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Degradation of Safranin O by thermally activated persulfate in the presence of mineral and organic additives: impact of environmental matrices

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ABSTRACT

This work explores the degradation of Safranin O (SO), an organic dye pollutant, in water by thermally activated persulfate (PS). The effect of operating parameters, i.e., PS and SO initial concentrations (100–2,000 mg L^{-1} for PS and 3–100 mg L^{-1} for SO), temperature (20°C–70°C) and initial solution pH (3–13) on the degradation rate of the dye was investigated. Additionally, the effect of several mineral (NaCl, K_2SO_4, $NaHCO_3$ and $FeSO_4$) and organic (humic acids [HAs] and surfactant) additives on the oxidation of SO was clarified. Besides, the efficiency of the heat-activated PS to remove SO from real environmental matrices such as natural mineral water and seawater was proven. The obtained results showed that SO (10 mg L^{-1}) was completely removed after ~1 h of treatment at 50°C with 2,000 mg L^{-1} of PS. The chemical probes experiments showed that $SO_4^{\bullet-}$ was the main species involved in the degradation of SO. The degradation rate of the dye increased significantly with increasing PS and SO initial concentrations, liquid temperature and initial solution pH. While K_2SO_4 has no impact on the degradation kinetics of SO, NaCl slightly inhibited it and a relatively more inhibition was observed with $NaHCO_3$. However, the presence of $FeSO_4$ drastically enhanced the degradation of the dye. The presence of HA decreased the efficiency of the heat/PS process toward the elimination of SO and the inhibition degree was much markedly at high HA concentrations. Unexpectedly, sodium dodecyl sulfate anionic surfactant enhanced the degradation rate of the dye at the initial stage of the treatment. The degradation of SO slightly decreased in mineral water and seawater compared with that observed in deionized water, making heat/PS treatment a promising technique for treating contaminated environmental samples.

Keywords: Degradation; Safranin O (SO); Persulfate (PS); Sulfate radical ($SO_4^{\bullet-}$); Hydroxyl radical ($\bullet$OH)

1. Introduction

Water pollution due to discharge of colored effluents from textile dye manufacturing is one of the major environmental concerns in today's world. 10%–25% of textile dyes are lost during the dyeing process, and 2%–20% are directly discharged as aqueous effluents in different environmental components [1]. The discharge of very small amounts of dyes is aesthetically displeasing, impedes light penetration, affects gas solubility damaging the quality of the receiving streams and may be toxic to treatment processes, to chain organisms and to aquatic life [1]. Moreover, these chemicals

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present a potential human health risk as some of them have been proven or are suspected to be carcinogenic as they generate toxic aromatic amine by hydrolysis [2]. Biological and physicochemical treatments and their various combinations are the most used methods for the elimination of dyes from polluted wastewater. However, these techniques are financially and often methodologically demanding, time consuming and mostly not very effective [3,4]. Recently, there has been increasing interest in the application of the so-called advanced oxidation processes (AOPs) as attractive alternative treatments for the degradation of dyes in wastewater [5,6]. These techniques are based on the in situ production and utilization of highly oxidative free radicals as oxidation agents [7].

Several AOPs based on the generation of $HO^\bullet$ such a Fenton (Fe^{2+}/H_2O_2), UV/H_2O_2, O_3/H_2O_2, photocatalysis and sonolysis have been widely applied in wastewater treatment and pollution control [8,9]. Lately, sulfate radical ($SO_4^{\bullet-}$) based AOPs gained growing attention as $SO_4^{\bullet-}$ has a relatively high standard reduction potential of 2.6 V [10], which is comparable to that of $HO^\bullet$ (E_0 = 2.8 V vs. NHE [10]). Second-order rate constant for the reaction of $SO_4^{\bullet-}$ with organic compound ranges from 10^6 to 10^9 M^{-1} s^{-1} [11,12]. Sulfate radical can be produced via activation of persulfate (PS) and peroxymonosulfate by ultraviolet light [13–15], transition metals [16–20], bases [21], sonolysis [22,23], radiolysis [24], microwaves [25] and organics [26,27].

Thermally activated PS is one of the promising techniques for the generations of sulfate radicals [11]. This technique, which was found to provide a prominent alternative for the decomposition of several organic contaminants, e.g., chlorinated hydrocarbons [28–31], aromatics [21,28,32], pharmaceuticals [33] and dyes [34,35], possesses several advantages compared with other activation approaches. For instance, heat activation required no additional chemicals, which minimizes the consumption of PS during its pre-mixing with activators [11]. Under the action of heat, the peroxide band of PS will be broken to generate two $SO_4^{\bullet-}$, as in Eq. (1). Once it is formed, $SO_4^{\bullet-}$ can rapidly attack oxidizable compounds including organic contaminants. Sulfate radical can be simultaneously transformed into sulfate ions and produce hydroxyl radical ($HO^\bullet$) as in Eqs. (2) and (3).

$$S_2O_8^{2-} \xrightarrow{\Delta H} 2SO_4^{\bullet-};\ k = 1.0\times10^{-5}\,s^{-1}\left(70\ °C\right) \qquad (1)$$

All pHs:

$$SO_4^{\bullet-} + H_2O \rightarrow HO^\bullet + H^+ + SO_4^{2-};\ k = 360\ s^{-1} \qquad (2)$$

Alkaline pH:

$$SO_4^{\bullet-} + HO^- \rightarrow HO^\bullet + H^+ + SO_4^{2-};\ k = 6.5\times10^7\,M^{-1}s^{-1} \qquad (3)$$

Eqs. (2) and (3) imply the potential coexistence of $SO_4^{\bullet-}$ and $HO^\bullet$, which has been evidenced by electron spin resonance (ESR) [36] and chemical probes method [37]. When pH is above 7, the conversion of $SO_4^{\bullet-}$ to $HO^\bullet$ via Eq. (3) becomes increasingly important. Both radicals are potentially responsible for the oxidation of organic contaminants, and either radical may predominate over the other depending on pH [36,37].

In this study, the degradation of Safranin O (SO) by thermally activated PS was assessed. SO is a phenazine dye of the quinone-imine class that has been widely used in textile and as a photosensitizer in electron- and energy-transfer reactions [38]. Also, it is used as a sensitizer in visible light photopolymerization [39]. Since the dye is known to be carcinogenic in nature [40], any presence of this dye in wastewater would have detrimental effects on aquatic life. Several $HO^\bullet$–based AOPs such as UV/H_2O_2 and photocatalysis have been successfully used for degrading SO [40–42] but, to the best of our knowledge, there has been no research investigating the degradation of this dye using sulfate radical generated by thermally activated PS. Additionally, despite the largely use of the heat/PS process, only very limited degradation studies have been tested in environmental samples or in synthetic samples containing dissolved natural organic matters (NOMs) existing usually in wastewater. It is of practical interest to examine this process in environmental matrices, as the various matrix components may significantly affect the degradation kinetics, and therefore, the overall treatment efficiency. In this paper, after clarifying the effect of operational parameters on the dye removal with the heat-activated PS, the degradation of SO was investigated in the presence of several mineral and NOMs such as salts, surfactant and HA and in real environmental samples such as seawater and natural mineral water.

