This is an early electronic version of an as-received manuscript that has been accepted for publication in the Journal of the Serbian Chemical Society but has not yet been subjected to the editing process and publishing procedure applied by the JSCS Editorial Office.


This “raw” version of the manuscript is being provided to the authors and readers for their technical service. It must be stressed that the manuscript still has to be subjected to copyediting, typesetting, English grammar and syntax corrections, professional editing and authors’ review of the galley proof before it is published in its final form. Please note that during these publishing processes, many errors may emerge which could affect the final content of the manuscript and all legal disclaimers applied according to the policies of the Journal.
Sulfate radicals based degradation of the antraquinone textile dye in a plug flow photoreactor

JELENA MITROVIĆ*, MILJANA RADOVIĆ VUČIĆ, MILOŠ KOSTIĆ, NENA VELINOVIĆ, SLOBODAN NAJDANOVIĆ, DANIJELA BOJIĆ and ALEKSANDAR BOJIĆ

University of Niš, Faculty of Sciences and Mathematics, Višegradska 33, 18 000 Niš, Serbia

(Received 13 March; revised 1 May; accepted 6 May 2019)

Abstract: The study evaluated the degradation of antraquinone textile dye Reactive Blue 19, frequently used dye in the textile industry, by means of sulfate radicals. Sulfate radicals were generated by activation of peroxodisulfate with UV-C (254 nm) irradiation. The UV irradiation alone did not affect removal efficiency, while with addition of the oxidant removal efficiency was significantly improved. The degradation rates of textile dye increased at higher initial dosages of oxidant, while the opposite trend was observed in the case of increase in the initial dye concentration. Acidic conditions were more convenient for degradation of the dye than neutral and basic. Degradation of the textile dye was not affected by the presence of bicarbonate and chloride anions within the concentrations range from 1 up to 200 mmol·L⁻¹. The presence of carbonate showed 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, dye removal efficiency increased. The use of methanol and tert-butyl alcohol as the scavengers revealed that both radicals, HO• and SO₄⁻, would be generated depending on initial pH value of 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 COD.² The amount of generated textile wastewater can reach more than 300 L per kg of product.³ The main adverse effect of dyes in the environment are their inhibitory effect on aquatic photosynthesis. Moreover, degradation by-products of
dyes, which can include a large variety of substituents in aromatic structures (e.g., amines), could be cancerogenic. Reactive Blue 19 is very stable and resistant anthraquinone reactive dye, which fixation effectiveness ranges between 75% and 80% due to the formation of vinyl sulfone and of 2-hydroxyethyl-sulfone.

Various physical, chemical and biological methods have been used for the removal of these type 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. Traditional AOPs are based on the generation of highly reactive hydroxyl radicals (‘OH, HR-AOPs), which are capable to react rapidly and non-selectively with organic pollutants, leading in ideal conditions to the formation of CO₂, H₂O and non-toxic inorganic ions. The second-order rate constants for reaction of ‘OH with organic pollutants were reported to be in the range of 10⁸ to 10¹⁰ M⁻¹ s⁻¹. Recently, application of AOPs was extended on the use of the other oxidation agents, and formation of the other radicals. Among them, the sulfate radicals are acquiring researchers’ interest, since that these radicals have higher redox potential (2.5-3.1 V) compared to that of the hydroxyl radicals (1.8-2.7 V) at pH 7, they are more selective, and possess longer life-time (t₁/₂ = 30-40 µs) than hydroxyl radicals (t₁/₂ = 10⁻³ µs). In the sulfate radicals-based AOPs (SR-AOPs), peroxymonosulfate (PMS, HSO₅⁻) and peroxydisulfate (PDS, S₂O₅²⁻) were used as a source of sulfate radicals (SO₄•⁻). Both of these oxidants could be activated in different ways to generate sulfate radicals. The most often used methods for activation are UV irradiation, alkali, heat and transition metals. The peroxydisulfate anion offers some advantages over the other oxidants; it is a solid oxidant at ambient temperature, its transport and storage are ease, it has high stability, and high water solubility. Two sulfate radicals (SO₄•⁻) are formed when peroxydisulfate is activated by UV irradiation (reaction (1)).

