²⁺ /UV	PPDS /UV	PPDS /Fe ²⁺	PPDS /Fe ²⁺ /UV
5 min	26.57	50.77	67.88	34.52	55.99	74.73
30 min	89.36	68.42	98.09	91.20	70.66	99.23
60 min	92.26	79.69	100	94.11	82.54	99.98

*PPDS: Potassium peroxydisulfate; *SPDS:Sodium peroxydisulfate.

Table 7

Summary of the degradation processes applied in treatment of RY 17.

Method	Operational condition	Analytical method	Results	Reference
Fenton	- [Fe ²⁺] = 0.005–0.15 Mm - [H ₂ O ₂] = 0.01–0.2 mM - [RY17] = 10 mg/L - nH = 3	UV-Vis	- RY 17 removal = 67.5% (20 min)	[40]
Photo-Fenton	- Black light (125 W) - [Fe ²⁺] = 0.01 mM - [H ₂ O ₂] = 0.1 mM - [RY17] = 10 mg/L - nH = 3	UV-Vis, COD	- RY 17 removal = 89 % (20 min) - COD removal = 93.08% (120 min)	[41]
Electro-Fenton	$ \begin{array}{l} -1 = 60 - 100 \text{ Ma} \\ - [\text{Fe}^{2+}] = 0.02 - 0.04 \text{ mM} \\ - [\text{RY}17] = 5 - 10 \text{ mg/L} \\ - [\text{Na}_2 \text{SO}_4] = 50 \text{ mM} \\ - \text{nH} = 3 \end{array} $	UV-Vis, COD, HPLC	- RY 17 removal = 87% (20 min) - COD removal = 89% (120 min)	[42]
Anodic Oxidation	-1 = 100 Ma - [RY17] = 5 mg/L $- [\text{Na}_2 \text{SO}_4] = 50 \text{ mM}$ - pH = 3	UV-Vis	- RY 17 removal = 94 % (60 min)	[41]
PDS/UV process	- Black light (125 W) - $[S_2O_8^{2-}] = 0.1-2 \text{ mM}$ - $[RY17] = 10 \text{ mg/L}$ - $pH = 3-10$	UV-Vis	RY 17 removal = 81 % (20 min)	Present study
Fe ²⁺ /PDS/UVProcess	- Black light (125 W) - $[Fe^{2+}] = 0.005 - 0.2 \text{ mM}$ - $[S_2O_8^{2-}] = 0.1 - 2 \text{ mM}$ - $[RY17] = 10 \text{ mg/L}$ - $pH = 3 - 10$	COD, UV-Vis, TOC	RY 17 removal = 95.4% (20 min) COD removal = 96.1% (120 min) TOC removal = 74.3% (120 min)	Present study

In addition, as reported by other researcher [39], the sodium peroxydisulfate is preferred for use in the field. Because, it is sufficiently stable at or below ambient temperature ($25 \circ C$), while it is stored in the solid form. With that, and the inadequacy of adding ammonia to water, $K_2S_2O_8$ and $Na_2S_2O_8$ are the best choice for using in the UV/peroxydisulfate oxidation process. Moreover, potassium peroxydisulfate and sodium peroxydisulfate are much less expensive than other oxidants such as hydrogen peroxide. From Fig. 7 and Table 6, the efficiency of $K_2S_2O_8/Fe^{2+}$ and $Na_2S_2O_8/Fe^{2+}$ processes increases rapidly with UV irradiations in the first minutes.

The RY17 discoloration with $K_2S_2O_8$ salt shows a strong degree of similarity with $Na_2S_2O_8$ salt. Accordingly, there is no salt effect. RY 17 mineralization degree in $S_2O_8^{2-}/Fe^{2+}/UV$ process was studied using two salts $Na_2S_2O_8$ and $K_2S_2O_8$. In this regards, the oxidation experiments were carried out for 10 mg/L RY 17 concentrations in optimum experimental conditions (0.05 mM iron dosage, 1.0 mM PDS dose and pH 3).



Fig. 7. Comparison of degradation efficiency of RY17 between two salts $Na_2S_2O_8$ and $K_2S_2O_8$. [RY17] = 10 mg/L, $[S_2O_8^{2-}] = 1$ mM, $[Fe^{2+}] = 0.05$ mM and pH = 3.

3.5. Comparison with the other advanced oxidation methods

Among different methods, the advanced oxidation process is a promising treatment for the removal of different azo dyes, especially RY 17. As shown in Table 7, many researchers have surveyed the RY17removal in aqueous solution through various advance oxidation processes. In comparison to the other studies (Table 7), the UV light with iron ions as activators of peroxydisulfate process is an effective method for the removal of RY 17, and it provide good removal efficiency. Additionally, the advantages of this method such as moderate cost, high stability, and aqueous solubility make it more suitable

4. Conclusion

In this study, Peroxydisulfate activated using Fe²⁺ an ion was evaluated as a process for RY17 removal from aqueous solution. The obtained results indicate that $S_2O_8^{2-}/Fe^{2+}/UV$ process provide a good performance compared to $S_2O_8^{2-}/UV$ for RY17 degradation. The degradation efficiency of $S_2O_8^{2-}/Fe^{2+}$, S₂O₈²⁻/UV and S₂O₈²⁻/Fe²⁺/UV processes was respectively 63.3%, 81.0% and 95.4% within 20 min of reaction. RY17 degradation was found to be affected by changing some parameters such as pH of the solution, initial concentrations of Fe²⁺ and $S_2O_8^{2-}$ with UV. The optimum conditions for a high RY17 removal were determined at pH=3, $[Fe^{2+}]=0.05$ mM, $[S_2O_8^{2-}] = 1 \text{ mM}, [RY17] = 10 \text{ mg/L}, \text{ and room temperature}.$ Although $S_2O_8^{2-}$ is essential for the generation of the sulfate radicals $SO_4^{-\bullet}$, a very high amount of $S_2O_8^{2-}$ and Fe^{2+} could reduce degradation efficiency, which may be due to the scavenging effect.

The kinetic studies indicated that the degradation of RY17 was well described by the BMG kinetics models. On other hand, the comparative study of the RY17 degradation efficiency between two salts Na₂S₂O₈ and K₂S₂O₈ shows similar results, and a total mineralization degree was obtained at the optimum conditions. Consequently, S₂O₈²⁻/Fe²⁺/UV process can be used for the treatment of water discharge containing azo dyes such as RY17; this process is very effective and less expensive than conventional processes.

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