2. Materials and methods

2.1. Reagents

SO (basic red 2; 3,7-diamino-2,8-dimethyl-5-phenylphenazinium chloride) and potassium persulfate (PPS) were supplied by Sigma-Aldrich (USA) and used without any purification. Table 1 lists relevant data for SO and PPS. All other reagents (ethanol, phenol, sodium chloride, iron(II) sulfate heptahydrate, sulfuric acid, sodium hydroxide, sodium bicarbonate, potassium sulfate, HA and sodium dodecyl sulfate [SDS]) were commercial products of the purest grade available (analytical grade).

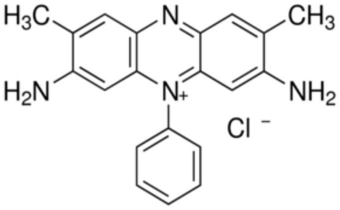
2.2. Experimental setup

Batch kinetic studies were conducted in a 500 mL cylindrical water-jacketed glass reactor mounted with a lid to ensure sealing and to avoid the evaporation of water (Fig. 1). The experiments were conducted at temperatures in the range of 30°C–70°C, with each temperature set was monitored using a thermocouple immersed in the reacting medium and maintained at desired value by circulating heating water, from a thermostatic bath (WiseCircu), through a jacket surrounding the cell. The solution pH during reaction period was followed with a pH meter (Jenway 3505).

2.3. Procedures

All solutions were prepared with distilled water. Degradation experiments were carried out under different conditions using constant solution volume of 300 mL.

Table 1
Physicochemical properties of SO and PS

Molecule	Safranin (SO)	Persulfate (PS)
CAS number	477-73-6	
C.I. number	50240	
Chemical class	Quinone-imine dye	–
Molecular formula	$C_{20}H_{19}ClN_4$	$K_2S_2O_8$
Chemical structure		
Molecular weight (g mol^{-1})	350.85	270.32
Solubility (g L^{-1}) at 20°C	50	52
pK_a	5.8	–
Maximum absorption wavelength (λ_{max})	518 nm (in water)	–
$^{\bullet}OH$ reaction rate constant (M^{-1} s^{-1})	9.30×10^9	8.00×10^4
$SO_4^{\bullet -}$ reaction rate constant (M^{-1} s^{-1})	3.59×10^7	6.00×10^4

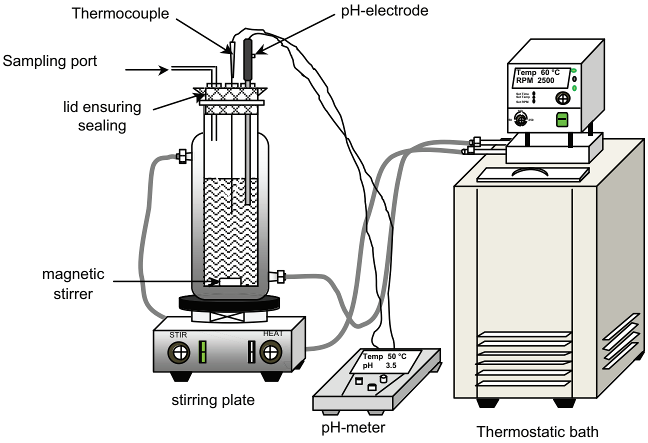


Fig. 1. Experimental setup.

Stock solutions of SO (0.5 g L^{-1}) and PS (10 g L^{-1}) were prepared and maintained in the dark at 4°C. Appropriate dilutions were then made from these stocks at desired operating concentrations of SO and PS. After adding reagents in the reactor, the mixed solution was continuously stirred at moderate speed using a magnetic stirrer. Aqueous samples were taken periodically from the solution and the concentrations of the dye were determined at 518 nm using a UV–visible spectrophotometer (Jasco V-730) equipped with quartz cuvettes of 1 cm light path. The pH of the solution was adjusted using sodium hydroxide or sulfuric acid. All experiments were repeated three times to ensure the reproducibility of the experimental results. The data were averaged and the error bars, which represent 95% confidence intervals, have been included in relevant plots.

3. Results and discussion

3.1. Characterization of SO degradation by the heat-activated PS

3.1.1. UV–visible spectra at varying reaction time

Fig. 2 shows the evolution of the UV–visible spectra of SO solution (C_0 = 10 mg L^{-1}) prior and during the oxidative treatment with the heat-activated PS (2 g L^{-1}) at 50°C and pH 3.5. As can be observed, the initial SO solution has two distinct bands: the first is that of the chromophoric group and is situated in the visible region, with λ_{max} = 518 nm, and the second is that of the aromatic rings and is located in the UV region, with λ_{max} = 275 nm. These two characteristic bands declined with increasing reaction time until no peaks were further observed after 100 min. This implies the degradation of the dye and the cleavage of the aromatic rings upon free radicals, presumably $SO_4^{\bullet -}$ and $HO^{\bullet}$, attack. Furthermore, the rate of the color disappearance was remarkably faster than that of the aromatic ranges decay, as shown in the inset of Fig. 2 (e.g., 98% of the initial absorbance at 518 nm were removed after 1 h whereas a lower degree of 73% was observed at 275 nm), signifying the priority of free radicals attack on the chromophore group of the dye and the increased mass of aromatic intermediates upon oxidation.

3.1.2. Predominant oxidizing species involved in the degradation process

In the heat-activated PS, both $SO_4^{\bullet -}$ and $HO^{\bullet}$ were likely formed and responsible for the elimination of contaminates. The formation of $SO_4^{\bullet -}$ and $HO^{\bullet}$ has previously confirmed by spectroscopic methods such as ESR as well as radical probes compounds, such as alcohols, aniline, phenol, etc. [36,37]. In the present study, to check the generation of these oxidizing species and then clarify the dominant radical involved in the degradation of SO, two radical scavengers, ethanol and phenol, of different reactivity toward radical species were employed as probes during the oxidation reaction. Ethanol reacts with $^{\bullet}$OH radical at a rate constant of 1.6 × 10^9 M^{-1} s^{-1} [43], which is much higher than its reaction rate constant with $SO_4^{\bullet-}$ (7.8 × 10^5 M^{-1} s^{-1} [11]) by a factor of ~2,050. However, phenol reacts with both radicals at higher and comparable rate constants (6.6 × 10^9 M^{-1} s^{-1} and 8.8 × 10^9 M^{-1} s^{-1}, respectively, for $^{\bullet}$OH and $SO_4^{\bullet-}$ [43,44]). Based on these proprieties, the addition of ethanol and phenol, in excess, should quench the radicals and affect the degradation rate of SO, which allows the identification of the dominant radical with the extent of the rate decrease.

