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Degradation of C.I. Acid Blue 25 in water using UV/$K_2S_2O_8$ process: effect of salts and environmental matrix

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ABSTRACT

The objective of this work was to evaluate the degradation of an anthraquinone dye, C.I. Acid Blue 25 (AB25), in aqueous phase using UV/$K_2S_2O_8$ (PPS) process. Experiments were conducted in batch mode using a low-pressure mercury lamp emitting mainly at 253.7 nm. The effect of operational conditions such as initial PPS and AB25 concentrations and initial solution pH on the degradation of AB25 was studied. Additionally, the influence of salts addition on the degradation of the dye was examined. Besides, degradation experiments were conducted using a natural mineral water instead of deionized water to check the applicability of UV/PPS oxidation system in a real matrix. It was found that the degradation rate of AB25 was improved significantly by the UV/PPS process compared with UV irradiation alone. The photolytic decay of PPS in water was evidenced spectrophotometrically, showing that $SO_4^{\bullet-}$ is the primarily radical involved in the degradation of AB25. The degradation rate increased considerably with increasing PPS concentration up to 400 mg L^{-1}, above which further increase enhanced insignificantly the abatement of the dye. Correspondingly, the degradation rate increased significantly with the increase of the initial dye concentration. Acidic condition (pH 2) offered the best conversion rate and the degradation decreased with pH increase in the interval 2–10. Addition of NaCl and Na_2SO_4 had practically no significant effect on the elimination of the pollutant. The degradation of AB25 was more effective in natural mineral water in the absence and presence of PPS, making UV/PPS an efficient treatment technique for the elimination of organic pollutants from natural waters.

Keywords: Acid Blue 25; UV/$K_2S_2O_8$ process; Degradation; $SO_4^{\bullet-}$ radical; Real matrix

1. Introduction

Pollution caused by industrial wastewaters has become a common problem for many countries. The effluents from dye manufacturing and consuming industries are highly colored coupled with high chemical oxygen demand (COD) and biochemical oxygen demand. Discharge of such effluents imparts color to receiving streams and affects its aesthetic value. Color interferes with penetration of sunlight into waters, retards photosynthesis, inhibits the growth of aquatic biota and interferes with gas solubility in water bodies [1]. Dyes may also be problematic if they are broken down anaerobically in the sediment, as toxic amines are often produced due to the incomplete degradation by bacteria [2]. Therefore, the removal of dyes from wastewater has given much attention in the last few decades by adopting different traditional technologies such as physical, chemical and biological treatments [3]. However, the physicochemical treatments are nondestructive and they only transform organic compound from one phase to another, which requires further

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treatment to avoid secondary pollution [4]. Additionally, most of organic dyes are persistent and may be toxic to the bacterial attack [4]. To overcome these problems, a new oxidation technology known as advanced oxidation processes (AOPs) have been proposed and employed for the treatment of hazardous materials in wastewater [4]. AOPs are based on the production of highly reactive species, hydroxyl radicals ($^{\bullet}$OH), which could degrade a variety of organic pollutants with rate constants in the order of 10^8–10^{11} M^{-1} s^{-1} [5].

Lately, sulfate radical-based AOPs has become an emerging approach for the removal of organic compounds in water and soil. These technologies, based on the production of sulfate radicals ($SO_4^{\bullet-}$), have attracted great scientific and technological interest in the area of water treatment and in situ chemical oxidation processes [6]. Generated generally from the activation of persulfate (PS) or peroxymonosulfate, $SO_4^{\bullet-}$ offers a high potential oxidation (E^0 = 2.6 V), comparable with that of $^{\bullet}$OH (E^0 = 2.7 V), and reacts with organic compounds with rate constants in the order of 10^6–10^9 M^{-1} s^{-1} [7]. In general, sulfate radicals are known by their longer half-life and higher selectivity for the oxidation of target organic compounds than that of hydroxyl radicals [8]. $SO_4^{\bullet-}$ can be achieved through thermal [9,10], ultraviolet (UV) irradiation [8,11], transition metal [12,13], sonolytic [14] and radiolytic [15] activation of PS. UV activation of PS has been found to provide a prominent alternative for the decomposition of organic contaminants including phenols [16,17], perfluorocarboxylic acids [11,18], dyes [19,20] and endocrine disruptor chemicals [21]. A summary of the PS activation chemistry can be presented by the following reactions [6]:

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

$$SO_4^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + H^+ + SO_4^{2-} \text{ at all pH values} \tag{2}$$

$$SO_4^{\bullet-} + HO^- \rightarrow {}^{\bullet}OH + H^+ + SO_4^{2-} \text{ mostly at alkaline pH values} \tag{3}$$

$$SO_4^{\bullet-} / HO^{\bullet} + \text{pollutant} \rightarrow \text{degradation products} \tag{4}$$

As can be seen in the above reactions, the degradation process proceeds with production of the sulfate and hydroxyl radicals, which is demonstrated experimentally by electron spin resonance (ESR) spin trapping technique [22]. Sulfate ion will be generated as the end product, which is practically inert and not considered to be a pollutant. The PS is ordinarily available as a salt associated with ammonium, sodium or potassium. It has been reported that potassium persulfate ($K_2S_2O_8$; PPS) gives better results in photooxidative removal of some organic materials than $(NH_4)_2S_2O_8$ under natural pH [23]. In view of this, and the general unsuitability of adding ammonia to waters, PPS can be the best choice for using in the UV/PS process. Alternatively, PPS is much cheaper than other oxidants like hydrogen peroxide [20].

To the best of our knowledge, the study of the degradation of Acid Blue 25 (AB25) using UV/PPS process has not been reported in the literature. Anthraquinone dyes represent the second most important class of commercial dyes after azo compounds and are mainly used for dyeing wool, polyamide and leather [24]. UV/PPS process was significantly affected by the properties of the aqueous matrix. For example, the matrix pH could influence the distribution and concentration of radical species [22], thus affecting the contaminant degradation. The background ions, e.g., Cl^- and SO_4^{2-}, could compete with target contaminants for reaction with radicals. Therefore, the influence of the aqueous matrix should also be considered when applying UV/PPS in practice. In this work, we investigated the degradation of AB25 dye, aiming at providing an insight into the ability of UV/PPS process for the remediation of AB25-contaminated natural water. First, the photodecomposition of PS in pure water was demonstrated. Furthermore, factors affecting the efficiency of AB25 oxidation, including PPS and AB25 concentrations, solution pH and mineral anions were also evaluated. Finally, the degradation of the dye was assessed in real natural mineral water to evaluate the impact of environmental matrix on the feasibility of the UV/PPS process.

2. Materials and methods

All materials were used as received without further purification. The anthraquinone dye AB25 (C.I. number: 62055; molecular formula: $C_{20}H_{13}N_2NaO_5S$; IUPAC name: 1-amino-9,10-dihydro-9,10-dioxo-4-(phenylamino)-2-anthracenesulfonic acid, monosodium salt; dye content 45%, molecular weight: 416.39 g mol^{-1}) and PPS were purchased from Sigma-Aldrich (USA). All other reagents (sodium chloride, sodium sulfate, sulfuric acid and sodium hydroxide) were commercial products of the purest grade available (analytical grade). Distilled water was used throughout this study.

Batch kinetic studies were carried out in a cylindrical water-jacketed glass reactor using a constant solution volume of 300 mL. A low-pressure mercury lamp (15 mW cm^{-2}, Oriel 6035, radiation wavelength <280 nm with a peak at 253.7 nm), placed in a quartz tube, was totally immerged in the solution and placed vertically at the center of the reactor. The temperature of the solution was controlled using a thermocouple immersed in the reacting medium and maintained constant at 20°C with circulating cooling water through a jacket surrounding the cell. During irradiation, the solution was agitated magnetically at a constant speed. Aqueous samples were taken from the solution at constant interval and the concentration of the dye was determined using a UV–vis spectrophotometer (Jenway 6405) at 602 nm, which is the maximum absorption wavelength of the dye in the visible region. The pH of the solution was adjusted using sodium hydroxide or sulfuric acid. The absorbance data of the dye solution, determined spectrophotometrically, indicated that change in the initial pH of the dye solution in the interval pH 2–10 has no effect on λ_{max}. All experiments were conducted in triplicate, and the mean values were reported.

