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The effects of various organic and inorganic anions on decolorization of textile dye Reactive Orange 16 by means of hydroxyl radicals have been studied. These anions are commonly present in wastewaters from textile industry and include chloride, sulfate, carbonate/bicarbonate, nitrate and acetate anions. The experiments were conducted in the presence of different concentrations of anions and at different initial pH values in a batch photoreactor equipped with UV-C (254 nm) lamps in the presence of hydrogen peroxide. It was obtained that decolorization efficiency was significantly affected by nature and concentration of the investigated anions. An inhibitory effect of acetate anions increased with increasing in their concentration and depended on whether protonated or deprotonated forms are favored. Carbonate anion showed specific, both positive and negative influence, depending on its concentration. Influence of bicarbonate, nitrate and chloride was more prominent at their higher initial concentrations. The presence of sulfate did not have noticeable impact on decolorization of RO16 dye under investigated conditions. (ORIGINAL SCIENTIFIC PAPER) UDC 677.281:677.027:54-76+546.215

Keywords: advanced oxidation processes, hydroxyl radicals, carbonate/bicarbonate anions, acetate anions

Introduction

Textile dyes are generally small molecules which contain chromophore, responsible for the color and the functional group that allows dye fixation onto fibers. In terms of the chemical structure, azo dyes represent the largest group (around 50%) of all textile dyestuff produced. Azo dyes contain one or more azo groups (-N=N-) mostly linked to benzene or naphthalene rings [1]. According to their mode of application, textile dyes can be classified as acid, reactive, metal complex, disperse, vat, mordant, direct, basic, and sulphur dyes [1]. Today, most commonly used are reactive dyes which form covalent bonds with the fibers and are used for dyeing of cotton, rayon, wool, silk, and nylon. The reactive dye molecule contains specific functional groups which can undergo the addition or substitution reactions with the -OH, -SH and -NH_a groups present in the fibers. Due to very good fastness of the substrate, the reactive dyes are one of the most important groups of dyes for dyeing textiles. However, the reactive dye fixation efficiency is generally low (up to 50%), which results in a highly colored dye effluent which is unfavorable on environmental grounds [2]. The strong color of discharged dyes, even in very small concentrations, has a huge impact on the aquatic ecosystem caused by their reduction of light transmittance (turbidity). Therefore, the effluents discharged from textile and dyestuff industries have to be treated due to their impact on water bodies and growing public concern over their toxicity and carcinogenicity [3].

Common treatment processes e.g. adsorption on activate carbon, flocculation, coagulation, reverse osmosis

and ultrafiltration are non-destructive and just transfer contaminants from one phase to another and form secondary waste [4]. The alternatives to non-destructive water treatment are advanced oxidation processes (AOPs), which are characterized by the generation of highly oxidative species, such as hydroxyl radicals [5]. Among AOPs, UV/H₂O₂ process has been successfully applied to treat different organic pollutants in water, such as pharmaceuticals (meprobamate, carbamazepine, dilantin, atenolol, primidone and trimethoprim) phenol, sunscreen ingredient PBSA, etc. [6-8]. In this process, UV light is absorbed directly by H₂O₂ and by its photolysis 'OH radicals are generated. These radicals are extremely powerful oxidizing agents, capable of oxidizing organic compounds by hydrogen abstraction, electron transfer, and electrophilic addition [5]. It was reported that second-order rate constants for the reaction of •OH radicals with organic compounds are in the range of 107 - 1010 M⁻¹s⁻¹, depending on the chemical structure of the pollutant [9]. Owing to high reactivity and non-selectivity of •OH radicals, their availability for a reaction towards the target organic pollutants depends on the concentration of scavengers of •OH radicals, either naturally occurring in the surface water or present in the industrial effluent, such as Cl⁻, SO₄⁻²⁻, CO₃⁻²⁻, HCO₃⁻, NO₃⁻ and CH₂COO⁻.

The main objective of this work was the investigation of the effects of various anions either present in textile waste streams or formed through oxidation treatment, such as chloride, sulfate, carbonate, bicarbonate, nitrate and ace-

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tate, on Reactive Orange 16 removal rate with UV-C irradiation (254 nm) in the presence of hydrogen peroxide as the oxidant. All experiments were done in a batch photoreactor, at different initial pH values of a dye solution.

Experimental

Materials

Reactive Orange 16 (RO16, chemical class: azo dye, molecular formula: $C_{20}H_{17}N_3Na_2O_{11}S_3$, molecular weight: 617, dye content: 50%) was purchased from Sigma Aldrich (USA) and was used as received. NaNO₃, NaCl, NaHCO₃, Na₂CO₃, Na₂SO₄ and NaOAc were supplied by Merck (USA) and used as purchased. All solutions were made using deionized water.