Fig. 3 depicts the effect of ethanol and phenol addition (166.66 mM, molar ratio additive/SO ≈ 5,333) on the degradation kinetics of SO (C_0 = 10 mg L^{-1}) by the heat-activated PS (2 g L^{-1}) at 50°C. It is clearly shown that the degradation of SO was significantly influenced with the addition of quenchers. The removal extent of SO after 60 min declined from 98% to 38% in the presence of phenol, as compared with non-phenol control, suggesting that both radicals (HO$^{\bullet}$ and $SO_4^{\bullet-}$) play an important role. However, ethanol showed a weak inhibitory effect and the SO removal efficiency decreased from 98% to 80%, indicating that $^{\bullet}$OH played a minor role in the degradation process. These results confirmed that $SO_4^{\bullet-}$ is predominately produced over HO$^{\bullet}$ during the heat-activated PS at acidic conditions and is the main species responsible for the degradation of SO. These observations were the same as those reported by Chen et al. [33] using methanol and *tert*-butyl alcohol as quenchers in their study investigating the degradation of diclofenac. Using various probes, including *tert*-butyl alcohol, phenol and nitrobenzene, for simultaneously identifying $SO_4^{\bullet-}$/HO$^{\bullet}$, Liang and Su [37] reported that sulfate radical is the predominant radical species in acidic solutions (pH < 7). It is worth noting that the solution pH during the control experiment (without additives) drops from 3.5 to 1.86 after 60 min of reaction, which was possibly due to the release of H^+ when sulfate radicals reacted with water (Eq. (2)) as well as the formation of aliphatic acids as degradation by-products.

3.2. Effect of operating parameters

3.2.1. Effect of initial SO concentration

Since the concentration of pollutants in wastewater effluents is generally variable, it is important to study the influence of pollutant concentration on the efficiency of the heat-activated PS treatment. In this work, the effect of initial SO concentration was studied in the range of 1–100 mg L^{-1} under 50°C and 2 g L^{-1} PS. The obtained results are shown in Fig. 4. As shown in this figure, the removal efficiency of SO decreased with increasing initial dye concentration. The SO elimination was completely achieved after 20 min for 3 mg L^{-1}, but lesser removal percentages of 80% for 5 mg L^{-1}, 66.4% for 10 mg L^{-1}, 38.1% for 50 mg L^{-1} and 31.4% for 100 mg L^{-1} were recorded. These results are in good agreement with that reported for the degradation of methylene blue [34]. However, the eliminated amount of SO increased significantly with increasing the dye concentration, e.g., 2.44–, 3.8– and 4.8-fold increase was recorded when the initial SO concentration increased from 3 mg L^{-1} to 20, 50 and 100 mg L^{-1}, respectively. On the other hand, even if the concentration profiles of SO exhibited an exponential

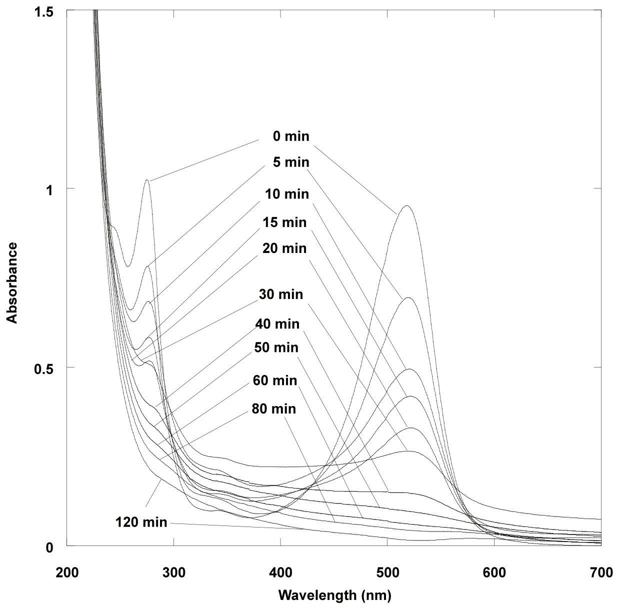


Fig. 2. Temporal variation of the UV–Vis spectra of SO solution upon treatment with heat-activated PS (conditions: volume, 300 mL; initial SO concentration, 10 mg L^{-1}; initial PS concentration, 2 g L^{-1}; temperature, 50°C ± 1°C; pH, ~3.5).

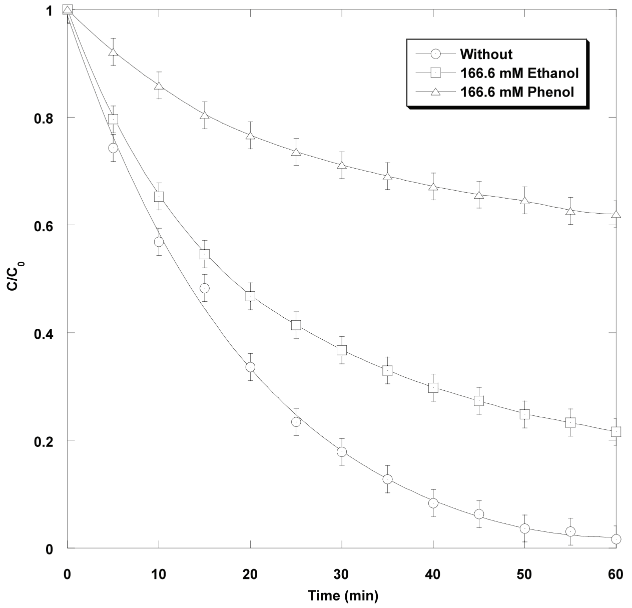


Fig. 3. Kinetics of SO degradation with heat-activated PS in the presence and absence of quenchers, ethanol and phenol, at 166.6 mM (conditions: volume, 300 mL; initial SO concentration, 10 mg L^{-1}; initial PS concentration, 2 g L^{-1}; temperature, 50°C ± 1°C; pH, ~3.5).

decay (Fig. 4), the degradation of SO cannot be described with first-order kinetics law. The initial degradation rate (calculated from Fig. 4 as $\Delta C/\Delta t$ after few reaction minutes) increased significantly with increasing initial concentration (Fig. 5), but linear relationship was not observed, as expected for a first-order kinetics law. Thus, the degradation of organic pollutants with the heat-activated PS could not be associated with pseudo-first-order kinetics model, as claimed by several literature reports [30,33,34,45]. The rise of the degradation rate with the rise of the initial pollutant concentration could simply be justified as follow: at fixed temperature and initial PS concentration, the overall production of reactive radicals was constant. Hence, with increasing the initial pollutant concentration, the portion of radicals scavenged by SO molecules increases and this leading to efficient degradation rates.

