

Original Research

**THERMALLY ACTIVATED PEROXYDISULFATE DEGRADATION OF
REACTIVE TEXTILE DYES**

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Abstract

This study examines the potential degradation of the anthraquinone textile dye Reactive Blue 19 (RB 19) and the azo dye Reactive Orange 16 (RO 16) through the application of thermally activated peroxydisulfate. The influence of basic operating parameters, such as the initial pH value of the solution, initial peroxydisulfate concentration, and temperature, was investigated. The degradation reaction followed pseudo-first-order kinetics for both dyes under investigated conditions. The degradation rate constants for these dyes increased with a rise in the concentration of peroxydisulfate up to a certain threshold, as well as with an increase in temperature, and in an acidic environment. The findings offer significant insights into the implementation of advanced oxidation processes utilizing thermally activated persulfate for the remediation of textile dye contaminated wastewater.

Keywords: wastewater, advanced oxidation processes, sulfate radicals, decolorisation.

INTRODUCTION

In the context of rapid industrial development, the daily discharge of wastewater is increasing, and the composition of organic pollutants within this wastewater is becoming progressively more complex [1]. This trend poses a significant threat to human health and the environment. Organic contaminants, such as pharmaceuticals, pesticides, and textile dyes, cannot be completely degraded using conventional wastewater treatment; therefore, developing an effective treatment to eliminate these pollutants from aqueous media and preventing the formation of toxic byproducts is required.

Advanced oxidation processes (AOPs) rely on the *in-situ* production of reactive species which have a high redox potential and are non-selective; therefore, they can oxidize any organic contaminant [2]. In the initial stages of research on advanced oxidation processes, the emphasis was predominantly on the role of hydroxyl radicals and the utilization of hydrogen peroxide as an oxidant. However, there has been a growing interest in processes that involve

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the activation of persulfates, such as peroxymonosulfate (PMS) or peroxydisulfate (PDS). Generally, persulfates without activation exhibit poor activity toward most organic pollutants. Persulfates achieve high oxidation capacity through two pathways: (a) radical oxidation via the generation of sulfate radicals ($\text{SO}_4^{\bullet-}$, 2.5–3.1 V) and hydroxyl radicals ($\cdot\text{OH}$, 1.8 V) and (b) non-radical processes based on singlet oxygen ($^1\text{O}^2$) and electron-transfer pathways [3]. Various methods have been employed for persulfate activation in the past decades, involving UV light, heat, ultrasound, alkalis, and catalysts [1].

One of the first methods used to activate persulfates in situ was heating. The production of two sulfate radicals can be accomplished by cleavage of the peroxide bond when an appropriate amount of energy equal to the bond dissociation energy is applied into the persulfate anion (equation 1) [4].



The activation energy for thermally activated persulfates decreased from 134 kJ/mol under neutral conditions to 116 kJ/mol and 129 kJ/mol under acidic and neutral conditions, respectively [5]. Practically, temperatures up to 30 °C resulted in negligible activation of the oxidant, with its half-life extending from days to month. Conversely, at temperatures ranging from 40 to 70 °C, the half-life is reduced to hours or even minutes.

While the heat-activated persulfate process is energy-intensive, it offers several advantages over alternative methods. Notably, it does not necessitate the use of rare or costly catalysts and is not constrained by size-scaling limitations associated with radiation-based techniques. Furthermore, the process requires minimal equipment and is relatively straightforward to manage. It presents a viable option for the industrial-scale application of heat or steam cogeneration. Additionally, integrating this process with renewable energy sources can mitigate its environmental and energy impacts.

In this study, the degradation of two textile dyes with different structures was examined using thermally activated peroxydisulfate. The investigation focused on the influence of varying initial peroxydisulfate concentrations, initial pH values, and reaction temperatures on the degradation characteristics. This research may offer an effective method for the removal of textile dyes in wastewater treatment processes.

MATERIALS AND METHODS

All used chemicals were reagent grade and were purchased from Sigma-Aldrich (USA). All solutions were prepared with ultrapure water from the Smart2Pure system with a conductivity of $0.055 \mu\text{S m}^{-1}$ (Thermo Scientific, USA).

