**Sulfate radicals based degradation of the antraquionone textile dye in plug flow photoreactor**

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*Abstract:* The study evaluated the degradation of antraquionone textile dye Reactive Blue 19, frequently used dye in textile industry, by means of sulfate radicals. Sulfate radicals were generated by activation of peroxydisulfate with UV-C (254 nm) irradiation. The UV irradiation alone did not affect removal efficiency, while it was improved significantly with addition of the oxidant. The degradation rates of textile dye increased with higher initial dosages of oxidant, while the opposite trend was observed in the case of increasing the initial dye concentration. Acidic conditions were more convenient for degradation of the dye then neutral and basic. Degradation of 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. Presence of carbonate showed suppressed effect on the removal efficiency especially at carbonate levels below 20 mmol∙L-1. However, at carbonate levels greater than 20 mmol∙L-1, RB 19 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 оf dye solution.

*Keywords:* Advance oxidation processes; Reactive Blue 19; carbonate/bicarbonate, chloride

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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 presence of strong color, suspended solids, chlorinated organics, surfactants, and heavy metals and they 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 effects 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.4 Reactive Blue 19 is one of the 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.5

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 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 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, H2Oand other 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-1.7 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).8 In the sulfate radicals-based AOPs (SR-AOPs), peroxymonosulfate (PMS, HSO5-) and peroxydisulfate (PDS, S2O82-) were used as a source of sulfate radicals (SO4•-).9 Both of the 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 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.15 Two sulfate radicals (SO4•-) are formed when peroxydisulfate is activated by UV irradiation (reaction (1)).16

S2O82- + hυ → 2SO4•- (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 efficiency of water treatment process.17 It was reported that these anions could have both positive or negative impact on performance of the hydroxyl and sulfate radicals-based oxidation technologies, depending on anions concentration, applied system variables, nature of 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 organic pollutants.

The aim ofthe present work was to evaluate the degradation of antraquionone textile dye C. I. Reactive Blue 19 by sulfate radicals, which were generated by irradiation of aqueous solution of the dye with UV-C light (254 nm) in the presence of peroxydisulfate as oxidant. All experiments were done in continuous conditions, in ideal plug flow photoreactor. In the first part, the influence of various operational parameters, including initial pH value, initial peroxydisulfateconcentration, flow rate and initial dye concentration, was investigated to determine the optimal degradation parameters. In the second part, the role of dominant oxidizing species in the applied system were 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, were elucidated.

EXPERIMENTAL

*Chemicals*

Textile dye Reactive Blue 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 I (SM). Regent grade K2S2O8 was provided by VWR (USA). Methanol and *tert-*butyl alcohol were ACS regent 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 antraquionone textile dye RB 19. The system consists of influent tank, peristaltic pump, photoreactor and effluent tank. Ten UV-C lamps of 28 W (Philips, Holland) emitting UV radiation at 254 nm wavelength were placed above the quartz tubes in 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. Peristaltic pump (PLP 380, Dülabo, Germany) was used for feeding the photoreactor with solution from influent tank. The experimental procedures consist of preparing of 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, 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, 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 known volume of the anions stock solution to the dye solution before the addition of 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 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, %), following formula was used (Eq (2)):

 (2)

where *c*0 and *c* are concentrations (mg∙L-1) of dye RB 19 before and after UV/S2O82- treatment, respectively.

According to the assumption that the degradation of dye RB 19 in UV/S2O82- system, mainly depends on SO4•- 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

 (3)

where *c* represents concentration of RB 19 dye (mg∙L-1); *k1* and *k2* are pseudo-first order rate constants of RB 19 dye with SO4•- and HO•, respectively; [SO4•-]ss and [HO•]ss are steady-state concentration of SO4•- and HO• radicals, respectively; *k* is overall pseudo-first order rate constants of RB 19 dye with total reactive species.

First order kinetic equation for plug flow reactor can be applied for calculation of overall pseudo-first order rate constant (Eq (4)).

 (4)

where *τ* is detention time, min; (τ = V/Q; V – volume of reactor, mL; Q – flow rate, mL∙min-1); *k* is first order rate constant, min-1; *c0* – initial dye concentration, mg∙L-1; *c* – 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® COD Vario tube test for the measuring range 0-150 mg∙L-1 and the Lovibond® Multidirect photometer (Lovibond, United Kingdom) was used for the determination of chemical oxygen demand.

