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Sulfate radical-based degradation of antraquinone textile dye in a plug flow photoreactor

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Abstract: The study evaluated the degradation of the antraquinone textile dye reactive blue 19, a frequently used dye in the textile industry, by means of sulfate radicals. Sulfate radicals were generated by activation of peroxydisulfate with UV-C (254 nm) irradiation. UV irradiation alone did not affect the removal efficiency, while with the addition of an oxidant, the removal efficiency was significantly improved. The degradation rates of the textile dye increased at higher initial dosages of oxidant, while the opposite trend was observed in the case of increasing initial dye concentration. Acidic conditions were more convenient for degradation of the dye then neutral or basic. Degradation of the textile dye was not affected by the presence of bicarbonate and chloride anions within the concentrations range from 1 to 200 mmol·L^{-1}. The presence of carbonate showed a suppressing effect on the removal efficiency, especially at carbonate levels below 20 mmol·L^{-1}. However, at carbonate levels greater than 20 mmol·L^{-1}, the dye removal efficiency increased. The use of methanol and *tert*-butanol as scavengers revealed that both radicals, $HO^{\bullet}$ and $SO_4^{\bullet -}$, would be generated depending on initial pH value of the dye solution.

Keywords: advanced oxidation processes; reactive blue 19; carbonate/bicarbonate; chloride.

INTRODUCTION

The textile industry is considered as the most polluting industrial sector due to the quantity and constituents of the produced effluents.[1] Dye effluents are characterized by the presence of strong color, suspended solids, chlorinated organics, surfactants, and heavy metals and also have variable pH, temperature and chemical oxygen demand (*COD*).[2] The amount of generated textile wastewater can reach more than 300 L per kg of product.[3] The main adverse effect of

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dyes in the environment are their inhibitory effect on aquatic photosynthesis. Moreover, degradation by-products of dyes, which can include aromatic structures with a large variety of substituents (*e.g.*, amines) that could be cancerogenic.[4] Reactive blue 19 is very stable and resistant anthraquinone reactive dye, with fixation effectiveness ranging between 75 and 80 % due to the formation of vinyl sulfone and of 2-hydroxyethyl-sulfone.[5]

Various physical, chemical and biological methods have been used for the removal of these types of pollutant from wastewater. Advanced oxidation technologies (AOPs) are consider as a promising alternative to the conventional wastewater treatment technologies for textile dye degradation, since they can eliminate non-biodegradable organic components and avoid the need to dispose of residual sludge.[6] Traditional AOPs are based on the generation of highly reactive $^{\bullet}OH$ (HR-AOPs), which are capable of reacting rapidly and non-selectively with organic pollutants, leading in ideal conditions for the formation of CO_2, H_2O and non-toxic inorganic ions. Second-order rate constants in the range of 10^8 to 10^{10} M^{-1} s^{-1} for reaction of $^{\bullet}OH$ with organic pollutants were reported.[7] Recently, application of AOPs has been extended on the use of other oxidation agents, and the formation of other radicals. Among them, the sulfate radicals are acquiring the interest of researchers, since that these radicals have higher redox potential (2.5–3.1 V) compared to those of hydroxyl radicals (1.8–2.7 V) at pH 7, they are more selective, and possess longer life-times ($t_{1/2}$ = 30–40 μs) than hydroxyl radicals ($t_{1/2}$ = 10^{-3} μs).[8] In the sulfate radicals-based AOPs (SR-AOPs), peroxymonosulfate (PMS, HSO_5^-) and peroxydisulfate (PDS, $S_2O_8^{2-}$) were used as a source of sulfate radicals ($SO_4^{\bullet-}$).[9] Both of these oxidants could be activated in different ways to generate sulfate radicals. The most often used methods for activation are UV irradiation,[10] alkali,[11] heat[12] and transition metals.[13,14] The peroxydisulfate anion offers some advantages over other oxidants, *i.e.*, it is a solid oxidant at ambient temperature, its transport and storage are easy, it has high stability, and high water solubility.[15] Two sulfate radicals are formed when peroxydisulfate is activated by UV irradiation (reaction (1)).[16]

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{\bullet-} \tag{1}$$

Various inorganic anions, such as chloride, carbonate/bicarbonate, sulfate, nitrate, phosphate and natural organic matter (NOM) could be present in surface and wastewater, which could influence the efficiency of the water treatment process.[17] It was reported that these anions might have both a positive or negative impact on the performance of hydroxyl and sulfate radicals-based oxidation technologies, depending on the concentration of the anions, variables of the applied system and the nature of the contaminants.[18] Therefore, it is necessary to understand the role and the effect of the anions commonly present in wastewaters on the oxidative removal of investigated organic pollutants.