3.2.2. Effect of initial PS concentration

For an economical point of view, it is important to optimize the amount of PS used in the heat/PS treatments. Thus, the effect of initial PS dosage on the degradation of SO was evaluated at 50°C and pH 3.5 by fixing initial SO concentration at 10 mg L^{-1} and varying PS dosage from 0.1 to 2 g L^{-1}. The obtained results, presented in Fig. 6, showed that the degradation rate of SO increased significantly with increasing PS concentration. 98% of initial SO was removed in 1 h when using 2 g L^{-1} of PS whereas lower oxidation degrees of 76.7%, 59.0% and 21.4% were attained, respectively, for 1.0, 0.5 and 0.1 g L^{-1} of PS (Fig. 6(a)). Correspondingly, the initial degradation rate becomes 5.42-, 12.61-, 18.25- and 25.6-fold much higher when the concentration of PS increased from 0.1 g L^{-1} to 0.3, 0.7, 1.0 and 2.0 g L^{-1}, respectively (Fig. 6(b)). This proportional relation between the degradation rate and the initial PS loading was also observed in the degradation of methyl tert-butyl ether [45], 1,1,1-trichloroethane [30], diclofenac [33] and carbamazepine [46] and was attributed to the release of higher $SO_4^{\bullet-}$ at high PS concentration. However, a much higher concentration of PS may lead to the release of excessive $SO_4^{\bullet-}$ and $^{\bullet}OH$, thus acting as scavengers (Eqs. (4)–(6)) and affecting negatively the degradation of the contaminant [47,48]. This phenomenon was not observed in this study, probably because the highest PS dose (2 g L^{-1}) did not reach the critical level that started to slow down the SO decomposition.

$$S_2O_8^{2-} + SO_4^{\bullet-} \rightarrow S_2O_8^{\bullet-} + SO_4^{2-};\ k = 6\times10^4 M^{-1}s^{-1} \tag{4}$$

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-};\ k = 4\times10^8 M^{-1}s^{-1} \tag{5}$$

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2;\ \ k = 5.5\times10^9 M^{-1}s^{-1} \tag{6}$$

3.2.3. Effect of liquid temperature

The performance of the heat-activated PS is strongly dependent to the temperature, which is the crucial factor that controls the decomposition rate of PS. Most research agrees that higher treatment temperature yields higher degradation performance [21,30–32,49]. Experimental and theoretical analysis revealed that PS decomposition rate increased with the rise of the liquid temperature up to ~80°C [35,50,51]. In this study, the effect of liquid temperature on the degradation of SO was investigated by

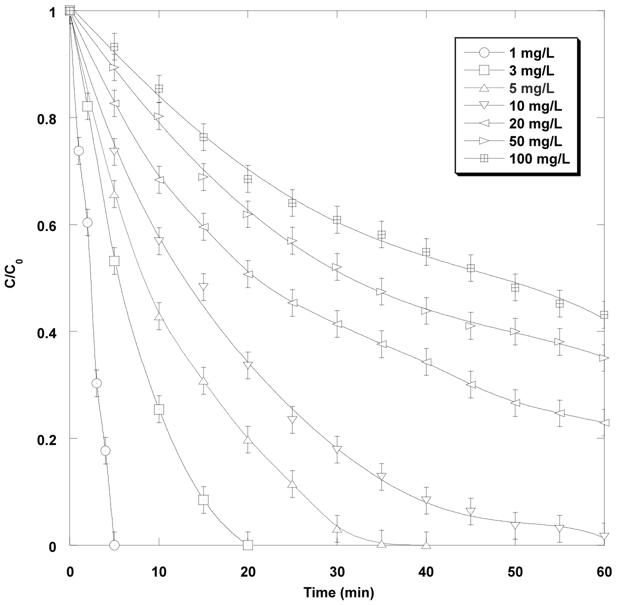


Fig. 4. SO degradation kinetics with the heat-activated PS at various initial concentrations (conditions: volume, 300 mL; initial SO concentration, 1–100 mg L^{-1}; initial PS concentration, 2 g L^{-1}; temperature, 50°C ± 1°C).

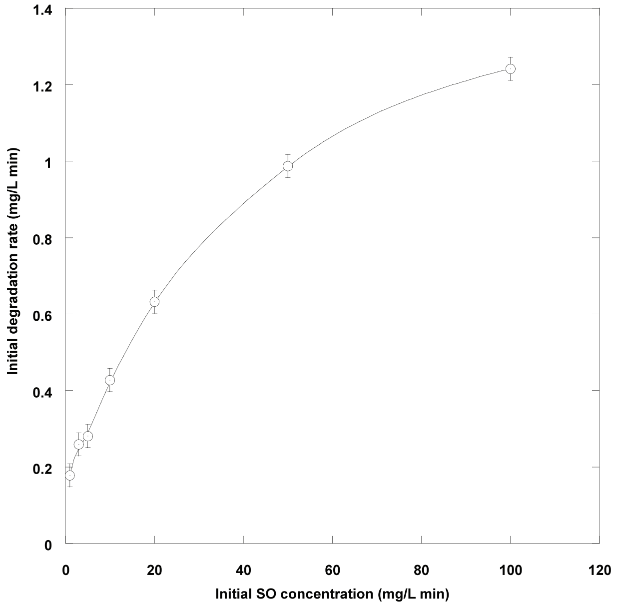


Fig. 5. Initial degradation rate vs. initial SO concentration (conditions: volume, 300 mL; initial SO concentration, 1–100 mg L^{-1}; initial PS concentration, 2 g L^{-1}; temperature, 50°C ± 1°C; pH, ~3.5).

keeping initial SO and PS concentrations, respectively, at 10 and 2,000 mg L^{-1} and varying the operating liquid temperature in the interval 30°C–70°C. The obtained results, summarized in Fig. 7, showed clearly that SO was highly temperature dependent. At 30°C, ~40% of SO was oxidized after 60 min, suggesting that a direct oxidation reaction may be occurring. It is also possible that a degree of thermal activation can occur at ambient temperature [52]. However, significant SO removal was observed as the temperature was increased above 30°C. 61% and 98% of SO removal were achieved after 60 min at 40°C and 50°C, respectively, and complete oxidation was observed in only 40 and 25 min, respectively, at 60°C and 70°C (Fig. 7(a)). Note that control tests in the absence of PS at 70°C exhibited no SO degradation (Fig. 7(a)). Therefore, more PS was activated at higher temperatures to generate more $SO_4^{\bullet-}$, resulting in the higher removal efficiency of SO. The initial degradation rate at 70°C is 9.45-fold much higher than that obtained at 30°C and 2.22-fold higher than that observed at 50°C. All these observations suggested that higher temperatures favor higher oxidative environment, leading to an efficient oxidation of contaminants.