RESULTS AND DISCUSSION

*Degradation of RB 19 dye under different oxidation conditions (UV alone, S2O82- alone and UV/S2O82-)*

The initial experiments were carried out in presence of only persulfate, under UV irradiation only and with 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 this dye is stable in water solution under the direct UV-C photolysis (Figure 1).



Figure 1.RB 19 residual concentrations after treatment with UV irradiation, S2O82- and UV/ S2O82-. *c*0(RB 19) = 50 mg∙L-1, *c*0(S2O82-) = 0.1 mmol∙L-1, flow rate 1.5 mL∙min-1, UV light intensity was 1950 μW∙cm–2, temperature was 25 ± 0.5 ºC.

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 S2O82- could be activated at alkaline conditions and sulfate radicals could be produced.11 Complete removal of the dye occurred at pH 3 when the solution was irradiated with UV-C light in the presence of S2O82-, whereas at pH 10 decrease of the initial dye concentration was also obtained, but at smaller extend (30 %). 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.

The changes in the UV/Vis absorption spectra at various initial peroxydisulfate concentrations during UV/S2O82- treatment of RB 19 dye was presented in Figure 2.



Figure 2. UV/Visible spectral changes during UV/S2O82- treatment of RB 19 dye. *c*0(RB 19) = 50 mg∙L-1, initial S2O82- 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 was 1950 μW∙cm–2, temperature was 25 ± 0.5 º C

The peak observed in the visible region corresponds to the blue color, while peak observed in the UV region was due to anthraquinone structure of the dye.20 It is evident that intensity of peak in 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 peak in the ultraviolet region of 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 combination of UV irradiation and peroxydisulfate was applied at acidic conditions (Figure 1-SM).

*The effect of initial S2O82- concentration*

The effect of initial S2O82- concentration on the removal of RB 19 was studied in the concentration range from 0.05 to 0.4 mmol∙L-1 of S2O82-, which is equivalent to RB 19/S2O82- molar ratio from 1:0.625 to 1:5, while the other parameters were constant (Figure 3).



Figure 3.Influence of different initial persulfate concentration on the removal efficiency of RB 19. *c*0(RB 19) = 50 mg∙L-1, flow rate 7 mL∙min-1, pH native (3.8 ± 0.1), UV light intensity was 1950 μW∙cm–2, temperature was 25 ± 0.5 º C

Removal efficiency increased from 39 % up to 84 % with increase in initial persulfate concentration from 0.05 to 0.2 mmol∙L-1 (RB 19/S2O82- 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 SO4•- radicals formation as the concentration of S2O82- increased (reaction (5)).

SO4•- + S2O82- → SO42- + S2O8•- (5)

When the initial S2O82- concentration increase from 0.2 to 0.4 mmol∙L-1, increase in removal efficiency is not proportional to the increase in oxidant concentration, and reached value of 98 %. This trend was probably consequence of the quenching of SO4•- radicals with S2O82- and SO4•- radicals themselves, when the peroxydisulfate was present in excess (reaction (6)).21

SO4•- + SO4•- → S2O82- (k = 5.2±0.7x108 M-1s-1) (6)

Similar results were reported for degradation of benzophenone in heat activated persulfate process,14 chloramphenicol in UV/persulfate system,22 remazol red with UV activated persulfate.4

*The effect of initial pH*

Results reveled that the removal of RB 19 dye in the UV/S2O82- system is more favorable in acidic conditions, in comparison to the neutral and basic (Figure 4).



Figure 4.Influence of different initial pH on the removal efficiency of RB 19. *c*0(RB 19) = 50 mg∙L-1, *c*0(S2O82-) = 0.1 mmol∙L-1, flow rate 7 mL∙min-1, UV light intensity was 1950 μW∙cm–2, temperature was 25 ± 0.5 º 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 value of 62 %. With further increasing in initial pH value from 5.0 up to 10.0, removal efficiency decreased to 30 %. Moreover, pseudo-first rate constant (Table II-SM) 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 raising in initial pH value up to 10.0, slight drop of rate constant was obtained (0.016 min-1). When initial pH value was lower than pH 7.0, SO4•- radicals play the major role in RB19 degradation, since it is supposed to be the dominant radicals in the UV/S2O82- system.23 In addition, due to the acid catalyzed decomposition of persulfate at lower pH values, greater amount of SO4•- radicals would be generated, so that degradation efficiency might be improved (reactions (7) and (8)).