\[ S_2O_5^{2-} + h\nu \rightarrow 2SO_4^{•-} \]  

(1)

Various inorganic anions, such as chloride, carbonate/bicarbonate, sulfate, nitrate, phosphate and natural organic matter (NOM), could be present in surface and wastewater, and could influence the efficiency of the water treatment process. It was reported that these anions might have both positive or negative impact on the performance of the hydroxyl and sulfate radicals-based oxidation technologies, depending on anions concentration, applied system variables, nature of contaminants. 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 anthraquinone 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 done in 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-butyl alcohol. Moreover, the effect of some anions, common constituents of wastewaters, was elucidated.

**EXPERIMENTAL**

**Chemicals**

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 shown in Table S1 (Supplementary Material, available on Journal web site)). Regent grade K$_2$S$_2$O$_8$ was provided by VWR (USA). Methanol and tert-butyl alcohol were ACS reagent grade and supplied from Merck (Germany). Sodium chloride, sodium bicarbonate and sodium carbonate were reagent grade and were purchased from Zorka Šabac (Serbia). All solutions were prepared with high water purity obtained from Smart2Pure system with a conductivity of 0.055 µSm$^{-1}$ (Thermo Scientific, USA).

**Degradation experiment**

A laboratory-scale plug flow photoreactor was used for oxidation treatment of anthraquinone textile dye RB 19. The system consists of an influent tank, peristaltic pump, photoreactor and effluent tank (Figure S1). 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. 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 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 stock solution, with 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 up 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-butyl alcohol 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 anions stock solution 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 percentage of the decolorization (removal efficiency, %), the following formula was used (Eq (2)):

\[
\text{Removal efficiency, } \% = \left(\frac{c_0 - c}{c_0}\right) \times 100
\] (2)
where \( c_0 \) and \( c \) are concentrations (mg L\(^{-1}\)) of dye RB 19 before and after UV/S\(_2\)O\(_8^2\)- treatment, respectively.

According to the assumption that the degradation of dye RB 19 in UV/S\(_2\)O\(_8^2\)- system, mainly depends on SO\(_4^•\) and HO\(^•\) 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)):\(^{19}\)

\[
\frac{dc}{dt} = -\left(k_1c_{SO_4^•ss} + k_2c_{HO^•ss}\right) = -kc
\]  

(3)

where \( c \) represents concentration of RB 19 dye (mg L\(^{-1}\); \( k_1 \) and \( k_2 \) are pseudo-first order rate constants of RB 19 dye with SO\(_4^•\) and HO\(^•\), respectively; \( c_{SO_4^•ss} \) and \( c_{HO^•ss} \) are steady-state concentration of SO\(_4^•\) and HO\(^•\) radicals, respectively; \( k \) is overall pseudo-first order rate constants of RB 19 dye with total reactive species.

The first order kinetic equation for plug flow reactor can be applied for calculation of overall pseudo-first order rate constant (equation (4)):\(^{20}\)

\[
\tau = \frac{1}{k} \ln \frac{c_0}{c}
\]  

(4)

where \( \tau \) is detention time, min; \( \tau = V/Q; V \) – volume of reactor, mL; \( Q \) – flow rate, mL\(\cdot\)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 using UV-Vis spectrophotometry (UV 1800, Shimadzu, Japan). The pH of the RB 19 dye solution was adjusted by pH meter (Orion Star A214, Thermo Scientific, USA). The thermoreactor (RD125, Lovibond, United Kingdom), the Lovibond\(^\circledR\) COD Vario tube test for the measuring range 0-150 mg L\(^{-1}\) and the Lovibond\(^\circledR\) Multidirect photometer (Lovibond, United Kingdom) were used for the determination of chemical oxygen demand.