3.2.4. Effect of initial pH

In order to investigate the effect of initial pH on SO degradation by the thermally activated PS, a series of experiments was conducted at various initial pH in the range of 3–13 for an initial SO concentration of 10 mg L^{-1} and PS loading of 2 g L^{-1}. The obtained results are reported in Fig. 8. As seen, the degradation of the dye was significantly affected by the pH. The SO degradation decreased from pH 3 to 5 and then slightly increased to pH 8.2. A faster degradation rates were observed at pH 11.4 and 13. The lower degradation rate was obtained at pH 5. At pH 3, the initial degradation rate is about 1.1-fold higher than that observed at pH 7 but it was 4-fold lower than that obtained at pH 13. Similarly, Liang and Huang [35] who investigated the degradation of methylene blue found that the degradation rate was highest at pH 11, followed by pH 3 and then pH 7.

In the heat-activated PS system, the solution pH plays an important role in the distribution of radical species. Liang and Su [37] researched active radical species in the thermally activated PS under various pH conditions using a chemical probe method. Their results revealed that $SO_4^{\bullet-}$ is the predominant radical oxidant at pH < 7; both $SO_4^{\bullet-}$ and

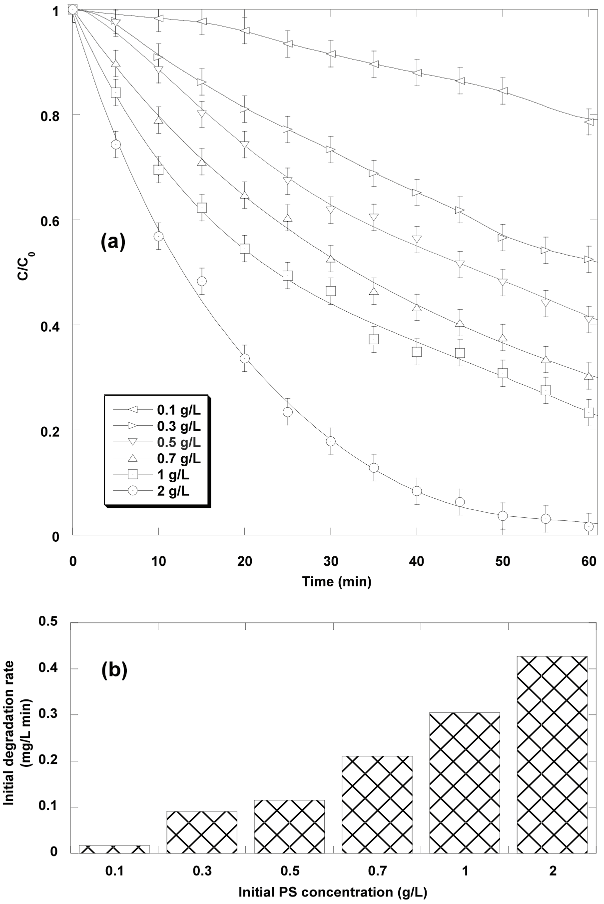


Fig. 6. Effect of initial PS concentration on: (a) the kinetics and (b) the initial degradation rate of SO with the heat-activated PS (conditions: volume, 300 mL; initial SO concentration, 10 mg L^{-1}; initial PS concentration, 0.1–2 g L^{-1}; temperature, 50°C ± 1°C; pH, ~3.5).

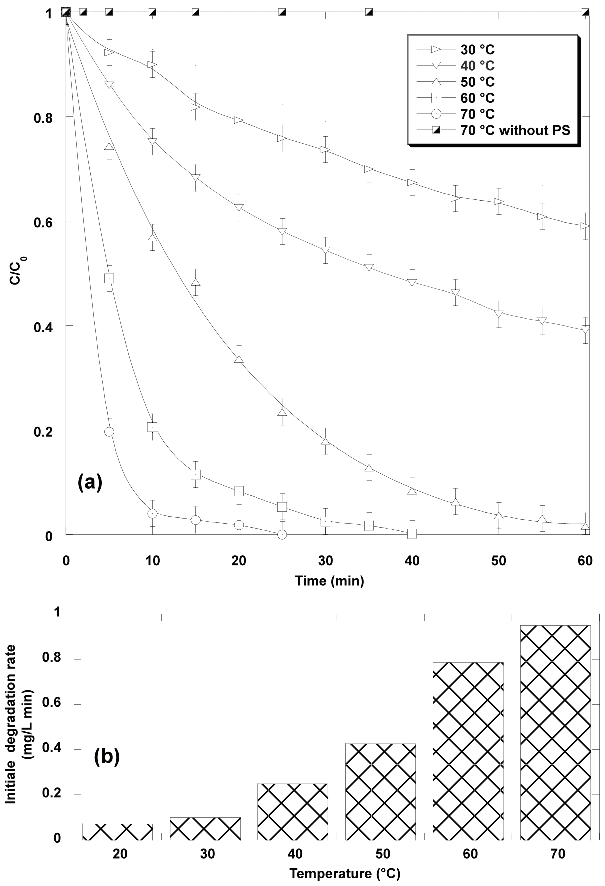


Fig. 7. Effect of liquid temperature on: (a) the kinetics and (b) the initial degradation rate of SO with the heat-activated PS (conditions: volume, 300 mL; initial SO concentration, 10 mg L^{-1}; initial PS concentration, 2 g L^{-1}; temperature, 20°C–70°C; pH, ~3.5).