3. Results and discussion

3.1. Characterization of AB25 degradation using UV/PPS process

Fig. 1 shows the UV–visible absorption spectra of AB25 solution (C_0 = 30 mg L^{-1}) during the UV/PPS treatment at natural pH (~6) and with 200 mg L^{-1} of PPS. It can be seen that

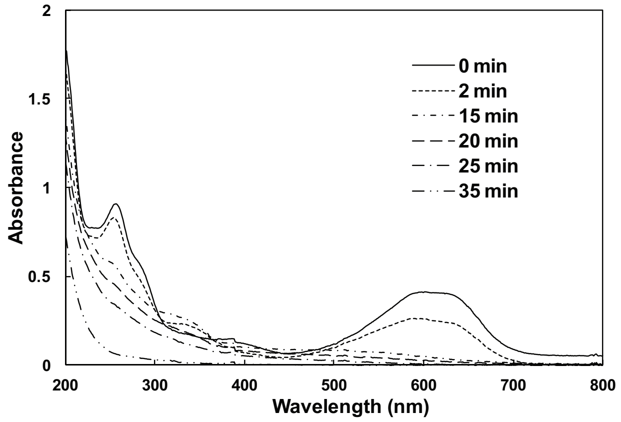

Fig. 1. UV–vis spectra of AB25 solution during the treatment with UV/PPS system (conditions: volume – 300 mL, initial dye concentration – 30 mg L^{-1}, initial PPS concentration – 200 mg L^{-1}, pH ~6, temperature – 20°C ± 2°C).

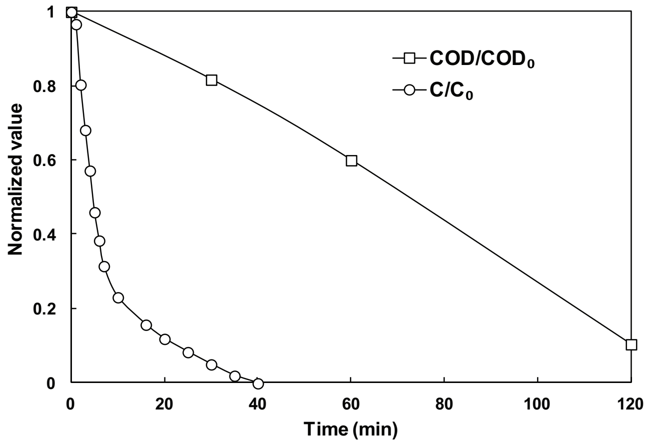

Fig. 2. Kinetics of AB25 removal and COD abatement during the treatment with UV/PPS process (conditions: volume – 300 mL, initial dye concentration – 30 mg L^{-1}, initial PPS concentration – 200 mg L^{-1}, pH ~6, temperature – 20°C ± 2°C).

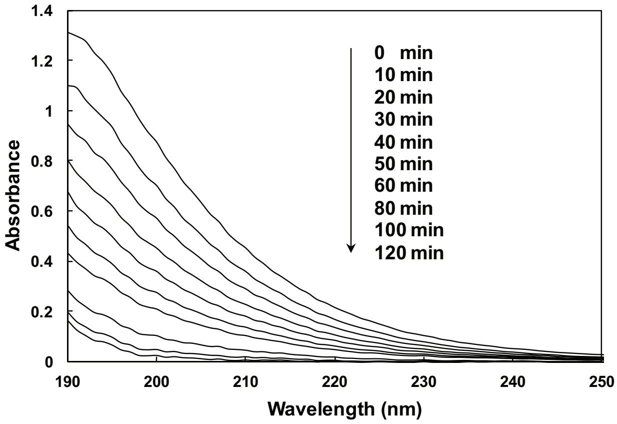

Fig. 3. Changes in UV spectra of persulfate ions during photolysis of PPS aqueous solution (conditions: volume – 300 mL, initial PPS concentration – 200 mg L^{-1}, pH ~6, temperature – 20°C ± 2°C).