Photoreactor

All experiments were conducted in a batch photoreactor equipped with ten low pressure mercury lamps, emitting at 253.4 nm (28 W, UV-C, Philips, Holland) which were fixed in parallel at the top of the photoreactor. The distance between the solution surface and UV lamps was kept constant at 220 mm. On the surface of the solution, the light intensity was measured by a UV radiometer Solarmeter model 8.0 UVC (Solartech, USA). The total UV intensity was controlled by turning on different numbers of UV lamps, from 2 up to 10 lamps, which gives the intensity from 730 up to 1950 µW cm⁻² (with all ten UV lamps on). The scheme of the photoreactor used for irradiation experiments is given elsewhere [10]. Due to the two fast decolorisation rates with maximum intensity, all experiments were done with the lowest intensity (730 µW cm⁻²) in order to have a better observation influence on the investigated anions.

Procedure

All experiments were conducted with 100 cm³ of the working solution, containing desired initial concentrations of the dye and H₂O₂ and appropriate pH values, in glass Petri dishes. For each set of experiments, the ratio $c_0(RO16)/c_0(H_2O_2)$ was kept constant at the optimal value of 246, while different amounts of organic and inorganic acids in form of sodium salts were added in order to evaluate their influence on RO16 degradation rate [10]. During the irradiation, the reaction mixture was magnetically stirred in a constant rate and the temperature was maintained at 25 ± 0.5 °C by thermostating. The pH of the solution was measured by Senslon3 pH-meter (HACH, USA) and adjusted by the addition of aqueous NaOH or dilute mineral acids. The samples were taken from the reaction mixture at defined intervals for the absorbance measurement, and then they were returned to the mixture to avoid the effect of reducing the volume. The remaining dye concentration was determined by means of UV/Vis spectrophotometer (Shimadzu, Japan), measuring the absorbance at 494 nm. None of the used inhibitors influenced UV/Vis spectrum of RO16 dye in the absence of UV light. The efficiency of the color removal was defined by the following expressions (1):

34 -

Decolorisation(%) =
$$\left(1 - \frac{c_t}{c_0}\right) \times 100$$
(1)

where c_0 is the initial RO16 dye concentration; c_t is RO16 dye concentration at irradiation time t.

It is reported [11] that dye degradation in the UV/H_2O_2 process occurs by an attack of strong oxidizing reagents, presumably hydroxyl radicals, which are formed upon hydrolysis of hydrogen peroxide (reaction (2)).

$$H_2O_2 + hv \rightarrow 2HO^{\bullet}$$
(2)

The hydroxyl radicals can react with dye molecules via reaction of hydrogen abstraction (reaction (3)), electrophile addition (reaction (4)) or electron transfer (reaction (5)).

$\mathrm{HO}^{\bullet} + \mathrm{RH} \rightarrow \mathrm{R}^{\bullet} + \mathrm{H}_{2}\mathrm{O}$.(3)
$\mathrm{HO}^{\bullet} + \mathrm{PhX} \rightarrow \mathrm{OHPhX}^{\bullet} \cdots \cdots$.(4)

$$HO^{\bullet} + RX \rightarrow RX^{+\bullet} + HO^{-}$$
(5)

Hydroxyl radicals also possess high reactivity towards the products formed through the above-mentioned reactions, which is probably true for the products formed from these products; *i.e.* for the secondary product, tertiary product, etc. which finally leads to complete dye mineralization. It has been previously shown [12] that dye degradation in AOPs follows a pseudo first reaction order with respect to the dye concentration, and can be described by using the following equation (6):

$$\ln \frac{c_t}{c_0} = -k_{app}t \dots (6)$$

where c_0 is the initial dye concentration, c_t is the dye concentration at time t, k_{app} is the apparent rate constant, t is the irradiation time. In the case of RO16 decolorization, a straight line with $R^2 > 0.98$ was observed when lnc_t/lnc_0 is plotted against the time which confirmed the proposed model.