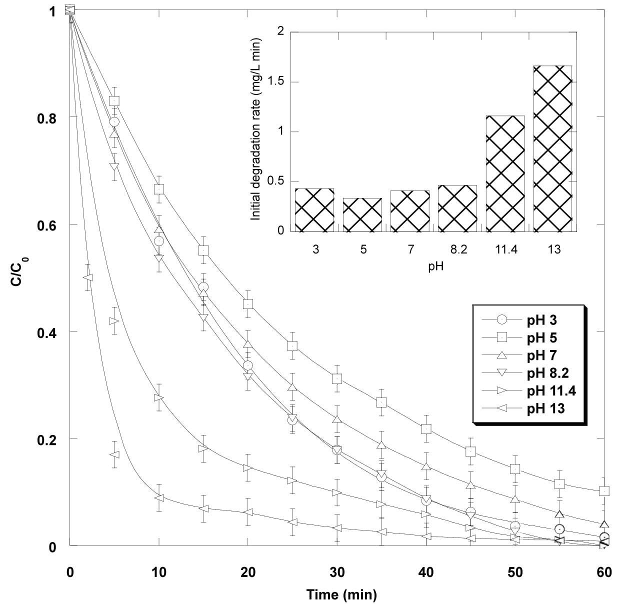


Fig. 8. Effect of initial solution pH on the degradation of SO with the heat-activated PS (conditions: volume, 300 mL; initial SO concentration, 10 mg L^{-1}; initial PS concentration, 2 g L^{-1}; temperature, 50°C ± 1°C; pH, 3–13).

$^{\bullet}OH$ are present at neutral pH; and $HO^{\bullet}$ is the predominant radical at more basic pH (pH > 9). Alternative spectroscopic method (ESR spin trapping) [36] also demonstrated that the predominant radical species at different pH conditions in the PS-activated system are similar to those reported by the chemical probe method. Based on the above literature analysis, the degradation of SO in alkaline conditions (pH 11.4 and 13) most likely occurred with $HO^{\bullet}$, which has a higher redox potential than $SO_4^{\bullet-}$, and this leads to faster removal rates. Additionally, PS is also known to be activated in alkaline conditions [53]. However, even if both $SO_4^{\bullet-}$ and $HO^{\bullet}$ contribute in the degradation at neutral conditions (pH ~ 5–7), lower degradation rates were obtained compared with that obtained at pH 3, which is due to the quench of radicals as in Eqs. (5)–(7). The rate constant of reaction (7) is 25-fold higher than that of reaction (5) and the recombination reaction of $^{\bullet}OH$ (Eq. (6)) is faster than that of $SO_4^{\bullet-}$by a factor of 13.75, which implies that lower amount of radicals will be available at neutral pHs than acidic conditions. Additionally, it has also been reported that PS may be activated by protons under acidic pH [30,33].

$$SO_4^{\bullet-} + {}^{\bullet}OH \rightarrow HSO_4^{-} + ½\,O_2; \quad k = 1.0\times10^{10}\,M^{-1}s^{-1} \tag{7}$$

3.3. *Effect of additives*

3.3.1. *Effect of mineral additives*

Since wastewaters can contain a significant quantity of salts, it is important to see the impact of the presence of salts on the efficacy of the heat/PS treatment. The effect of several individual salts (NaCl, K_2SO_4, $NaHCO_3$ and $FeSO_4$) on the degradation of SO (C_0 = 10 mg L^{-1}) by the thermally activated PS (2 g L^{-1}) was assessed at 50°C and the results are illustrated in Fig. 9. As can be seen, over the concentration range of 0–50 mM, sulfate ions have no impact on the efficiency of the process (Fig. 9(a)), which is in accord with the statement reported by Gu et al. [30]. The same comportment was observed for NaCl and $NaHCO_3$ at low concentrations and only low degrees of inhibition, e.g., 6.3% for Cl^- and 11.5% for HCO_3^-, were reached when these species present at high concentration levels (50 mM) (Fig. 9(b) and (c)). However, Gu et al. [30] showed a more quenching effect of Cl^- and HCO_3^- toward the degradation of 1,1,1-trichloroethane. On the other hand, Yuan et al. [54] reported that the addition of Cl^- enhanced the degradation of acid orange 7 in UV/PS system up to certain dose above which Cl^- starts to inhibit the degradation process. HCO_3^- and Cl^- at higher concentrations can scavenge $SO_4^{\bullet-}$ (Eqs. (8)–(11)) and, therefore, result in competition with $SO_4^{\bullet-}$ for reaction with SO. Additionally, the chlorine and carbonate radicals generated from the reaction of sulfate radical with HCO_3^- and Cl^- are less reactive toward organic compounds [12] and could not play a significant role in the degradation of the target contaminate, which was supported by the kinetic results of Fig. 9.

$$SO_4^{\bullet-} + Cl^- \rightleftharpoons SO_4^{2-} + Cl^{\bullet}; \quad k_f = 4.7\times10^{8}\,M^{-1}s^{-1}, \quad k_r = 2.5\times10^{8}\,M^{-1}s^{-1} \tag{8}$$

$$Cl^{\bullet} + Cl^- \rightleftharpoons Cl_2^{\bullet-}; \quad k_f = 8.0\times10^{9}\,M^{-1}s^{-1}, \quad k_r = 4.2\times10^{4}\,M^{-1}s^{-1} \tag{9}$$

$$Cl_2^{\bullet-} + Cl_2^{\bullet-} \rightarrow Cl_2 + 2Cl^-; \quad k = 1.3\times10^{9}\,M^{-1}s^{-1} \tag{10}$$

$$SO_4^{\bullet-} + HCO_3^- \rightarrow SO_4^{2-} + CO_3^{\bullet-} + H^+; \quad k = 9.1\times10^{6}\,M^{-1}s^{-1} \tag{11}$$

On the other hand, the assistance of the heat-activated PS oxidation treatment with low amount of bivalent iron drastically enhanced the degradation of the dye, as shown in Fig. 9(d). The degradation rate increased with increasing Fe^{2+} concentration up to 0.358 mM (20 mg L^{-1}). The total removal of the dye in the presence of 0.358 mM of Fe^{2+} required only 25 min instead of ~100 min in the absence of iron. Compared with the non-iron control test, the initial degradation rate was 4.5-fold higher at 0.090 mM (5 mg L^{-1}) of Fe^{2+} and 7-fold higher at 0.358 mM (20 mg L^{-1}).