**RESULTS AND DISCUSSION**

**Degradation of RB 19 dye under different oxidation conditions (UV alone, S\(_2\)O\(_8^2\)- alone and UV/S\(_2\)O\(_8^2\))**

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

The decrease of the dye concentration was not considerable when experiments were carried out with persulfate alone at pH 3, while at pH 10 about 8 % of color removal was obtained after 24 h. This result could be attributed to the fact that by activation of S\(_2\)O\(_8^2\)- at alkaline conditions sulfate radicals might be produced.\(^{11}\)

The complete removal of the dye occurred at pH 3 when the solution was irradiated with UV-C light in the presence of S\(_2\)O\(_8^2\)-, whereas at pH 10 decrease of the initial dye concentration was also obtained, but at smaller extent (30 %).
The activation of peroxydisulfate anion with the UV light, and formation of reactive species, probably sulfate and hydroxyl radicals, significantly enhanced removal of RB 19 dye.

![Figure 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 ºC.](image)

The changes in the UV/Vis absorption spectra at various initial peroxydisulfate concentrations during $UV/S_2O_8^{2-}$ treatment of RB 19 dye was presented in Figure S2. 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. 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 initial peroxydisulfate concentration. At the same time, the reduction in the intensity of a peak in the ultraviolet region of the spectrum was considered as the evidence of chromophore degradation in the dye molecule. It appeared that both the color removal and certain degree of RB 19 molecule degradation were achieved under UV activated peroxydisulfate. Moreover, results of COD measurements revealed decrease of 54 % of COD when the combination of UV irradiation and peroxydisulfate was applied at acidic conditions (Figure S3).

The effect of initial $S_2O_8^{2-}$ concentration

The effect of 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/$S_2O_8^{2-}$ molar ratio from 1:0.625 to 1:5, while the other parameters were constant (Figure 2).
Figure 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 ºC

Removal efficiency increased from 39 % up to 84 % with increasing in initial persulfate concentration from 0.05 to 0.2 mmol·L$^{-1}$ (RB 19/S$_2$O$_8^{2-}$ molar ratio from 1:0.625 to 1:1.25). The enhancement in removal efficiency of RB 19 dye can be attributed to the increasing in rate of SO$_4^{•-}$ radicals formation as the concentration of S$_2$O$_8^{2-}$ increased (reaction (5)).

$$\text{SO}_4^{•-} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4^{2-} + \text{S}_2\text{O}_8^{•-} \quad (5)$$

Further increase in the initial S$_2$O$_8^{2-}$ concentration from 0.2 to 0.4 mmol·L$^{-1}$ led to the not proportional increase in the removal efficiency which reached a value of 98 %. This trend was probably a consequence of the quenching of SO$_4^{•-}$ radicals with S$_2$O$_8^{2-}$ and SO$_4^{•-}$ radicals themselves when the peroxydisulfate was present in excess (reaction (6)):

$$\text{SO}_4^{•-} + \text{SO}_4^{•-} \rightarrow \text{S}_2\text{O}_8^{2-} \quad (k = 5.2±0.7x10^8 \text{ M}^{-1}\text{s}^{-1}) \quad (6)$$

Similar results were reported for degradation of benzophenone in heat activated persulfate process, chloramphenicol in UV/persulfate system, remazol red with UV activated persulfate.
The effect of initial pH

The results revealed that the removal of RB 19 dye in the UV/S$_2$O$_8^{2-}$ system is more favorable in the acidic conditions, in the comparison to the neutral and basic (Figure 3).