The aim of the present work was to evaluate the degradation of the antraquinone textile dye C. I. reactive blue 19 with sulfate radicals, which were generated by irradiation of an aqueous solution of the dye with UV-C light (254 nm) in the presence of peroxydisulfate as the oxidant. All experiments were performed under continuous conditions, in a plug flow photoreactor. In the first part, the influence of various operational parameters, including initial pH values, initial peroxydisulfate concentrations, flow rates and initial dye concentrations, was investigated to determine the optimal values. In the second part, the role of dominant oxidizing species in the applied system was interpreted *via* selective quenching of sulfate and hydroxyl radicals with methanol and *tert*-butanol. Moreover, the effect of some anions, common constituents of wastewaters, was elucidated.

EXPERIMENTAL

Chemicals

The textile dye reactive blue 19 (RB 19, dye content about 50 %) was purchased from Sigma–Aldrich (St. Louis, MO, USA) and used without further purification. The general characteristics of RB 19 dye are given in Table S-I of the Supplementary material to this paper. Regent grade $K_2S_2O_8$ was provided by VWR (USA). Methanol and *tert*-butanol were ACS reagent grade and supplied by Merck (Germany). Sodium chloride, sodium bicarbonate and sodium carbonate were reagent grade purchased from Zorka Šabac (Serbia). All solutions were prepared with high water purity obtained from a Smart2Pure system (Thermo Scientific, USA) with a conductivity of 0.055 μS m^{-1}

Degradation experiment

A laboratory-scale plug flow photoreactor was used for the oxidative treatment of the antraquinone textile dye RB 19. The system consists of an influent tank, peristaltic pump, photoreactor and effluent tank (Fig. S-1, Supplementary material). Ten UV-C lamps of 28 W (Philips, Holland) emitting UV radiation at 254 nm wavelength were placed above the quartz tubes in the photoreactor. The length of quartz tubes through which the solution flows was 1000 cm. The detention time was 22 min, and 2 h for flow rates 7 and 1.5 mL·min^{-1}, respectively. A peristaltic pump (PLP 380, Dülabo, Germany) was used for feeding the photoreactor with a solution from the influent tank. The experimental procedures consisted of preparing working dye solution (50 mg·L^{-1}, 250 mL) by the appropriate dilution of a stock solution to give the desired initial peroxydisulfate concentrations (0.05, 0.1, 0.2 and 0.4 mmol·L^{-1}) and at the appropriate initial pH values (3.0, 5.0, 7.0, 9.0 and 10.0). To investigate the influence of the initial dye concentrations, the concentration of the working solutions was varied from 20 to 100 mg·L^{-1}, while the other parameters were kept constant. The effect of the flow rate was examined at four different values 30, 15, 7 and 1.5 mL·min^{-1}. For identification of the predominant radicals, the working dye solutions (50 mg·L^{-1}) with 100 mmol·L^{-1} of methanol and *tert*-butanol at three initial pH values (3.0, 7.0 and 10.0) were irradiated. The effect of carbonate, bicarbonate and chloride (10, 20, 50, 100 and 200 mmol·L^{-1}) was assessed by adding a known volume of the stock solutions of the anions to the dye solution before the addition of an oxidant. After a specific resident time, which depends on the selected flow rate, samples of the treated solution were withdrawn from the effluent tank and the residual dye concentration was measured. All the tests were performed in triplicate and the average of the three values are presented. In order to determined the percentage of decolorization (removal efficiency, %), the following formula was used (Eq. (2)):

$$\text{Removal efficiency, \%} = 100\frac{c_0 - c}{c_0} \tag{2}$$

where c_0 and c are concentrations (mg·L^{-1}) of dye RB 19 before and after UV/$S_2O_8^{2-}$ treatment, respectively.

According to the assumption that the degradation of dye RB 19 in UV/$S_2O_8^{2-}$ system, mainly depends on $SO_4^{\bullet -}$ and $HO^{\bullet}$ generated from the activated peroxydisulfate, and that the concentration of peroxydisulfate could be assumed to be stable during the irradiation period, the degradation of RB 19 dye may be described as follows (Eq. (3)):[19]

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = -\left(k_1 c_{\mathrm{SO_4^{\bullet -}ss}} + k_2 c_{\mathrm{HO^{\bullet}ss}}\right) = -kc \tag{3}$$

where c represents the concentration of RB 19 dye (mg·L^{-1}); k_1 and k_2 are the pseudo-first order rate constants of RB 19 dye degradation with $SO_4^{\bullet -}$ and $HO^{\bullet}$, respectively; $c_{\mathrm{SO_4^{\bullet -}ss}}$ and $c_{\mathrm{HO^{\bullet}ss}}$ are the steady-state concentration of $SO_4^{\bullet -}$ and $HO^{\bullet}$, respectively; k is the overall pseudo-first order rate constant of RB 19 dye degradation with the total reactive species.