there are two main characteristic absorption bands of AB25. One in UV region with λ_{max} = 257 nm and another in the visible region with λ_{max} = 602 nm. The strong absorption band of the chromophore group at 602 nm is responsible for the blue color of the solution whereas that at 257 nm represents the absorbance of the aromatic content of the dye, and the decrease of absorbance at this band indicates the degradation of aromatic parts of dye. During the UV/PPS treatment, the absorption band of AB25 at 602 nm became weaker along with the reaction time and the whole UV–visible spectrum decreased rapidly with time and finally disappeared after 35 min. The decrease of the absorbance in the visible band may reasonably be due to the elimination of the auxochromes and indicated complete removal of the conjugated structure of the dye. The decrease in the absorbance in the UV region at 257 nm indicated that aromatic rings of AB25 were destroyed. This result demonstrated that there is no simple discoloration of AB25 solution but a degradation which resulted in a decrease in the amount of organic matter in the reacting medium. To confirm this statement, measurement of COD abatement during the oxidative treatment was carried out and the results are shown in Fig. 2 together with the normalized AB25-concentration profile. As can be observed from Fig. 2, at time when AB25 was completely disappeared, COD abatement was only 30% but it was ~90% after 120 min of treatment. These results evidenced that an efficient mineralization of the AB25 aqueous solution took place by the UV/PPS process. These results are in good agreement with those of Soleymani et al. [20] who reported that COD abatement of C.I. Direct Red 16 solution in UV/peroxymonosulfate system was 7% after 30 min of treatment and 77% after 180 min. Similarly, Saien et al. [25] reported COD removal values of 45% and 60% at, respectively, 30 and 60 min during the degradation of Triton X-100 surfactant by UV/PPS system. It should be mentioned that ecotoxicity analysis of the solution during the treatment period is important as the degradation intermediates/byproducts are sometime more toxic than the initial pollutant. However, even if this analysis was not conducted in this work, the hard reduction in the initial COD (90%) at the final treatment (2 h) gives confidence that the final discharged effluent will not be toxic.

As mentioned in the introduction, after the cleavage of the peroxide bond in $S_2O_8^{2-}$ via homolysis to the sulfate radical, the latter will further react with water to produce $^{\bullet}OH$ (Eqs. (1) and (2)). At neutral pH, both radicals coexist in the reacting medium as already demonstrated by Dogliotti and Hayon [22] using ESR spin-trapping technique. Thus, both radicals are suspected to be involved in the degradation of the dye. In our study, the generation of these reactive species, particularly $SO_4^{\bullet-}$ radical, was verified by monitoring the photodecomposition of PS ions during photolysis. In Fig. 3, the PS UV spectra during photolysis of 300 mL of PPS (initial concentration: 200 mg L^{-1}) solution at natural pH (~6) was shown. Initially (t = 0 min), the absorption spectrum of PS in water was characterized by a band with an intense absorption at 190 nm. Application of UV irradiation clearly caused a progressive decrease in the intensity of UV band, evidencing the decomposition of PS ions into sulfate radical according to Eq. (1) [22].

3.2. Effect of initial pH

Fig. 4 shows the effect of initial solution pH (2, 6 and 10) on the degradation of AB25 (C_0 = 30 mg L^{-1}) with UV/PPS in the presence of 200 mg L^{-1} of PPS at 20°C. As can be observed high conversion degrees of AB25 were obtained for the three tested initial pHs. However, the degradation rate decreased progressively from low pH to high pH levels. The initial degradation rates are 4.17, 3.18 and 2.54 mg L^{-1} min^{-1} for, respectively, pH 2, 6 and 10. These finding are in line with those of Li et al. [26] who investigated the degradation of methyl orange by PS activated with zero-valent zinc. Likewise, similar results were reported for the degradation of methyl *tert*-butyl ether [27] and 1,1,1-trichloroethane [9] by the thermally activated PS.