S2O82- + H+ → HS2O8- (7)

HS2O8- → SO4•- + SO42- + H+ (8)

When initial pH value was greater than pH 7.0, it is assumed that both radicals, SO4•- and HO•, existed in the UV/S2O82- system.23 Since that HO• radicals possessed lower oxidation potential than SO4•-, decreased in removal efficiency could be expected as initial pH value increased. Moreover, in alkali conditions, excessive amount of OH- can react with SO4•- and further generated HO•, so that inhibition effect was probably dominant (reactions (9) and (10)).21

SO4•- + -OH → SO42- + HO• (k = 5.6 x 107 M-1s-1) (9)

SO4•- + HO• → HSO4- + 1/2O2 (10)

Similar results were obtained when degradation of sulphamethoxazole under UV light activated persulfate was performed.24

*The effect of flow rate*

The effect of flow rate on the removal efficiency of textile dye RB 19 was presented in Figure 2-SM. Up to four flow rates were tested in the range from 1.5 up to 30 mL∙min-1. Results demonstrated that removal efficiency is inversely proportional to the flow rate. Namely, complete removal of the dye was evaluated when flow rate was 1.5 mL min-1. Calculated pseudo first rate constant for these conditions was 0.282 min-1 (Table II-SM). 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 behaviour can be explained by the fact that at lower flow rates residence time is longer, so that the exposure of dye to the UV irradiation and attack of sulfate radicals better, leading to the higher percentage of dye degradation. On the contrary, due to the shorter resident time at higher flow rates, 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 decrease in the rate constants and efficiencies of color removal (Figure 3-SM). 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 increased in the initial dye concentration up to 100 mg∙L-1 led to decline in the value of removal efficiency to 26 %. Similar decreasing trend of pseudo first rate constants with increasing in initial dye concentration was obtained (Table II-SM). This observation was primarily due to the fact that higher concentration of the dye enhanced the number of dye molecules, but not the oxidative species concentration, so the removal rate becomes slower. At higher initial dye concertation 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.25 In addition, possibility of the generation of more inorganic anions with the increase in RB 19 dye concentration increased, so that competing reaction between dye molecules and oxidation species.26

*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.27, 28 Contribution of SO4•- 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, rate constant between methanol and SO4•- was 1.1x107 M-1s-1, while rate constant for reaction with HO• was 9.7x108 M-1s-1.7, 29 Therefore, it is assumed that methanol effective scavenges both hydroxyl and sulphate radicals. On the other side, rate constants of *tert*-butyl alcohol with SO4•- and HO• radicals vary in the range 4-9.1x105 M-1s-1 and 3.8-7.6x108 M-1s-1, respectively, so that *tert*-butyl alcohol has approximately three orders of magnitude higher rate of scavenging for HO• radicals than that for SO4•- radicals.30,31 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)).10

Bering in mind above mentioned facts, experiments were carried out in the presence of 100 mmol∙L-1 of methanol and *tert*-butyl alcohol at three initial pH values 3, 7 and 10 to identify predominant reactive species (Figure 5).

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Figure 5.Removal efficiency of RB 19 dye in UV/S2O82- process in the presence of *tert*-butyl alcohol and methanol at different initial pH values. *c*0(RB 19) = 50 mg∙L-1, *c*0(S2O82-) = 0.1∙mmol L-1, flow rate 7 mL∙min-1, UV light intensity was 1950 μW∙cm–2, temperature was 25 ± 0.5 ºC

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∙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∙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 ability to react with SO4•- and HO•, formed during the UV irradiation of peroxydisulfate, leading to formation of carbonate radicals (reactions (11) – (14)).32, 33, 21

HCO3- + HO• → HCO3• + HO- (k = 8.5 x 106 M-1s-1) (11)

CO32- + HO• → CO3•- + HO- (k = 4.2 x 108 M-1s-1) (12)

SO4•- + HCO3- → HCO3•- + SO42- (k = 1.6±0.2 x 106 M-1s-1 at pH 8.4) (13)

SO4•- + CO32- → CO3•- + SO42- (k = 6.4±0.4 x 106 M-1s-1 at pH > 11) (14)