The first order kinetic equation for a plug flow reactor could be applied for the calculation of overall pseudo-first order rate constant (Eq. (4)):[20]

$$\tau = \frac{1}{k}\ln\frac{c_0}{c} \tag{4}$$

where τ is the retention time, min; ($\tau = V/Q$; V – volume of reactor, mL; Q – flow rate, mL·min^{-1}); k – first order rate constant, min^{-1}; c_0 – the initial dye concentration, mg·L^{-1}; c – the dye concentration after treatment, mg L^{-1}.

Analytical methods

The residual RB 19 concentration was determined by UV–Vis spectrophotometry (UV 1800, Shimadzu, Japan). The pH of the RB 19 dye solution was adjusted using a pH meter (Orion Star A214, Thermo Scientific, USA). A thermoreactor (RD125, Lovibond, UK), a Lovibond® *COD* Vario tube test for the measuring range 0–150 mg·L^{-1} and a Lovibond® Multidirect photometer (Lovibond, UK) were used for the determination of the chemical oxygen demand.

RESULTS AND DISCUSSION

Degradation of RB 19 dye under different oxidation conditions (UV alone, $S_2O_8^{2-}$ alone and UV/$S_2O_8^{2-}$)

The initial experiments were performed in the presence of only persulfate, under UV irradiation only and with a combination of the oxidant and UV light, at two different initial pH values (pH 3 and 10). The results showed that there are no changes in the initial dye concentration when only UV light was applied at both the studied initial pH values, probably since the RB 19 dye is stable in water solution under direct UV-C photolysis (Fig. 1).

The decrease of the dye concentration was not considerable when experiments were realized with persulfate alone at pH 3, while at pH 10 about 8 %

color removal was obtained after 24 h. This result could be attributed to the fact that sulfate radicals might be produced by activation of $S_2O_8^{2-}$ under alkaline conditions.[11]

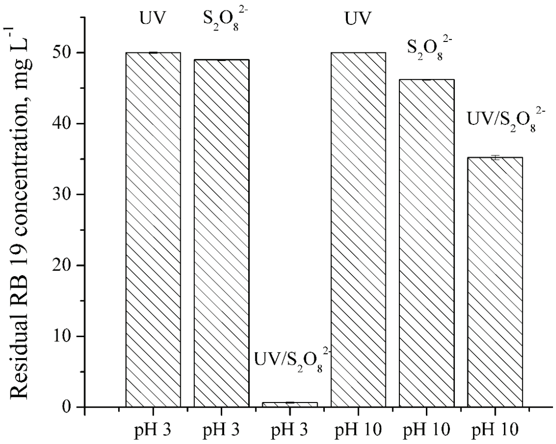

Fig. 1. RB 19 residual concentrations after treatment with UV irradiation, $S_2O_8^{2-}$ and UV/ $S_2O_8^{2-}$. c_0(RB 19) = 50 mg·L^{-1}, $c_0(S_2O_8^{2-})$ = 0.1 mmol·L^{-1}, flow rate = 1.5 mL·min^{-1}, UV light intensity = 1950 µW·cm^{-2}, temperature = 25±0.5 °C.

The complete removal of the dye occurred at pH 3 when the solution was irradiated with UV-C light in the presence of $S_2O_8^{2-}$, whereas at pH 10, a decrease of the initial dye concentration was also obtained, but to a smaller extent (30 %). The activation of peroxydisulfate anions with UV light and the formation of reactive species, probably sulfate and hydroxyl radicals, significantly enhanced the removal of RB 19 dye.

The changes in the UV/Vis absorption spectra at various initial peroxydisulfate concentrations during $UV/S_2O_8^{2-}$ treatment of RB 19 dye is presented in Fig. S-2 of the Supplementary material. The peak observed in the visible region corresponds to the blue color, while the peak observed in the UV region was due to the anthraquinone structure of the dye.[21] It is evident that the intensity of a peak in the visible region of the spectrum decreased when the initial oxidant concentrations increased, and completely disappeared under the optimal value of the initial peroxydisulfate concentration. Simultaneously, the reduction in the intensity of a peak in the ultraviolet region of the spectrum was considered as the evidence of degradation of the chromophore in the dye molecule. It appeared that both color removal and, to a certain degree, degradation of the RB 19 molecules were achieved under UV activated peroxydisulfate. Moreover, the results of *COD* measurements revealed a decrease of 54 % of *COD* when a combination of UV irradiation and peroxydisulfate was applied under acidic conditions (Fig. S-3).