It has been reported that the pH of the solution affects the distribution of the radical species ($SO_4^{\bullet-}$ and $^\bullet OH$) in the reacting medium [22,28]. ESR spin-trapping studies during photolysis of PS showed that $SO_4^{\bullet-}$ is the main product species at pH < 8.5. For pH > 8.5, $SO_4^{\bullet-}$ decays rapidly into $^\bullet OH$ via Eq. (2) and only $^\bullet OH$ was detected for pH > 10.8 [22]. Alternative chemical probes method in heat activated PS system revealed that $SO_4^{\bullet-}$ is the predominant radical oxidant at pH < 7; both $SO_4^{\bullet-}$ and $^\bullet OH$ are present at neutral pH; and $^\bullet OH$ is the predominant radical at more basic pH (pH > 9) [28]. Based on these analyses, the degradation of AB25 should be increased with increasing pH from acidic to basic medium. However, the opposite trend was obtained, which may be explained as follow: the radicals-AB25 reactions were always accompanied by radical-radical recombination reactions, as illustrated by Eqs. (5)–(7) [29].

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \quad k_5 = 4\times10^8 M^{-1}s^{-1} \tag{5}$$

$$SO_4^{\bullet-} + {}^\bullet OH \rightarrow HSO_4^- + 1/2O_2 \quad k_6 = 1.0\times10^{10} M^{-1}s^{-1} \tag{6}$$

$$ {}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2 \quad k_7 = 5.5\times10^9 M^{-1}s^{-1} \tag{7}$$

Compared with $^\bullet OH$, $SO_4^{\bullet-}$ radicals are less reactive toward organic compounds [7]. However, the importance of $SO_4^{\bullet-}$ may overweight $^\bullet OH$ due to its longer life-time and, thus, higher steady-state concentration in the aqueous phase. Indeed, the $SO_4^{\bullet-}$–$SO_4^{\bullet-}$ recombination rate constant is 13.75-fold lesser than that of $^\bullet OH$–$^\bullet OH$ (Eq. (7)), allowing more time residence of $SO_4^{\bullet-}$ radicals in the solution [29]. The beneficial effect of acidic condition is that high amount of sulfate radicals will be available to react with AB25 molecules, resulting in higher degradation rate. Acid-catalysis activation of PS could also be a source for generating more $SO_4^{\bullet-}$ in the reacting medium [9,30,31]. Moving pH from 2 to 6, a part of sulfate radical was converted into $^\bullet OH$ radical according to Eq. (2). This conversion was accompanied with higher consumption of radicals as $SO_4^{\bullet-}$–$^\bullet OH$ recombination reaction (Eq. (6)) is 25 times more rapid than that of $SO_4^{\bullet-}$–$SO_4^{\bullet-}$ (Eq. (5)), which lowers the available amount of radicals compared with that offered by acidic conditions. Thus, it is reasonably to observe a decline in the degradation rate at pH 6, compared with pH 2. Under basic conditions, $^\bullet OH$ is the main oxidizing species and, as mentioned, their recombination reaction (Eq. (7)) is 13.75-fold faster than that of sulfate radical with itself (Eq. (5)). As a result, the amount of $^\bullet OH$ available to react with AB25 molecules is low and induced lower chemical transformation than that observed with $SO_4^{\bullet-}$ at pH 2.

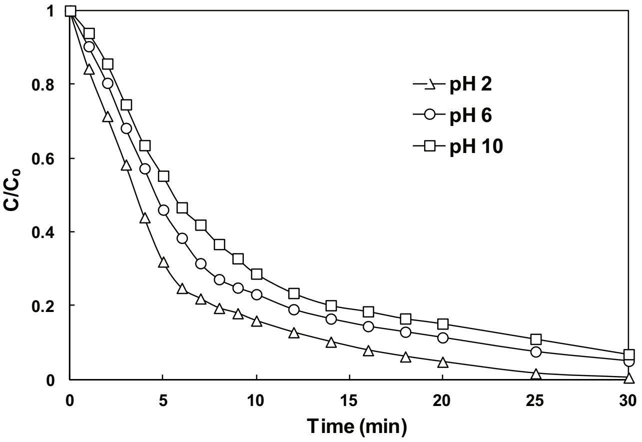

Fig. 4. Effect of initial pH on the degradation of AB25 with UV/PPS process (conditions: volume – 300 mL, initial dye concentration – 30 mg L^{-1}, initial PPS concentration – 200 mg L^{-1}, temperature – 20°C ± 2°C).