Figure 3. The influence of different initial pH on the removal efficiency of RB 19 (inset represents changes of $k$ at different pH), $c_0$(RB 19) = 50 mg·L$^{-1}$, $c_0$(S$_2$O$_8^{2-}$) = 0.1 mmol·L$^{-1}$, flow rate = 7 mL·min$^{-1}$, UV light intensity = 1950 μW·cm$^{-2}$, temperature = 25 ± 0.5 °C

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, removal efficiency decreased to 30%. Moreover, pseudo-first rate constant dropped significantly from 0.155 to 0.042 min$^{-1}$ when initial pH value raised from 3.0 up to 5.0, while with further rising in initial pH value up to 10.0, a slight drop of rate constant was obtained (0.016 min$^{-1}$). When initial pH value was lower than pH 7.0, SO$_4^{•-}$ radicals play the major role in RB19 degradation, since it is supposed to be the dominant radicals in the UV/S$_2$O$_8^{2-}$ system. In addition, due to the acid catalyzed decomposition of persulfate at lower pH values, a greater amount of SO$_4^{•-}$ radicals would be generated, so that degradation efficiency might be improved (reactions (7) and (8)).

$$\text{S}_2\text{O}_8^{2-} + \text{H}^+ \rightarrow \text{HS}_2\text{O}_8^- \quad (7)$$
$$\text{HS}_2\text{O}_8^- \rightarrow \text{SO}_4^{•-} + \text{SO}_4^{2-} + \text{H}^+ \quad (8)$$

When the initial pH value was greater than pH 7.0, it is assumed that both radicals, SO$_4^{•-}$ and HO', existed in the UV/S$_2$O$_8^{2-}$ system. Since that HO' radicals possessed lower oxidation potential than SO$_4^{•-}$, the decrease in removal efficiency
could be expected as initial pH value increased. Moreover, in the alkali conditions, an excessive amount of OH\(^-\) can react with SO\(_4\)^{2-} and further generated HO\(^\cdot\), so the inhibition effect was probably dominant (reactions (9) and (10)).

\[
\text{SO}_4^{2-} + \text{OH} \rightarrow \text{SO}_4^{2-} + \text{HO}^\cdot \quad (k = 5.6 \times 10^7 \text{M}^{-1}\text{s}^{-1}) \\
\text{SO}_4^{2-} + \text{HO}^\cdot \rightarrow \text{HSO}_4^{-} + \frac{1}{2}\text{O}_2 \quad (10)
\]

Similar results were obtained with degradation of the same dye in thermal activated peroxydisulfate and when degradation of sulphamethoxazole under UV light activated persulfate was performed.\textsuperscript{25,26}

The effect of flow rate

The effect of flow rate on the removal efficiency of textile dye RB 19 was presented in Figure S4. Up to four flow rates were tested in the range from 1.5 up to 30 mL\cdot min\(^{-1}\). Results demonstrated that the removal efficiency was inversely proportional to the flow rate. Namely, the complete removal of the dye was evaluated when the flow rate was 1.5 mL min\(^{-1}\). The calculated pseudo first rate constant for these conditions was 0.282 min\(^{-1}\). As the flow rate increased up to 30 ml min\(^{-1}\), removal efficiency as well as pseudo first constant, decreased and reached values 12 % and 0.005 min\(^{-1}\), respectively. Such behavior can be explained by the fact that at the lower flow rates residence time was longer, so that the exposure of dye to the UV irradiation and attack of sulfate radicals was better, leading to the higher percentage of dye degradation. On the contrary, due to the shorter resident time at higher flow rates, the removal of dye was retarded.

The 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 (Figure S5). Values of RB 19 dye removal decreased dramatically from 91 % to 45 %, when the initial dye concentration increased from 20 to 60 mg\textperiodcentered L\(^{-1}\). A further increasing in the initial dye concentration up to 100 mg\textperiodcentered L\(^{-1}\) led to decline in the value of removal efficiency to 26 %. The similar decreasing trend of pseudo first rate constants with increase in the initial dye concentration was obtained. This observation was primarily due to the fact that a higher concentration of the dye enhanced the number of dye molecules, but not the oxidative species concentration, so the removal rate became slower. At higher initial dye concentrations more absorption of UV-C light would be achieved by the dye molecules itself; lower amounts of sulfate radicals are expected which consequently resulted in decreasing of the removal efficiency.\textsuperscript{27} In addition, the possibility of the generation of more inorganic anions increased with the increasing in RB 19 dye concentration, so competing reaction between dye molecules and oxidation species.\textsuperscript{28}