Effect of the initial $S_2O_8^{2-}$ concentration

The effect of the initial $S_2O_8^{2-}$ concentration on the removal of RB 19 was studied in the concentration range from 0.05 to 0.4 mmol·L^{-1} of $S_2O_8^{2-}$, which is equivalent to RB 19/$S_2O_8^{2-}$ mole ratio from 1:0.625 to 1:5, while the other parameters were constant (Fig. 2).

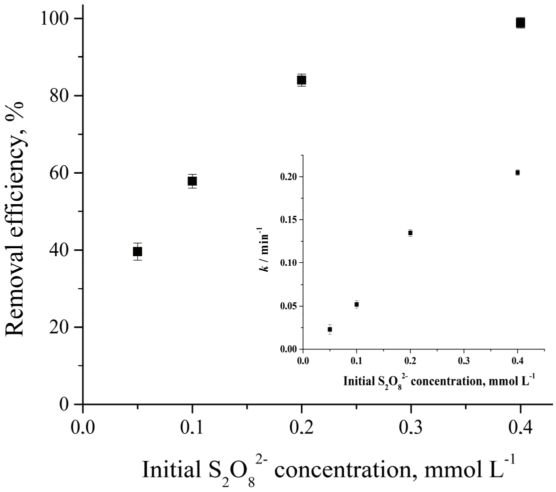

Fig. 2. The influence of different initial persulfate concentrations on the removal efficiency of RB 19 (inset represents changes of *k* at different persulfate concentrations). c_0(RB 19) = 50 mg·L^{-1}, flow rate = 7 mL·min^{-1}, pH native (3.8±0.1), UV light intensity = 1950 μW·cm^{-2}, temperature = 25±0.5 °C.

Removal efficiency increased from 39 up to 84 % with increasing initial persulfate concentration from 0.05 to 0.2 mmol·L^{-1} (RB 19/$S_2O_8^{2-}$ mole ratio from 1:0.625 to 1:1.25). The enhancement in the removal efficiency of RB 19 dye could be attributed to the increasing rate of $SO_4^{\bullet-}$ formation as the concentration of $S_2O_8^{2-}$ increased (reaction (5)):[14]

$$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-} \quad (5)$$

Further increase in the initial $S_2O_8^{2-}$ concentration from 0.2 to 0.4 mmol·L^{-1} led to a not-proportional increase in the removal efficiency, reached a value of 98 %. This trend was probably a consequence of the quenching of $SO_4^{\bullet-}$ with $S_2O_8^{2-}$ and $SO_4^{\bullet-}$ themselves when the peroxydisulfate was present in excess (reaction (6)):[22]

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \ (k = (5.2\pm0.7)\times10^8\ M^{-1}\ s^{-1}) \quad (6)$$

Similar results were reported for degradation of benzophenone in a heat activated persulfate process,[14] chloramphenicol in a UV/persulfate system,[23] and remazol red with UV activated persulfate.[4]

Effect of initial pH

The results revealed that the removal of RB 19 dye in the UV/$S_2O_8^{2-}$ system is more favorable in acidic conditions, in the comparison to neutral and basic conditions (Fig. 3).

Complete color removal was obtained at pH 3.0, while with increasing in pH value up to pH 5.0, removal efficiency drastically decreased, and reached a value of 62 %. With further increase in the initial pH from 5.0 up to 10.0, the removal efficiency decreased to 30 %. Moreover, the pseudo-first rate constant dropped significantly from 0.155 to 0.042 min^{-1} when the initial pH value was raised from 3.0 up to 5.0, while with further increase in the initial pH value up to 10.0, a slight decrease in rate constant was observed (0.016 min^{-1}). When the initial pH value was lower than pH 7.0, $SO_4^{\bullet-}$ plays the major role in RB19 degradation, since they are supposed to be the dominant radicals in the UV/$S_2O_8^{2-}$ system.[24] In addition, due to the acid catalyzed decomposition of persulfate at lower pH values, a larger number of $SO_4^{\bullet-}$ would be generated, so that degradation efficiency might be improved (reactions (7) and (8)):[10]