All experiments were conducted using 100 cm^3 of working solution, which contained the specified initial oxidant ($\text{S}_2\text{O}_8^{2-}$) concentration, the textile dye RB 19 or RO 16, and at the corresponding pH values. The influence of each effect was examined by varying its value while keeping the other parameters constant. The degradation experiments were carried out in a thermostat in batch condition. Sampling of the dye solution was carried out at the beginning of the treatment and at time intervals of 5, 10, 15, 20 and 25 minutes, respectively. The absorbance of RB 19 dye was measured using a UV-Vis spectrophotometer UV-1800

(Shimadzu, Japan) at the wavelength of the maximum absorption of this dye of 592 nm, while the absorbance of RO 16 was measured at a wavelength of 494 nm.

The pseudo-first-order kinetic model, represented by equation (2), was employed to monitor the kinetics of each textile dye degradation [6]:

$$\ln \frac{c_t}{c_0} = -k_{\text{app}} t \quad (2)$$

where c_0 is the initial dye concentration, c_t is textile dye concentration at treatment time t , k_{app} is the apparent pseudo-first-rate constant, t is the treatment time. By plotting $\ln(c_t/c_0)$ against time, the k_{app} values were derived from the experimental data. The obtained values of the coefficient of determination r^2 for each investigated conditions were sufficiently high to confirm that the degradation kinetics of the textile dyes RB 19 and RO 16 by thermally activated peroxydisulfate followed pseudo-first-order reaction kinetics.

RESULTS AND DISCUSSION

Effect of initial pH

The results presented in Figure 1a show a decrease in the pseudo-first-order rate constant with an increase in the initial pH for thermally activated persulfate degradation of textile dye RB 19. The obtained pseudo-first-order rate constant was 0.117 min^{-1} ($r^2 = 0.93$) in acidic medium and decreased significantly in neutral medium to 0.072 min^{-1} ($r^2 = 0.98$). Further increases in pH led to a slight decrease in the pseudo-first-order rate constant, which was 0.061 min^{-1} ($r^2 = 0.99$) in an alkaline medium. The results presented in Figure 1b show that the pseudo-first-order rate constant for thermally activated persulfate degradation of textile dye RO 16 decreased with increasing initial pH values. The pseudo-first-order rate constant was 0.09 min^{-1} ($r^2 = 0.93$) in acidic medium and decreased significantly to 0.06 min^{-1} ($r^2 = 0.88$) in neutral medium. Further increases in pH led to a slight decrease in the pseudo-first-order rate constant, which reached value 0.052 min^{-1} ($r^2 = 0.87$) in an alkaline medium.

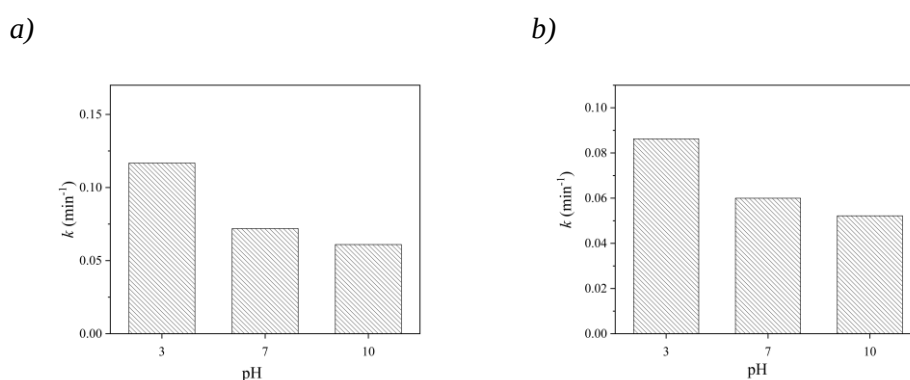
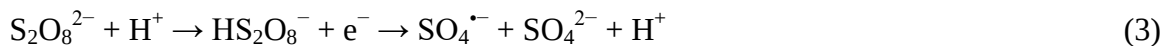


Figure 1 Effect of initial pH value on pseudo-first-order rate constant for thermally activated peroxydisulfate degradation of textile dyes: a) RB 19; b) RO 16

Generally, the initial pH of the solution can favor, hinder, or have no effect on organic pollutant elimination. The pH of aqueous solutions can affect the distribution and yield of

reactive species, which directly affects the rate of micropollutant degradation. Under neutral conditions, there is a contribution from both reactive species ($\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$), whereas under acidic conditions, persulfate can undergo acid-catalyzed degradation with the formation of a larger amount of $\text{SO}_4^{\bullet-}$ according to the reaction (3) [7].