Identification of predominant radicals at different initial pH values

The most often used method for the identification of major radical species in the oxidation processes is free radicals quenching method, usually with alcohols,
such as methanol, ethanol, tert-butyl alcohol. Contribution of SO$_4^{•-}$ and HO$^•$ radicals to pollutant degradation can be made due to the different second order reaction rate constants of these radicals with alcohols. For instance, the rate constant between methanol and SO$_4^{•-}$ was $1.1 \times 10^7$ M$^{-1}$s$^{-1}$, while the rate constant for reaction with HO$^•$ was $9.7 \times 10^8$ M$^{-1}$s$^{-1}$. Therefore, it is assumed that methanol effective scavenges both hydroxyl and sulphate radicals. On the other side, the rate constants of tert-butyl alcohol with SO$_4^{•-}$ and HO$^•$ radicals vary in the range 4-9.1 $\times 10^5$ M$^{-1}$s$^{-1}$ and 3.8-7.6 $\times 10^8$ M$^{-1}$s$^{-1}$, respectively, so the tert-butyl alcohol has approximately three orders of magnitude higher rate of scavenging for HO$^•$ radicals than that for SO$_4^{•-}$ radicals. According to previous investigations, it can be expected that sulphate radicals are predominant radicals at acidic and neutral conditions, whereas hydroxyl radicals should be only present at high pH values, due to the conversion of sulfate radical into hydroxyl radicals (reaction (9)).

Bering in mind above mentioned facts, experiments were carried out in the presence of 100 mmol$\cdot$L$^{-1}$ of methanol and tert-butyl alcohol at three initial pH values 3, 7 and 10 to identify predominant reactive species (Figure 4).

![Figure 4. The removal efficiency of RB 19 dye in UV/S$_2$O$_8^{2-}$ process in the presence of tert-butyl alcohol & methanol at different initial pH values. c$_0$(RB 19)=50 mg L$^{-1}$, c$_0$(S$_2$O$_8^{2-}$)=0.1 mmol L$^{-1}$, flow rate = 7 mL min$^{-1}$, UV light intensity = 1950 μW cm$^{-2}$, temperature = 25 ± 0.5 ºC.](image-url)

In the absence of alcohols at acidic conditions, removal efficiency of the RB 19 dye was found to be almost 100 %, whereas removal efficiency was strongly suppressed by the presence of 100 mmol$\cdot$L$^{-1}$ of methanol (72 %). The presence of tert-butyl alcohol at acidic conditions did not affect removal efficiency significantly. Removal of RB 19 dye was 58 % at neutral conditions and decreased to 30 % and 51 % after addition of 100 mmol$\cdot$L$^{-1}$ of methanol and tert-butyl alcohol, respectively. Percentage of RB 19 removal was 40 % at pH 10
when tert-butyl alcohol and methanol are no present, whereas, obtained removal efficiency in the presence of 100 mmol·L⁻¹ of methanol and tert-butyl alcohol was 25 % and 15 %, respectively. It is evident that, in the case of RB 19 dye decolourisation, scavenging effect of tert-butyl alcohol was prominent at alkali conditions, whereas the presence of methanol affect significantly removal of the dye in acidic and neutral conditions, and at lower extend at alkali conditions. These findings suggested that sulfate radicals are mainly responsible for the removal of the investigated dye in acidic and neutral conditions. At alkali conditions, removal of the RB 19 dye was inhibited to the greater extend in the presence of tert-butyl alcohol, implying that hydroxyl radicals could participate, together with sulfate radicals, in dye degradation.