It was reported that carbonate radicals have enough redox potential (1.6V at pH 8.4, 1.59V at pH 12) for degradation of organic pollutants, and that these radicals are more selective toward organic pollutants compared to the SO4•- and HO• radicals.21 In general, both, the positive and negative impact of bicarbonate and carbonate anions on the performances of advanced oxidation processes, were reported in the literature.34-35 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 positive influence of carbonate/bicarbonate anions. The effect of carbonate and bicarbonate anions on removal efficiency of RB 19 dye was studied at different concentrations (0, 10, 20, 50, 100 and 200 mmol∙L-1). Results (Figure 4-SM) revealed that when the concentrations of added carbonate anions increased from 0 up to 20 mmol∙L-1, removal efficiency slightly decreased from 73 % to 66 %, whereas further increased carbonate concentration to 50 mmol∙L-1, increased removal efficiency to 80 %. No significant changes in removal efficiency was observed with further increasing of carbonate concentration up to 200 mmol∙L-1. Reactive carbonate radicals, produced by reaction of carbonate anions with sulfate and hydroxyl radicals, with a redox potential of 1.6V, are probably capable to degrade RB 19 dye in similar manner as sulfate radicals or catalyse propagation reaction, which produced more reactive oxidation species.17 This adverse behaviour at lower carbonate concentrations might be attributed to the fact that the reactivity of CO3•- was not sufficient to prevail the importance of SO4•- and HO• radicals, 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 high bicarbonate concentrations (Figure 4-SM). The bicarbonate radical HCO3•-, generated by the reaction of SO4•- with HCO3- (reaction (13)) was reported to yield redox potential ∼1.65 V at pH 7 and could participate in degradation process or enhancement the propagation reactions. In addition, HCO3- reacts with SO4•- at much slower reaction rate (k = 1.6±0.2 x 106 M-1s-1) compared with that of CO32- (k = 6.4±0.4 x 106 M-1s-1)which could explain that the influence of bicarbonate is less significant in the removal of textile dye RB 19 with UV/S2O82- system.

Complex reactions are involved in the interaction between chloride anions and sulfate/hydroxyl radicals. Species like Cl•, Cl2•-, ClHO•- can be generated during the UV activation of peroxydisulfate in presence of chloride anions, according to reactions (15) - (20).36-38

SO4•- + Cl- → Cl• + SO42- (k = 4.7 x 108 M-1s-1) (15)

Cl• + Cl- → Cl2•- (k = 8 x 109 M-1s-1) (16)

2Cl2•- → 2Cl- + Cl2 (k = 1.3 x 109 M-1s-1) (17)

Cl• + H2O → ClHO•- + H+ (k = 1.3 x 103 M-1s-1) (18)

ClHO•- ↔ HO• + Cl- (k = 6.1 x 109 M-1s-1) (19)

Cl- + HO• → ClHO•- (k = 4.3 x 109 M-1s-1) (20)

It was assumed that chloride anions has overall negative impact on the degradation of organic contaminants with the advanced oxidation processes, due to their possible involvement in scavenging of SO4•- and HO• radicals.39 However, different researches reported improved effect of chloride anions, which at higher concentrations could promote the propagation reactions and production of more SO4•-.22, 40 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.27 Moreover, some studies reported the dual effect of chloride anions, reducing at lower Cl- anions concentrations, and accelerating at higher Cl- anions concentrations.41 Figure 5-SM 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/S2O82- 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 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•, Cl2•-, ClHO•-), which probably participate in the decolorisation of investigated textile dye. Similar trend was observed with degradation of diethyl phthalate (DEP) by UV/persulfate and p-nitrosodimethylaniline with iron activated persulfate at neutral pH.19, 17

CONCLUSION

This work showed that activation of peroxydisulfate with UV irradiation is efficient technology for complete removal of anthraquinone textile dye RB 19 from wastewater. Complete decolorisation of RB 19 dye solution was obtained under optimal operational conditions. Moreover, 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; values for removal efficiency was higher in acidic then those obtained in neutral and alkali medium. The removal efficiency was significantly enhanced when the flow rate decreased. Increasing the RB 19 concentration had negative impact on the performance of applied technology. The presence of wastewater matrix components, such as carbonate, bicarbonate and chloride, affect removal efficiency of investigated dye to different degrees. Carbonate showed specific effect, both positive and negative, depending on concentration, while influence of bicarbonate and chloride was neglected. Contribution of sulfate radicals in the removal of the dye was confirmed by the quenching method with methanol at acidic, neutral and alkali conditions.

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И З В О Д

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

ЈЕЛЕНА МИТРОВИЋ1, МИЉАНА РАДОВИЋ ВУЧИЋ1, МИЛОШ КОСТИЋ1, НЕНА ВЕЛИНОВ1, СЛОБОДАН НАЈДАНОВИЋ1, ДАНИЈЕЛА БОЈИЋ1 и АЛЕКСАНДАР БОЈИЋ1

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У овом раду је испитана деградација антрахинонске текстилне боје Reactive Blue 19, боје која се често користи у текстилној индустрији, у присуству сулфатних радикала. Сулфатни радикали 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 kонцентрација 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.

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