The combination of thermal activation of PS with iron could yield intensive generation of sulfate radical in the aqueous system. In this case, in addition to the thermal decomposition of PS, $SO_4^{\bullet-}$ also generated through the Fe^{2+}-catalytic effect on PS (Eq. (12)) [11]. The iron-activated PS has been widely applied to the degradation of various organic pollutants such as trichloroethylene [55], propachlor [56],

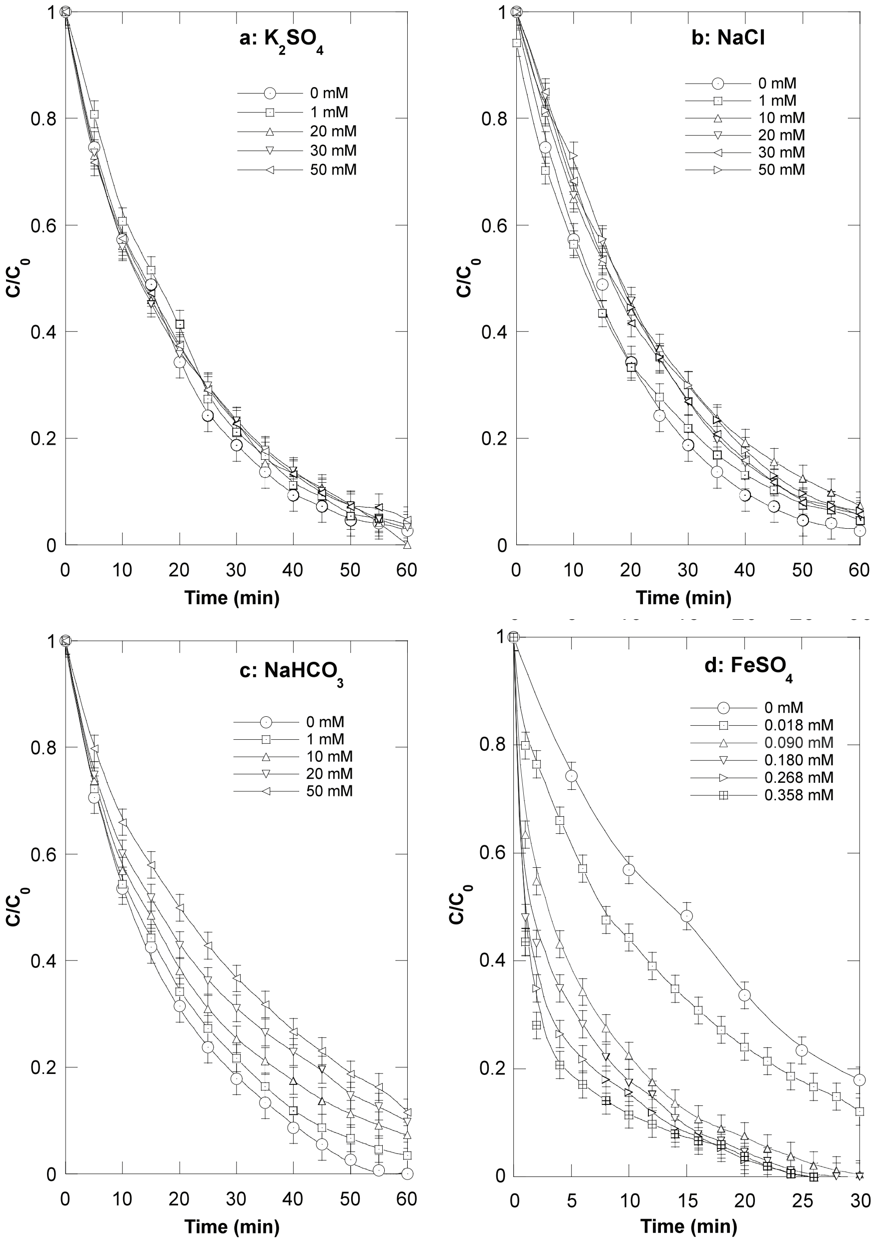


Fig. 9. Effect of mineral salts, NaCl, K_2SO_4, $NaHCO_3$ and $FeSO_4$, on the degradation of SO with the heat-activated PS (conditions: volume, 300 mL; initial SO concentration, 10 mg L^{-1}; initial PS concentration, 2 g L^{-1}; temperature, 50°C ± 1°C; pH 7 for (a) and (b); pH 8.4 for (c) and pH 3 for (d)).

toluene [17], polychlorinated biphenyls [57], bisphenol A [58], cibacron black and acid orange 7 dyes [59,60]. In some cases [61,62], a detrimental effect of iron was observed and was attributed to the fact that excessive of Fe^{2+} may act as a scavenger for $SO_4^{\bullet-}$ (Eq. (13)). This phenomenon was not observed here, which was may be due to the low doses of iron used in this study.

$$Fe^{2+} + S_2O_8^{\ 2-} \rightarrow SO_4^{\bullet-} + SO_4^{\ 2-} + Fe^{3+};\ k = 15.33\ M^{-1}s^{-1} \quad (12)$$

$$Fe^{2+} + SO_4^{\bullet-} \rightarrow SO_4^{\ 2-} + Fe^{3+};\ k = 4.6 \times 10^9 M^{-1}s^{-1} \quad (13)$$

3.3.2. Effect of organic additives

The investigation of pollutants degradation in the presence of NOM is an important topic in the water treatment technique. One of the reasons for the high total organic carbon value of water sample is the presence of humic substances, i.e., humic acids (HA). Additionally, surfactants are used as additive in dyeing processes and are widely discharged along with the dye solutions. These chemical compounds which are also used in different industries become an important class of NOM. Therefore, it will be interesting to look at the effect of HA and surfactants on the performance of the heat-activated PS process for removing SO pollutant.

Fig. 10 illustrates the effect of HA and SDS anionic surfactant, over the concentration range of 10–50 mg L^{-1}, on the degradation of SO (C_0 = 10 mg L^{-1}) by the heat-activated PS (2 g L^{-1}) at 50°C and pH 3.5. The results of this figure indicated that SO degradation was significantly inhibited in the presence of HA. 10 mg L^{-1} of HA reduced the SO removal by 12%, and the inhibitory effect further increased to 25% and 52%, respectively, for 30 and 50 mg L^{-1} of HA (Fig. 10(a)), indicating that HA is a potential competitor to SO for consuming sulfate radicals. It should be noted that control experiments with HA and SDS (50 mg L^{-1} for each one) in the absence of PS showed that no degradation occur in these conditions (data not shown). Gu et al. [30] and Chen et al. [33] evaluated the in situ heat-activated PS oxidation of diclofenac and 1,1,1-trichloroethane in aqueous solutions and reported that a retardation was observed in the presence of HA. On the other hand, the presence of surfactant, even at high concentration, had no inhibiting effect as observed for HA, but it obviously increases the initial degradation rate of the dye, as show in Fig. 10(b). 50 mg L^{-1} of surfactant induced a twice increase in the initial degradation rate of SO. The reason of this enhancement was not clear and needs further studies.