The influence of inorganic anions

Many anions present in the wastewater can influence the activity of main oxidizing species in the application of UV activated peroxydisulfate for wastewater treatment. The most common investigated scavenging species are carbonate/bicarbonate, chloride, sulfate, nitrate and phosphate anions. Carbonate and bicarbonate anions usually exist in the water and wastewater systems. They have the ability to react with \( \text{SO}_4^{2-} \) and \( \text{HO}^\cdot \), formed during the UV irradiation of peroxydisulfate, leading to the formation of carbonate radicals (reactions (11) – (14)).\(^{22,34,35}\)

\[
\begin{align*}
\text{HCO}_3^- + \text{HO}^\cdot &\rightarrow \text{HCO}_3^\cdot + \text{HO}^- (k = 8.5\times10^6 \text{ M}^{-1}\text{s}^{-1}) \\
\text{CO}_3^{2-} + \text{HO}^\cdot &\rightarrow \text{CO}_3^\cdot + \text{HO}^- (k = 4.2\times10^8 \text{ M}^{-1}\text{s}^{-1}) \\
\text{SO}_4^{2-} + \text{HCO}_3^- &\rightarrow \text{HCO}_3^\cdot + \text{SO}_4^{2-} (k = 1.6\pm0.2\times10^6 \text{ M}^{-1}\text{s}^{-1} \text{ at pH 8.4}) \\
\text{SO}_4^{2-} + \text{CO}_3^{2-} &\rightarrow \text{CO}_3^\cdot + \text{SO}_4^{2-} (k = 6.4\pm0.4\times10^6 \text{ M}^{-1}\text{s}^{-1} \text{ at pH > 11})
\end{align*}
\]

It was reported that the carbonate radicals have enough redox potential (1.6V at pH 8.4, 1.59V at pH 12) for degradation of organic pollutants, and these radicals are more selective toward organic pollutants compared to the \( \text{SO}_4^{2-} \) and \( \text{HO}^\cdot \) radicals.\(^{22}\) In general, both the positive and the negative impact of bicarbonate and carbonate anions on the performances of advanced oxidation processes, were 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 anions. 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). Results (Figure S6) revealed that when the concentrations of added carbonate anions 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 removal efficiency were observed with further increase of carbonate concentration up to 200 mmol·L⁻¹. Reactive carbonate radicals, produced by the reaction of carbonate anions with sulfate and hydroxyl radicals,
with a redox potential of 1.6 V, are probably capable to degrade RB 19 dye in a similar manner as sulfate radicals or catalyse propagation reaction, which produced more reactive oxidation species. This adverse behavior at lower carbonate concentrations might be attributed to the fact that the reactivity of SO$_4^-$ was not sufficient to prevail the importance of SO$_4^-$ and HO' radicals when the initial concentration of carbonate was low.

The removal of textile dye RB 19 slightly increased with increasing in bicarbonate concentrations up to 50 mmol L$^{-1}$ and remained almost unchanged at higher bicarbonate concentrations (Figure S5). The bicarbonate radical HCO$_3^-$, generated by the reaction of SO$_4^-$ with HCO$_3^-$ (reaction (13)) was reported to yield redox potential $\sim 1.65$ V at pH 7 and could participate in degradation process or enhancement the propagation reactions. In addition, HCO$_3^-$ reacts with SO$_4^-$ at much slower reaction rate ($k = 1.6 \pm 0.2 \times 10^6$ M$^{-1}$s$^{-1}$) compared with that of CO$_3^-$ ($k = 6.4 \pm 0.4 \times 10^6$ M$^{-1}$s$^{-1}$) which could explain that the influence of bicarbonate is less significant in the removal of textile dye RB 19 with UV/S$_2$O$_8^-$ system.

Complex reactions are involved in the interaction between chloride anions and sulfate/hydroxyl radicals. Species like Cl$^+$, Cl$_2^+$, ClHO$^+$ can be generated during the UV activation of peroxydisulfate in presence of chloride anions, according to reactions (15) - (20).