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \tag{7}$$

$$HS_2O_8^- \rightarrow SO_4^{\bullet-} + SO_4^{2-} + H^+ \tag{8}$$

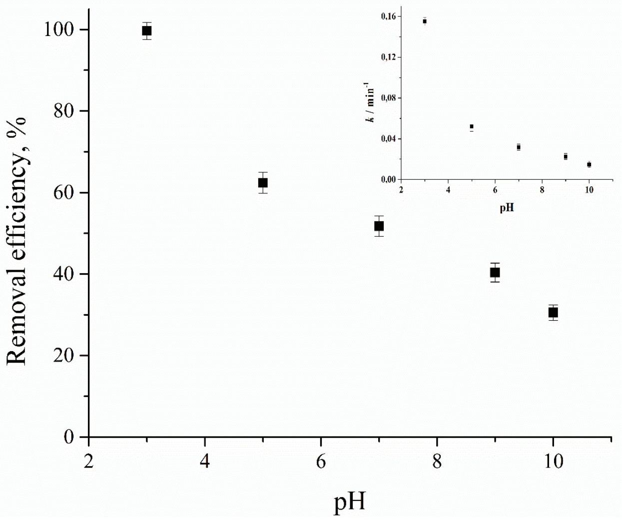

Fig. 3. The influence of different initial pH on the removal efficiency of RB 19 (the inset represents changes in *k* at different pH values). c_0(RB 19) = 50 mg·L^{-1}, $c_0(S_2O_8^{2-})$ = 0.1 mmol·L^{-1}, flow rate = 7 mL·min^{-1}, UV light intensity = 1950 μW·cm^{-2}, temperature = 25±0.5 °C

When the initial pH value was greater than pH 7.0, it is assumed that both $SO_4^{\bullet-}$ and $HO^\bullet$, existed in the UV/$S_2O_8^{2-}$ system.[23] Since $HO^\bullet$ possesses a lower oxidation potential than $SO_4^{\bullet-}$, a decrease in the removal efficiency could be expected as the initial pH value increased. Moreover, under alkali conditions, an excessive amount of OH^- could react with $SO_4^{\bullet-}$ and further generate $HO^\bullet$, and hence, the inhibition effect was probably dominant (reactions (9) and (10)):[22]

$$SO_4^{\bullet-} + {}^-OH \rightarrow SO_4^{2-} + HO^\bullet \; (k = 5.6\times10^7\ \mathrm{M^{-1}\ s^{-1}}) \tag{9}$$

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

Similar results were obtained for the degradation of the same dye in thermally activated peroxydisulfate and for the degradation of sulphamethoxazole under UV light activated persulfate.[25,26]

Effect of flow rate

The effect of flow rate on the removal efficiency of textile dye RB 19 is presented in Fig. S-4 of the Supplementary material. Up to four flow rates were tested in the range from 1.5 up to 30 mL·min^{-1}. The results demonstrated that the removal efficiency was inversely proportional to the flow rate. Namely, complete removal of the dye was evidenced when the flow rate was 1.5 mL min^{-1}. The calculated pseudo first order rate constant under these conditions was 0.282 min^{-1}. As the flow rate increased up to 30 ml min^{-1}, the removal efficiency and the pseudo first constant decreased and reached values 12 % and 0.005 min^{-1}, respectively. Such behavior could be explained by the fact that at lower flow rates, the residence time was longer, and hence, the exposure of dye to the UV irradiation and attack of sulfate radicals was promoted, leading to a higher percentage of dye degradation. On the contrary, due to the shorter resident time at higher flow rates, the removal of dye was retarded.

Effect of initial dye concentration

It was found that an increase in the initial dye concentration generally resulted in a decrease in the rate constants and the efficiencies of color removal (Fig. S-5 of the Supplementary material). Values of RB 19 dye removal decreased dramatically from 91 to 45 %, when the initial dye concentration increased from 20 to 60 mg·L^{-1}. A further increase in the initial dye concentration up to 100 mg·L^{-1} led to a decline in the value of removal efficiency to 26 %. A similar decreasing trend of the pseudo first order rate constants with increasing initial dye concentration was obtained. This observation was primarily because a higher concentration of the dye enhanced the number of dye molecules, but not of the concentration of the oxidative species, and thus, the removal rate became slower. At higher initial dye concentrations, the dye molecules themselves absorb more of the UV-C light and hence, lower amounts of sulfate radicals are expected, consequently resulting in decreasing removal efficiency.[27] In addition, the possibility of the generation of more inorganic anions increased with increasing RB 19 dye concentration, leading to competition between the dye molecules and the oxidation species.[28]