Effect of initial peroxydisulfate concentration

The results presented in Figure 2a revealed that there is a significant increase in the pseudo-first-order reaction rate constant for thermally activated peroxydisulfate degradation of textile dye RB 19 from 0.032 min^{-1} ($r^2 = 0.96$) to 0.22 min^{-1} ($r^2 = 0.99$) with an increase in the initial peroxydisulfate concentration from 5 to 40 mmol dm^{-3} . Further increasing the initial peroxydisulfate concentration decreased the pseudo-first-order reaction rate constant, whose value was 0.14 min^{-1} ($r^2 = 0.98$) for an initial peroxydisulfate concentration of 80 mmol dm^{-3} . The results from Figure 2b revealed that there is a significant increase in the value of the pseudo-first-order reaction rate constant from 0.005 min^{-1} ($r^2 = 0.9$) to 0.113 min^{-1} ($r^2 = 0.97$) with an increase in the initial peroxydisulfate concentration from 5 to 40 mmol dm^{-3} in case of thermally activated peroxydisulfate degradation of textile dye RO 16. Further increasing the initial peroxydisulfate concentration led to a slight increase in the pseudo-first-order reaction rate constant, whose value was 0.12 min^{-1} ($r^2 = 0.98$) for an initial peroxydisulfate concentration of 80 mmol dm^{-3} .

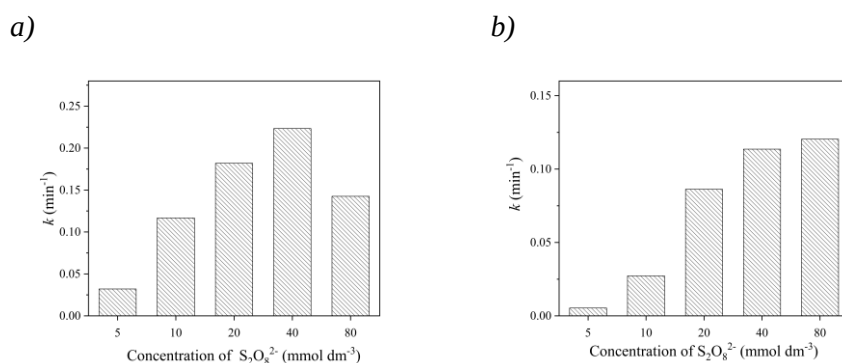


Figure 2 Effect of initial peroxydisulfate concentration on pseudo-first-order rate constant for thermally activated peroxydisulfate degradation of textile dyes: a) RB 19; b) RO 16

The increase in the removal efficiency of the investigated textile dyes RB 19 and RO 16 with an increase in the initial peroxydisulfate concentration may be due to an increase in the rate of formation of sulfate anion radicals, according to equation 1. An increase in the initial concentration of peroxydisulfate from 40 to 80 mmol dm^{-3} did not lead to a proportional increase in the removal efficiency of the investigated textile dyes. This trend is probably due to the reaction of the sulfate anion radical with the peroxydisulfate anion, as well as the sulfate anion radicals with each other, when the peroxydisulfate anion is present in excess, as shown by the reactions (5) and (6) [8].



Finally, the addition of large amounts of oxidants should be performed with caution. Although this usually increases the efficiency of the process, it also increases the cost of supplying the chemicals. Simultaneously, upon activation, each persulfate ion is converted into two sulfate ions, which present in high concentrations can be considered as pollutants.

Effect of temperature

The results from Figure 3a depict that the pseudo-first-order reaction rate constant increases slightly from 0.01 min^{-1} ($r^2 = 0.98$) to 0.03 min^{-1} ($r^2 = 0.98$) with an increase in temperature from 40 to 50 °C in case of thermally activated peroxydisulfate degradation of textile dye RB 19. Further increasing the temperature to 60 °C and 70 °C led to a significant increase in the pseudo-first-order reaction rate constant to 0.117 min^{-1} ($r^2 = 0.93$) and 0.132 min^{-1} ($r^2 = 0.82$), respectively. The results for thermally activated peroxydisulfate degradation of textile dye RO 16 (Figure 3b) revealed that the pseudo-first-order reaction rate constant increases slightly from 0.06 min^{-1} ($r^2 = 0.89$) to 0.008 min^{-1} ($r^2 = 0.88$) with an increase in temperature from 40 to 50 °C. Further increasing the temperature to 60 °C and 70 °C led to a significant increase in the pseudo-first-order reaction rate constant to 0.089 min^{-1} ($r^2 = 0.93$) and 0.162 min^{-1} ($r^2 = 0.91$), respectively.