3.3. Effect of initial PPS concentration

The effect of PPS dosage on the degradation of AB25 by UV/PPS process was investigated at pH ~6 for different initial PPS concentrations ranging from 200 to 1,000 mg L^{-1} when the initial dye concentration was 30 mg L^{-1}. The results are shown in Fig. 5. Additionally, control experiments were carried out in the absence and presence of either UV light or $K_2S_2O_8$ alone. Results showed that mere $K_2S_2O_8$ was not sufficient for the degradation of AB25 as no color loss was observed in the absence of UV irradiation. With only UV light irradiation, there was about 44% degradation of AB25 within 60 min reaction time, while there was 93% with UV/PPS ($[PPS]_0$ = 200 mg L^{-1}) treatment system at the same reaction time, which indicated that UV/PPS was superior to UV alone in terms of dye removal efficiency. As can be seen from Fig. 5, the degradation rate of AB25 increased considerably with increasing PPS loading up to 400 mg L^{-1}, which is mainly due to the generation and use of an important quantity of radicals, $SO_4^{\bullet-}$ and $^\bullet OH$, in the degradation process. Similar enhancement was reported by Gao et al. [32] for the degradation of sulfamethazine and by Hori et al. [18] for the degradation of fluorotelomer unsaturated carboxylic acid in water. Higher PPS concentration implies that high photons could be absorbed to generated higher quantity of sulfate radical through Eq. (1). However, increasing PPS concentration above 400 mg L^{-1} increased insignificantly the dye removal (Fig. 5), which is in this case due to: (i) the quench of $SO_4^{\bullet-}$ and $^\bullet OH$ by the excess of PS as in Eqs. (8) and (9) and (ii) the radical–radical recombination reactions (Eqs. (5)–(7)) may overweight the radical–organic degradation reaction due to the higher suspected quantity of radicals at higher concentration of PS. A similar circumstance was reported by Peyton [33] for thermally activated PS at high reaction temperature and by Ferkous et al. [29] for

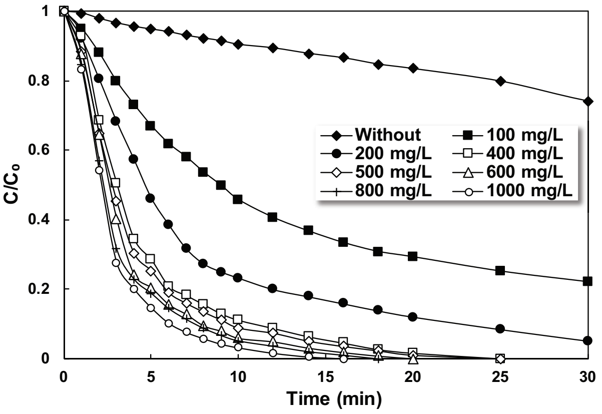

Fig. 5. Effect of initial PPS concentration on the degradation of AB25 with UV/PPS process (conditions: volume – 300 mL, initial dye concentration – 30 mg L^{-1}, pH ~6, temperature – 20°C ± 2°C).

sono-activated PS at high PS concentration. Lau et al. [21] reported a steady concentration of PS for the degradation of hydroxyanisole by UV/PS oxidation system. Gadipelly et al. [34] observed a detrimental effect of PS at high concentration level toward the degradation of cetirizine hydrochloride by UV/PS treatment.

$$S_2O_8^{2-} + {}^{\bullet}OH \rightarrow OH^- + S_2O_8^{\bullet-} \tag{8}$$

$$S_2O_8^{2-} + SO_4^{\bullet-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-} \tag{9}$$