Identification of predominant radicals at different initial pH values

The most often used method for the identification of major radical species in oxidation processes is the free radical quenching method, usually with alcohols, such as methanol, ethanol, *tert*-butanol.[29,30] The contribution of $SO_4^{\bullet-}$ and $HO^{\bullet}$ to pollutant degradation could be determined due to the different second order reaction rate constants of these radicals with alcohols. For instance, the rate constant in the reaction between methanol and $SO_4^{\bullet-}$ was 1.1×10^7 M^{-1} s^{-1}, while the rate constant for the reaction with $HO^{\bullet}$ was 9.7×10^8 M^{-1} s^{-1}.[7,31] Therefore, it is assumed that methanol effectively scavenges both hydroxyl and sulfate radicals. On the other hand, the rate constants of *tert*-butanol with $SO_4^{\bullet-}$ and $HO^{\bullet}$ vary in the range 4.0–9.1×10^5 M^{-1} s^{-1} and 3.8–7.6×10^8 M^{-1} s^{-1}, respectively, and hence, *tert*-butanol has approximately three orders of magnitude higher rate of scavenging for $HO^{\bullet}$ than that for $SO_4^{\bullet-}$.[32,33] According to previous investingations, it could be expected that sulfate radicals are the predominant radicals in acidic and neutral conditions, whereas hydroxyl radicals should only be present at high pH values, due to the conversion of sulfate radical into hydroxyl radicals (reaction (9)).[10]

Bearing in mind the above-mentioned facts, experiments were performed in the presence of 100 mmol·L^{-1} of methanol and *tert*-butanol at three initial pH values 3, 7 and 10 to identify predominant reactive species (Fig. 4).

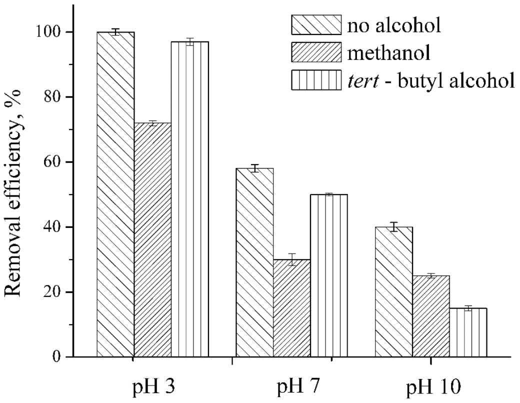

Fig. 4. The removal efficiency of RB 19 dye in UV/$S_2O_8^{2-}$ process in the presence of *tert*-butanol & methanol at different initial pH values. c_0(RB 19) = = 50 mg·L^{-1}, $c_0(S_2O_8^{2-})$ = 0.1·mmol L^{-1}, flow rate = 7 mL·min^{-1}, UV light intensity = 1950 μW·cm^{-2}, temperature = = 25±0.5 °C.

In the absence of alcohols under acidic conditions, the removal efficiency of the RB 19 dye was found to be almost 100 %, whereas the removal efficiency was strongly suppressed in the presence of 100 mmol·L^{-1} methanol (72 %). The presence of *tert*-butanol under acidic conditions did not significantly affect the removal efficiency. Removal of RB 19 dye was 58 % under neutral conditions and decreased to 30 and 51 % after the addition of 100 mmol·L^{-1} of methanol and *tert*-butanol, respectively. The percentage RB 19 removal was 40 % at pH 10 when *tert*-butanol and methanol were absent, whereas, obtained removal efficiencies in the presence of 100 mmol·L^{-1} of methanol and of *tert*-butanol were 25 and 15 %, respectively. It is evident that in the case of RB 19 dye decolorization, the scavenging effect of *tert*-butanol was prominent in alkali conditions, whereas the presence of methanol significantly affected the removal of the dye in acidic and neutral conditions, and to a lower extent in alkali conditions. These findings suggested that sulfate radicals are mainly responsible for the removal of the investigated dye in acidic and neutral conditions. In alkali conditions, the removal of the RB 19 dye was inhibited to the greater extent in the presence of *tert*-butanol, implying that hydroxyl radicals could participate, together with sulfate radicals, in dye degradation.

Influence of inorganic anions

The presence of many anions could influence the activity of the main oxidizing species in the application of UV activated peroxydisulfate for the treatment of wastewater. The most common scavenging species present are carbonate/bicarbonate, chloride, sulfate, nitrate and phosphate. Carbonate and bicarbonate usually exist in water and wastewater systems. They have the ability to react with $SO_4^{\bullet-}$ and $HO^{\bullet}$, formed during the UV irradiation of peroxydisulfate, leading to the formation of carbonate radicals (reactions (11)–(14)):[22,34,35]

$$HCO_3^- + HO^{\bullet} \rightarrow HCO_3^{\bullet} + HO^- \ (k = 8.5\times10^6\ M^{-1}\ s^{-1}) \tag{11}$$

$$CO_3^{2-} + HO^{\bullet} \rightarrow CO_3^{\bullet-} + HO^- \ (k = 4.2\times10^8\ M^{-1}\ s^{-1}) \tag{12}$$

$$SO_4^{\bullet-} + HCO_3^- \rightarrow HCO_3^{\bullet-} + SO_4^{2-} \ (k = 1.6\pm0.2\times10^6\ M^{-1}\ s^{-1} \text{ at pH 8.4}) \tag{13}$$

$$SO_4^{\bullet-} + CO_3^{2-} \rightarrow CO_3^{\bullet-} + SO_4^{2-} \ (k = 6.4\pm0.4\times10^6\ M^{-1}\ s^{-1} \text{ at pH} > 11) \tag{14}$$