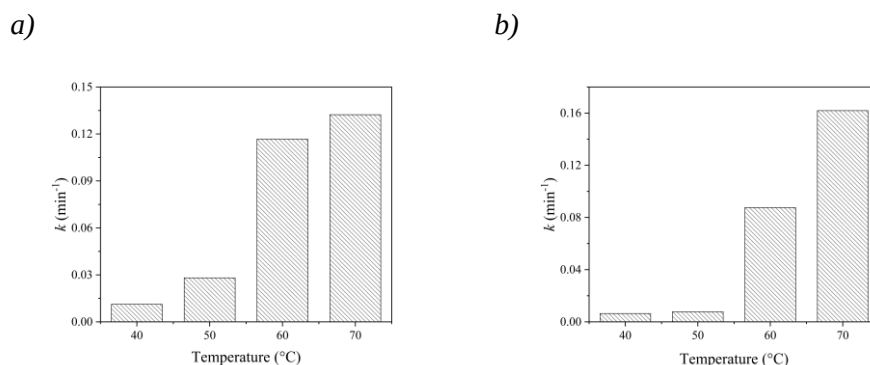


Figure 3 Effect of temperature on pseudo-first-order rate constant for thermally activated peroxydisulfate degradation of textile dyes: a) RB 19; b) RO 16

It can be assumed that the rate of pollutant degradation by thermally activated persulfate increases with increasing temperature, because the concentration of generated reactive species, such as $\text{SO}_4^{\bullet-}$, which are available for pollutant degradation increases (reaction 1). Although increased temperatures generally favor thermally activated persulfate processes owing to the increase in the concentration of generated radicals, the energy costs are high at very high temperatures. In addition, the rapid formation of radicals, specific to high-temperature processes, is accompanied by a faster rate of interaction of sulfate radicals, which can lead to unnecessary consumption of persulfate [9]. Dominguez et al. (2020) suggested that persulfate degradation consists of two simultaneous/parallel reactions: a) the production of sulfate radicals and b) non-productive persulfate degradation [10]. The activation energy of persulfate is between 128.48 and 140.16 kJ/mol, while the apparent activation energy of

organic pollutants ranges from 80 to 160 kJ/mol [11]. Therefore, for certain organic pollutants, increasing the temperature favors non-productive persulfate degradation rather than the oxidation of organic pollutants. Moreover, from an engineering point of view, the choice of process temperature requires a preliminary calculation of energy and chemical costs to achieve the required efficiency in a time frame that allows industrial application.

The temperature dependence of k_{app} can be estimated using the Arrhenius equation [4]. The apparent activation energy for each organic pollutant was calculated using a linear regression of the graphical dependence of $\ln k_{app}$ as a function of $1/T$. In general, a higher activation energy of an organic pollutant indicates that it is more difficult to degrade using thermally activated persulfate. Based on the experimental results, the apparent activation energies of the textile dyes RB 19 and RO16 were 79 kJ/mol and 107.6 kJ/mol, respectively. The lower values of the apparent activation energy of the textile dye RB 19 by thermally activated peroxydisulfate indicate that the degradation of this dye is favored over the degradation of the textile dye RO 16. Based on data from the literature on the apparent activation energies of some organic pollutants, such as trimethoprim (177.8 kJ/mol), ketoprofen (169.74 kJ/mol), atrazine (141 kJ/mol), p-nitrophenol (127.8 kJ/mol), and bisphenol A (133.5 kJ/mol), it can be concluded that both tested textile dyes are more susceptible to degradation by thermally activated peroxydisulfate than the above-mentioned compounds [11].

CONCLUSION

It can be concluded that the thermally activated peroxydisulfate degradation of the textile dyes RB 19 and RO 16 was favored in acidic environments compared to neutral and alkaline environments. The pseudo-first-order rate constant of the tested textile dyes depended on the initial peroxydisulfate concentration and increased with increasing its concentration up to 40 mmol dm⁻³. Further increases in the oxidant concentration led to a significant decrease in the pseudo-first-order rate constant of the textile dye RB 19, whereas the rate constant of the dye RO 16 changed slightly. An increase in the treatment temperature led to an increase in the degradation rate constants of the tested dyes. The apparent activation energies for the degradation of textile dye RB 19 and RO 16 were 79 and 107.6 kJ/mol, respectively, indicating that the degradation of RB 19 dye was favored over the degradation of textile dye RO 16 by thermally activated peroxydisulfate.

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