3.4. Effect of initial AB25 concentration

To confirm the rate-enhancing effect of PPS toward the degradation of organic contaminates, degradation experiments in UV/PPS system were conducted at pH 6 for 10, 20 and 30 mg L^{-1} of AB25 initial concentrations when the PPS concentration was kept at 200 mg L^{-1}. Fig. 6 shows the normalized concentration profiles for the three dye concentrations. As can be observed, the removal efficiency at 5 min decreased from 92% for 10 mg L^{-1} of AB25 to 74% for 20 mg L^{-1} of AB25 and 54% for 30 mg L^{-1} of AB25. However, the removed amount of AB25, after 5 min, increased significantly from 9.2 and 10 mg L^{-1} of AB25 to 14.8 and 16.2 mg L^{-1} for, respectively, 20 and 30 mg L^{-1}, reflecting higher degradation rate at higher initial dye concentration. Correspondingly, significant lesser reaction times were required for complete removal of AB25 at low dye concentrations. For example, AB25 disappeared completely in 7 min for 10 mg L^{-1} of AB25 instead of 50 min for 30 mg L^{-1} of AB25. All these observations are in line with those reported by Gadipelly et al. [34] for the degradation of cetirizine hydrochloride. In general, at fixed dosage of PPS, the amount of free radicals, $SO_4^{\bullet-}$ and ${}^{\bullet}OH$, induced by PS photolysis is constant. Increasing AB25 initial concentration in the solution results in increasing the probability of radicals' scavenger by the dye molecules and this conducted to higher conversion rates.

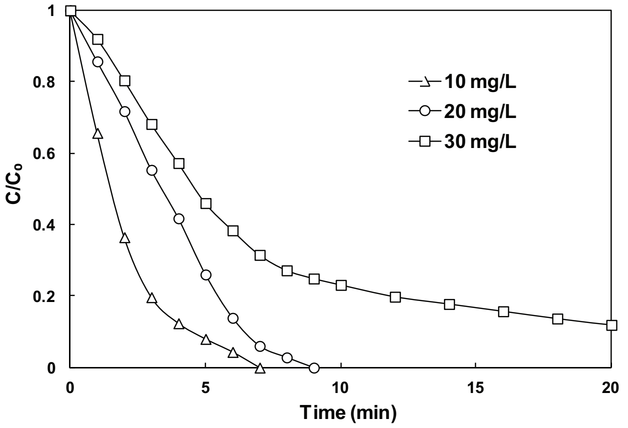

Fig. 6. Effect of initial dye concentration on the degradation of AB25 with UV/PPS process (conditions: volume – 300 mL, initial PPS concentration – 200 mg L^{-1}, pH ~6, temperature – 20°C ± 2°C).

3.5. Effect of salts addition and degradation tests in real natural matrice

To evaluate the effect of addition of inorganic anions on the degradation of AB25 by UV/PPS system, NaCl and Na_2SO_4 salts were added at different concentrations ranging from 0.2 to 10 g L^{-1}. Figs. 7(a) and (b) plot the effect of addition of NaCl and Na_2SO_4 on the degradation of AB25 at pH ~6, a PPS dose of 200 mg L^{-1}, an initial AB25 concentration of 30 mg L^{-1} and a temperature of 20°C. Even if inorganic anions are known to have an inhibiting effect, it is clearly seen from Fig. 7(a) that the addition of sodium chloride up to 10 g L^{-1} have practically no effect on the degradation of the dye. On the other hand, the degradation of AB25 slightly increased in the presence of Na_2SO_4.

The study of salt addition on the dye removal was completed by degradation experiments using real natural matrice. The purpose of the study is to check applicability of UV/PPS in real environmental water. Degradation of AB25 was studied by dissolving 30 mg L^{-1} of the dye in natural mineral water. The main characteristics of the natural water are pH 7.2, Ca^{2+} = 81 mg L^{-1}, Mg^{2+} = 24 mg L^{-1}, Na^+ = 15.8 mg L^{-1}, Cl^- = 72 mg L^{-1}, SO_4^{2-} = 53 mg L^{-1}, HCO_3^- = 265 mg L^{-1}. The obtained results, presented in Fig. 8, show that AB25 degradation was more effective in natural water compared with distilled water in the absence and presence of PS ions, making UV/PPS a promising process for treating real contaminated groundwater. It seems that the salts contained in the mineral water promote the degradation of AB25 by UV irradiation.