It was reported that carbonate radicals have a sufficient redox potential (1.6 V at pH 8.4, 1.59 V at pH 12) for the degradation of organic pollutants, and these radicals are more selective toward organic pollutants compared to $SO_4^{\bullet-}$ and $HO^{\bullet}$.[22] In general, both the positive and negative impact of bicarbonate and carbonate on the performances of advanced oxidation processes have been reported in the literature.[36,37] The negative effect was mainly ascribed to the scavenging action of the anions to the main oxidizing species, whereas the role of carbonate radicals was emphasized to explain the positive influence of carbonate/ /bicarbonate. The effect of carbonate and bicarbonate anions on the removal efficiency of RB 19 dye was studied at different concentrations (0, 10, 20, 50, 100 and 200 mmol·L^{-1}). The results (Fig. S-6 of the Supplementary material) revealed that when the concentrations of added carbonate was increased from 0 up to 20 mmol·L^{-1}, the removal efficiency slightly decreased from 73 to 66 %, whereas further increase in carbonate concentration to 50 mmol·L^{-1}, increased removal efficiency to 80 %. No significant changes in the removal efficiency were observed with further increase in the carbonate concentration up to 200 mmol·L^{-1}. Reactive carbonate radicals, produced by the reaction of carbonate with sulfate and hydroxyl radicals, with a redox potential of 1.6 V, are probably capable of degrading RB 19 dye in a similar manner as sulfate radicals or catalyze propagation reaction, whereby more reactive oxidation species are produced.[17] This adverse behavior at lower carbonate concentrations might be attributed to the fact that the reactivity of $CO_3^{\bullet-}$ was not sufficient to exceed the importance of $SO_4^{\bullet-}$ and $HO^\bullet$ when the initial concentration of carbonate was low.

The removal of textile dye RB 19 slightly increased with increasing bicarbonate concentrations up to 50 mmol L^{-1} and remained almost unchanged at higher bicarbonate concentrations (Fig. S-6). The bicarbonate radical $HCO_3^{\bullet-}$, generated by the reaction of $SO_4^{\bullet-}$ with HCO_3^- (reaction (13)) was reported to have redox potential of ≈1.65 V at pH 7 and could participate in the degradation process or enhance the propagation reactions. In addition, HCO_3^- reacts with $SO_4^{\bullet-}$ at a much slower reaction rate (k = 1.6±0.2×10^6 M^{-1} s^{-1}) compared with that of CO_3^{2-} (k = 6.4±0.4×10^6 M^{-1} s^{-1}), which could explain why the influence of bicarbonate is less significant in the removal of textile dye RB 19 with the $UV/S_2O_8^{2-}$ system.

Complex reactions are involved in the interaction between chlorides and sulfate/hydroxyl radicals. Species such as $Cl^\bullet$, $Cl_2^{\bullet-}$, $ClHO^{\bullet-}$ could be generated during UV activation of peroxydisulfate in the presence of chlorides, according to reactions (15)–(20):[38–40]

$$SO_4^{\bullet-} + Cl^- \rightarrow Cl^\bullet + SO_4^{2-}\ (k = 4.7\times10^8\ M^{-1}\ s^{-1}) \tag{15}$$

$$Cl^\bullet + Cl^- \rightarrow Cl_2^{\bullet-}\ (k = 8\times10^9\ M^{-1}\ s^{-1}) \tag{16}$$

$$2Cl_2^{\bullet-} \rightarrow 2Cl^- + Cl_2\ (k = 1.3\times10^9\ M^{-1}\ s^{-1}) \tag{17}$$

$$Cl^\bullet + H_2O \rightarrow ClHO^{\bullet-} + H^+\ (k = 1.3\times10^3\ M^{-1}\ s^{-1}) \tag{18}$$

$$ClHO^{\bullet-} \leftrightarrows HO^\bullet + Cl^-\ (k = 6.1\times10^9\ M^{-1}\ s^{-1}) \tag{19}$$

$$Cl^- + HO^\bullet \rightarrow ClHO^{\bullet-}\ (k = 4.3\times10^9\ M^{-1}\ s^{-1}) \tag{20}$$