\begin{align*}
\text{SO}_4^+ + \text{Cl}^- &\rightarrow \text{Cl}^+ + \text{SO}_4^2^- \quad (k = 4.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}) \quad (15) \\
\text{Cl}^+ + \text{Cl}^- &\rightarrow \text{Cl}_2^+ \quad (k = 8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}) \quad (16) \\
2\text{Cl}_2^+ &\rightarrow 2\text{Cl}^+ + \text{Cl}_2 \quad (k = 1.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}) \quad (17) \\
\text{Cl}^- + \text{H}_2\text{O} &\rightarrow \text{CIHO}^+ + \text{H}^+ \quad (k = 1.3 \times 10^7 \text{ M}^{-1}\text{s}^{-1}) \quad (18) \\
\text{CIHO}^+ &\leftrightarrow \text{HO}^- + \text{Cl}^+ \quad (k = 6.1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}) \quad (19) \\
\text{Cl}^- + \text{HO}^- &\rightarrow \text{CIHO}^- \quad (k = 4.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}) \quad (20)
\end{align*}

It was assumed that chloride anions have an overall negative impact on the degradation of organic contaminants with the advanced oxidation processes, due to their possible involvement in scavenging of SO$_4^-$ and HO' radicals. However, different researches reported the improved effect of chloride anions, which at higher concentrations could promote the propagation reactions and production of more SO$_4^-$, $^{21,42}$ In addition, the positive effect of chloride anions could be explained by the fact that formed chlorine radicals possess enough high redox potential for degradation of organic contaminants. Moreover, some studies reported the dual effect of chloride anions, reducing at lower Cl$^-$ anions concentrations, and accelerating at higher Cl$^-$ anions concentrations. Figure S7 illustrated the effects of different concentrations of chloride anions (0, 10, 20, 50, 100 and 200 mmol·L$^{-1}$) on the degradation of textile dye RB 19 by the UV/S$_2$O$_8^-$ process. The RB 19 removal percentage was almost unchanged at low concentrations of Cl$^-$ anions (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 and the other reactive oxidizing species (Cl\(^-\), Cl\(_2\)\(^-\), ClHO\(^-\)), which probably participate in the decolorisation of investigated textile dye. A similar trend was observed with degradation of diethyl phthalate (DEP) by UV/persulfate and p-nitrosodimethylaniline with iron activated persulfate at neutral pH.\(^{17,19}\)

CONCLUSION

This work showed that activation of peroxydisulfate with UV irradiation is an efficient technology for the removal of anthraquinone textile dye RB 19 from wastewater. The almost complete decolorisation of RB 19 dye solution was obtained under optimal operational conditions. Moreover, the reduction of COD value confirmed that applied technology is suitable for satisfying degree of dye mineralisation. Degradation of the dye was affected by the initial pH value; value for removal efficiency was higher in acidic than those obtained in neutral and alkali medium. The removal efficiency was significantly enhanced when the flow rate decreased. Increasing in the RB 19 concentration had a negative impact on the performance of applied technology. The presence of wastewater matrix components, such as carbonate, bicarbonate and chloride, affected 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 neglected. The contribution of sulfate radicals in the removal of the dye was confirmed by the quenching method with methanol at acidic, neutral and alkali conditions.

SUPPLEMENTARY MATERIAL

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

Acknowledgements: This work was supported by the grant from the Ministry of Education, Science and Technological Development of the Republic of Serbia (TR34008).
концентрации 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-бутил алкохола као хватача радикала је показала да, у зависности од почетне pH вредности раствора боје, може доћи до генерисања и хидроксилних и сулфатних радикала.

(Примљено 13. марта; ревијирено 1. маја; прихваћено 6. маја 2019)

REFERENCES
15. J. Sharma, I. M. Mishra, V. Kumar, J. Environ. Manage. 156 (2015) 266 (https://doi.org/10.1016/j.jenvman.2015.03.048)
SUPPLEMENTARY MATERIAL TO
Sulfate radicals based degradation of the antraquinone textile dye
in a plug flow photoreactor

JELENA MITROVIĆ, MILJANA RADOVIĆ VUČIĆ, MILOŠ KOSTIĆ,
NENA VELINOV1, SLOBODAN NAJDANOVIĆ, DANIJELA BOJIĆ
and ALEKSANDAR BOJIĆ