3.4. Degradation of SO in real environmental matrices

It is of practical interest to examine the heat-activated PS process in environmental matrices, as the various matrix components may significantly affect the oxidation kinetics, and therefore, the overall treatment efficiency. To test the viability of the heat/PS process to remove SO from real matrices, experiments with 2 g L^{-1} of PS and 10 mg L^{-1} of SO have been conducted at 50°C in natural mineral water and seawater. The natural mineral water characteristics are: pH = 7, Ca^{2+} = 81 mg L^{-1}, Mg^{2+} = 24 mg L^{-1}, Na^+ = 15.8 mg L^{-1}, Cl^- = 72 mg L^{-1}, SO_4^{2-} = 53 mg L^{-1}, HCO_3^- = 265 mg L^{-1}. The seawater (pH ~8.4) has a high salinity (~35 g L^{-1}), which is composed mainly of Na^+ ≈ 11 g L^{-1}, Mg^{2+} = 1.3 g L^{-1}, Ca^{2+} ≈ 0.4 g L^{-1}, Cl^- ≈ 20 g L^{-1}, SO_4^{2-} = 3 g L^{-1}. The obtained results are shown in Fig. 11. It was observed that mineral water engenders a slight reduction in the degradation rate of SO (~4.3% after 60 min, compared with control test in deionized water at pH 7) and a relatively more inhibition was observed in seawater (~11% after 60 min, compared with control test in deionized water at pH 8.4). Overall, these low degrees of retardation in the removal rate of SO in real matrices even if huge concentration of salts is present, makes heat-activated PS a promising technique for treating real waters contaminated with organic dyes.

4. Conclusion

This wok demonstrated the performance of the heat-activated PS process toward the degradation of a phenazine dye, SO, in aqueous media and illustrated clearly the influence of various factors such as PS and SO initial concentrations, liquid temperature, initial solution pH, mineral and organic additives on the degradation rate of the dye. Additionally, the effectiveness of heat/PS oxidation process for removing SO from real matrices was proven. The experimental results showed that SO removal was significantly influenced by the operating parameters and was favored at high liquid temperature, pH and PS dosage. The presence of mineral anions such as Cl^-, SO_4^{2-} and HCO_3^- at natural concentrations had practically no significant effect on SO decomposition and only a low inhibitive effect was observed for Cl^- and HCO_3^- at high

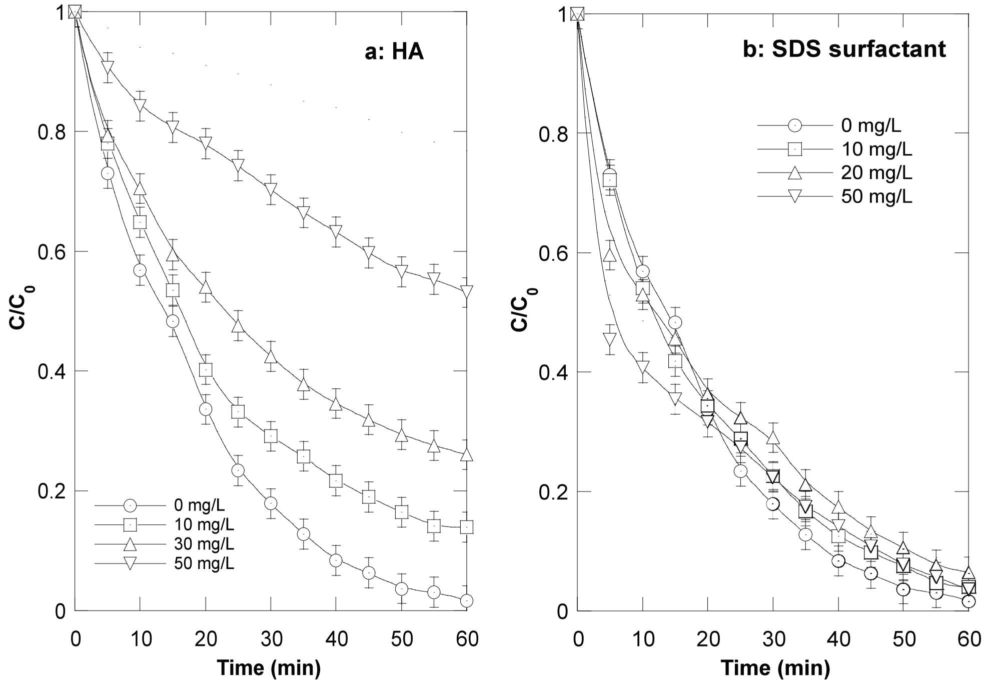


Fig. 10. Effect of: (a) humic acid (HA) and (b) SDS surfactant on the degradation of SO with the heat-activated PS (conditions: volume, 300 mL; initial SO concentration, 10 mg L^{-1}; initial PS concentration, 2 g L^{-1}; temperature, 50°C ± 1°C; pH, 3.5).

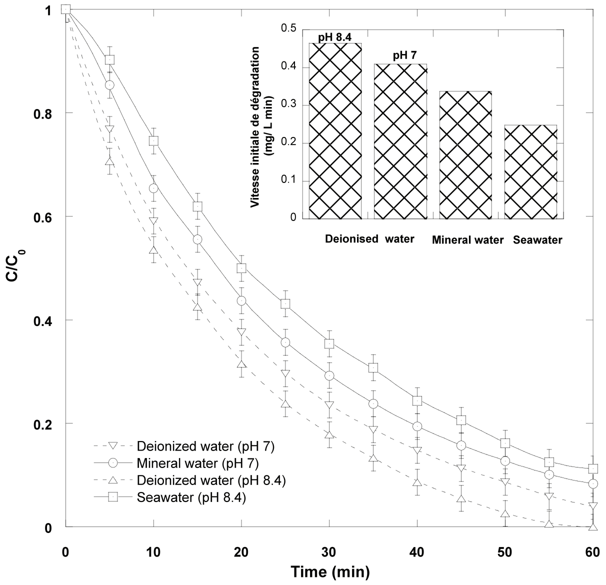


Fig. 11. Kinetics of SO degradation with the heat-activated PS in mineral water (pH 7), seawater (pH 8.4) and deionized water (pH 7 and 8.4) (conditions: volume, 300 mL; initial SO concentration, 10 mg L^{-1}; initial PS concentration, 2 g L^{-1}; temperature, 50°C ± 1°C).

concentrations. However, HA had a significant inhibitive effect on the degradation of SO, particularly at high concentrations. In contrast, anionic surfactant (SDS) did not alter the oxidation of the dye but it accelerates the degradation at the initial stage of the treatment. The SO removal was decreased by only 11% in seawater and 6% in natural mineral water, making thermally activated PS process a highly promising technique for removing organic dyes from natural contaminated waters.

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