It was assumed that chloride anions have an overall negative impact on the degradation of organic contaminants with advanced oxidation processes, due to their possible involvement in scavenging of $SO_4^{\bullet-}$ and $HO^\bullet$.[41] However, different researches reported the improved effect of chloride anions, which at higher concentrations could promote the propagation reactions and the production of more $SO_4^{\bullet-}$.[23,42] In addition, the positive effect of chloride anions could be explained by the fact that the formed chlorine radicals possess a sufficiently high redox potential for degradation of organic contaminants.[29] Moreover, some studies reported the dual effect of chlorides, reducing at lower Cl^-concentrations and accelerating at higher Cl^- concentrations.[43] The effects of different concentrations of chlorides (0, 10, 20, 50, 100 and 200 mmol·L^{-1}) on the degradation of textile dye RB 19 by the $UV/S_2O_8^{2-}$ process are illustrated in Fig. S-7. The RB 19 removal percentage was almost unchanged at low concentrations of Cl^- (up to 50 mmol L^{-1}) and slightly reduced with increasing Cl^- dosage up to 200 mmol L^{-1}. Overall, it is obvious that the degradation of RB 19 dye was insignificantly influenced by the presence of chloride anions. Besides sulfate radicals, there may exist other reactive oxidizing species ($Cl^\bullet$, $Cl_2^{\bullet-}$, $ClHO^{\bullet-}$), which probably participate in the decolonization of investigated textile dye. A similar trend was observed with the degradation of diethyl phthalate (DEP) by UV/persulfate and *p*-nitrosodimethylaniline with iron activated persulfate at neutral pH.[17,19]

CONCLUSIONS

This work showed that the activation of peroxydisulfate with UV irradiation is an efficient technology for the removal of the anthraquinone textile dye RB 19 from wastewater. Almost complete decolonization of RB 19 dye solution was achieved under optimal operational conditions. Moreover, the reduction of *COD* value confirmed that applied technology is suitable for a satisfying degree of dye mineralization. Degradation of the dye was affected by the initial pH value; the value for the removal efficiency was higher in acidic than those obtained in neutral and alkali medium. The removal efficiency was significantly enhanced when the flow rate was reduced. Increasing in the RB 19 concentration had a negative impact on the performance of the applied technology. The presence of wastewater matrix components, such as carbonate, bicarbonate and chloride, affected the removal efficiency of investigated dye to different degrees. Carbonate showed a specific effect, both positive and negative, depending on concentration, while the influence of bicarbonate and chloride was negligible. The contribution of sulfate radicals in the removal of the dye was confirmed by the quenching method with methanol under acidic, neutral and alkali conditions.

SUPPLEMENTARY MATERIAL

Additional data are available electronically from the journal web site: http:////www.shd.org.rs/JSCS/, or from the corresponding author on request.

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ИЗВОД

ДЕГРАДАЦИЈА ТЕКСТИЛНЕ АНТРАХИНОНСКЕ БОЈЕ ПОД ДЕЈСТВОМ СУЛФАТНИХ РАДИКАЛА У РЕАКТОРУ СА КЛИПНИМ ПРОТИЦАЊЕМ

ЈЕЛЕНА МИТРОВИЋ, МИЉАНА РАДОВИЋ ВУЧИЋ, МИЛОШ КОСТИЋ, НЕНА ВЕЛИНОВ,
СЛОБОДАН НАЈДАНОВИЋ, ДАНИЈЕЛА БОЈИЋ и АЛЕКСАНДАР БОЈИЋ

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У овом раду је испитана деградација антрахинонске текстилне боје reactive blue 19 у присуству сулфатних радикала који су генерисани активацијом пероксидисулфата UV-C (254 nm) зрачењем. Самостална примена UV зрачења није утицала на ефикасност уклањања боје, док је ефикасност уклањања значајно побољшана у присуству оксиданса. Проценат уклањања текстилне боје расте са порастом почетне концентрације оксиданса, док је са повећањем почетне концентрације боје уочен супротан тренд. Кисела средина је погоднија за деградацију боје, у поређењу са неутралном и базном. На деградацију текстилне боје не утиче присуство бикарбонатног и хлоридног анјона у опсегу концентрација од 1 до 200 mmol L^{-1}. Присуство карбоната показује негативан утицај на ефикасност уклањања, посебно уколико је концентрација карбонатног анјона мања од 20 mmol

L^{-1}. Међутим, при концентрацијама карбонатног анјона већим од 20 mmol L^{-1}, ефикасност уклањања боје расте. Примена метанола и терц-бутанола као хватача радикала је показала да, у зависности од почетне pH вредности раствора боје, може доћи до генерисања и хидроксилних и сулфатних радикала.

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