University of Niš, Faculty of Sciences and Mathematics, Višegradska 33, 18 000 Niš, Serbia

TABLE SI. General characteristic of RB 19 dye

<table>
<thead>
<tr>
<th>Properties</th>
<th>Dye</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial name</td>
<td>Remazol Brilliant Blue R</td>
</tr>
<tr>
<td>C. I. number</td>
<td>61200</td>
</tr>
<tr>
<td>Apparent color</td>
<td>Blue</td>
</tr>
<tr>
<td>Purity</td>
<td>~ 50 %</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>626 g mol⁻¹</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C₂₂H₁₆N₂Na₂O₁₁S₃</td>
</tr>
</tbody>
</table>

![Chemical structure]

- Maximum absorption wavelength: 592 nm
- Water solubility: 10 g dm⁻³
Figure S1. Scheme of irradiation system with plug flow reactor

Figure S2. UV/Visible spectral changes during UV/S$_2$O$_8^-$ treatment of RB 19 dye. $c_0$(RB 19) = 50 mg·L$^{-1}$, initial S$_2$O$_8^-$ concentration: a) before treatment, and after treatment with: b) 0.05, c) 0.1, d) 0.2, e) 0.4 and f) 0.6 mmol·L$^{-1}$, flow rate = 7 mL·min$^{-1}$, pH 3.0 ±0.1, UV light intensity = 1950 μW·cm$^{-2}$, temperature = 25 ± 0.5 ºC
Figure S3. COD changes before and after UV/S₄O₆²⁻ treatment. \( c_0(\text{RB 19}) = 50 \text{ mg L}^{-1}, \ c_0(\text{S}_2\text{O}_8^{2-}) = 1 \text{ mmol L}^{-1}, \) flow rate 1.5 mL min⁻¹, pH 3 ± 0.1, UV light intensity was 1950 μW cm⁻², temperature was 25 ± 0.5 °C.

Figure S4. The influence of flow rate on RB 19 dye degradation (inset represents changes of \( k \) at different flow rates). \( c_0(\text{RB 19}) = 50 \text{ mg L}^{-1}, \ c_0(\text{S}_2\text{O}_8^{2-}) = 0.1 \text{ mmol L}^{-1}, \) native pH (3.8 ± 0.1), UV light intensity = 1950 μW cm⁻², temperature = 25 ± 0.5 °C.
Figure S5. The influence of different initial RB 19 concentration on its degradation (inset represents changes of $k$ at different dye concentrations). $c_0(S_2O_8^{2-}) = 0.1$ mmol·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.

Figure S6. Influence of different carbonate and bicarbonate anions concentrations on the removal efficiency of RB 19. $c_0$(RB 19) = 50 mg·L$^{-1}$, $c_0$(S$_2$O$_8^{2-}$) = 0.1 mmol·L$^{-1}$, flow rate 7 mL·min$^{-1}$, pH 8.0±0.1 (for bicarbonate) 12±0.1 (for carbonate), UV light intensity was 1950 μW·cm$^{-2}$.
Figure S7. Influence of different chloride anions concentrations on the removal efficiency of RB 19. $c_0$(RB 19) = 50 mg L$^{-1}$; $c_0$(S$_2$O$_8^{2-}$) = 0.1 mmol L$^{-1}$; flow rate 7 mL min$^{-1}$; pH native (3.8 ± 0.1), UV light intensity was 1950 μW cm$^{-2}$.

Example of $k$ calculation according to equation 4:

Experimental conditions:
- initial pH value = 3.00 ±0.1
- initial S$_2$O$_8^{2-}$ concentration = 0.1 mmol L$^{-1}$
- flow rate = 7 mL min$^{-1}$
- UV light intensity = 1950 μW cm$^{-2}$
- $c_0$(RB 19) = 50 mg L$^{-1}$ (before treatment)
- $c$(RB 19) = 1.64 mg L$^{-1}$ (after treatment)
- $\tau$ = 22 min

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

$k = 1/22 \ln 50/1.64 = 0.155$ min$^{-1}$