4. Conclusion

The present work revealed that the UV/PPS process supplies good performance in the degradation of anthraquinone dye AB25 in water. The degradation rate of the dye by UV/PPS process was drastically higher compared with direct UV irradiation alone. This significant improvement in the degradation of the dye is due to the formation of $SO_4^{\bullet-}$ and ${}^{\bullet}OH$ reactive radicals that are generated simultaneously in the AB25 solution. The degradation rate increased with the increase in PPS and AB25 concentrations and decreased with

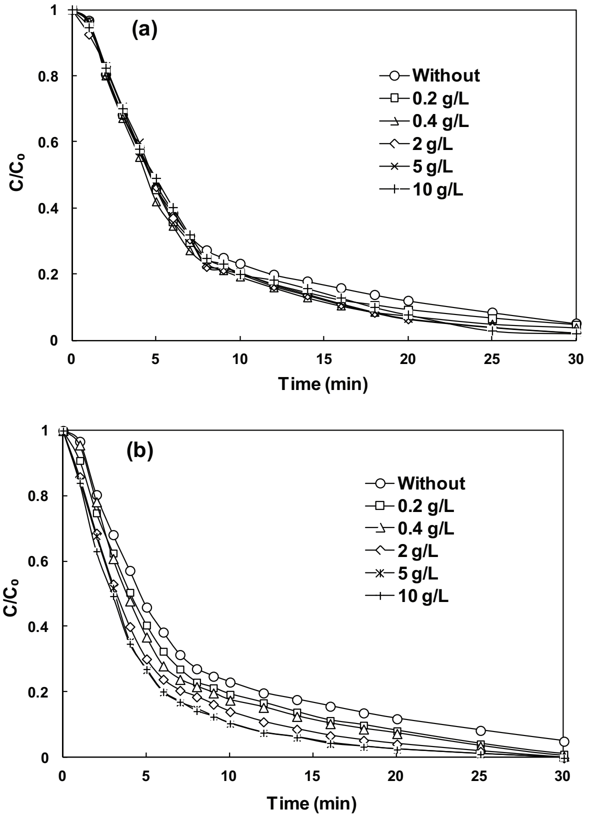

Fig. 7. Effect of (a) NaCl and (b) Na_2SO_4 addition on the degradation of AB25 with UV/PPS process (conditions: volume – 300 mL, initial dye concentration – 30 mg L^{-1}, initial PPS concentration – 200 mg L^{-1}, pH ~6, temperature – 20°C ± 2°C).

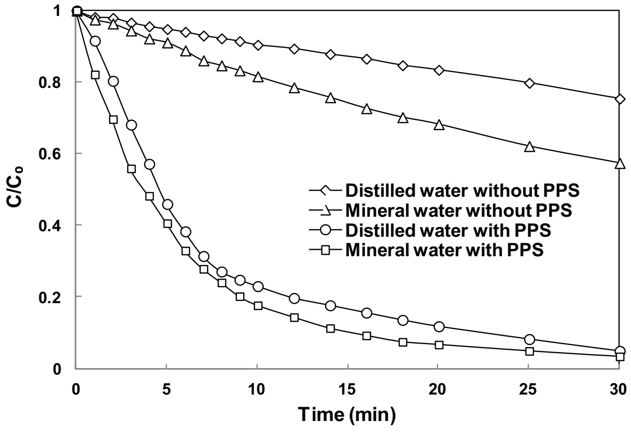

Fig. 8. Degradation kinetics of AB25 by UV and UV/PPS in deionized and mineral waters (conditions: volume – 300 mL, initial dye concentration – 30 mg L^{-1}, initial PPS concentration – 200 mg L^{-1}, pH ~6, temperature – 20°C ± 2°C).

increasing initial solution pH. The presence of inorganic anion, even at very high concentrations (10 g L^{-1}), had practically no significant effect on the elimination of the pollutant. The realized experiments using a natural water showed that the degradation of AB25 is more effective in a natural water compared with distilled water in the absence and presence of PPS, making UV/PPS a promising process for treating real contaminated waters.

Acknowledgments

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