Results and discussion -

Effect of organic anions

During the three usual steps (pre-treatment, dyeing, and rinsing after dyeing) of the dyeing process in textile industries, various salts are added to the bath in order to improve the exhaustion of the dye and color fastness. In case of dyeing cotton fibers, high pH is needed in the dyeing phase to complete the reaction between the dye and cellulose. After this, especially in the case of vinyl sulphone reactive dyes and because of their poor alkaline washing fastness, neutralization takes place. For this purpose, a large amount of acetic acid was usually added. Therefore, the effect of different acetic acid concentrations (1, 10 and 100 mmol L⁻¹) on the color removal of azo dye RO16 in UV/H₂O₂, the process was investigated at two initial pH values, pH 3.0 and 9.0. Ac-

cording to Fig. 1, decolorisation of RO16 was strongly affected by the presence of CH₃COO-/CH₃COOH ions at both studied pH values.



Figure 1. Effect of acetate on decolorisation of RO16 azo dye with UV/H₂O₂ process. $c_0(RO16) = 50.0 \text{ mg L}^{-1}$, $c_0(H_2O_2) = 25.0 \text{ mmol L}^{-1}$, a) pH 3.0 ± 0.2, b) pH 9.0 ± 0.2, UV light intensity was 730 µW cm⁻², the temperature was 25 ± 0.5 °C.

With increasing the concentration of CH₂COO⁻/CH₂COOH, ions from 0 mmol L⁻¹ up to 100 mmol L⁻¹, k_{app} at pH 3.0 decreased from 0.221 min⁻¹ to 0.099 min⁻¹, while at pH 9.0 a decrease in kapp from 0.195 min⁻¹ to 0.057 min⁻¹ was obtained. Considering the distribution diagram of ionic species of acetic acid in relation to the pH value (pKa 4.76), the predominant species at pH 3.0 is protonated CH₂COOH, while at pH 9.0 the predominant species is dissociated CH₂COO-. It is evident that both forms have an inhibitory effect on the RO16 removal rate, but a greater decline of kapp was achieved at pH 9.0 compared with pH 3.0. Hence, the removal rate of RO16 was more influenced by CH₂COO⁻ ions and the percentage of decolorization in the presence of 100 mmol L⁻¹ CH₂COO-/CH₂COOH after 20 min of the treatment at pH 9.0 is 79% in comparison with 91% at pH 3.0. The presence of CH₃COO-/ CH₃COOH ions led to the competition of these anions

with dye molecules for the reaction with HO[•] radicals. Furthermore, the increase in CH₃COO-/CH₃COOH concentrations decreased the effective HO[•] radical concentrations and, as a consequence, the degradation rate of target dye molecules declined. Dissociated species CH₃COO- react with HO[•] radicals with the rate constant k = 8.5x07 M⁻¹s⁻¹, which is higher than the rate constant for the reaction of HO[•] and protonated species CH₃COOH, k = 1.5x107 M⁻¹s⁻¹ [13], so that it is expected that CH₃COOions slightly more retard the removal rate of RO16 dye (reactions (7) and (8)).

HO[•] + CH₃COOH → [•]CH₂COOH + H₂O, k =
$$1.5 \times 10^7 M^{-1} s^{-1} \dots (7)$$

HO[•] + CH₃COO⁻ → [•]CH₂COO⁻ + H₂O, k = $8.5 \times 10^7 M^{-1} s^{-1} \dots (8)$

Effect of inorganic anions

Many inorganic anions, such as CO_3^{2-} , HCO_3^{-} , NO_3^{-} , SO_4^{2-} , Cl^- , could be present in textile effluents and hence significantly influence the removal of organic pollutants with AOP processes [14-16]. Among all anions, the influence of carbonate and bicarbonate are the most investigated ones, since they can be present in a significant amount both in surface waters and in wastewaters. Scavenging of 'OH radicals in the presence of carbonate and bicarbonate and bicarbonate anions was well documented in literature [17, 18]. On the other hand, carbonate radicals are formed through the reaction between carbonate and bicarbonate anions with hydroxyl radicals (equations (9) and (10)).

$HCO_{3}^{-} + OH \rightarrow H_{2}O + CO_{3}^{-}, k = 8.5 \times 10^{6} M^{-1} s^{-1}$ (9)
$CO_3^{2-} + OH \rightarrow OH^- + CO_3^{-0}, k = 3.9 \times 10^8 M^{-1} s^{-1}$ (10)

These radicals possess significant and selective reactivity towards organic compounds, high oxidation potential (E_o = 1.78 V vs. SHE at pH 7) and longer half-life time than hydroxyl radical so that they may take part in a degradation process [19]. Canonica et al. showed that the reaction of carbonate radicals may be a significant way of transformation of organic contaminants with second order rate constants from 4x10⁶ to 1x10⁸ M⁻¹s⁻¹ [20]. Mazellier et al. reported that when the starting concentration of bicarbonate in UV/H₂O₂ system is high enough, the elimination of fungicide carbendazim by carbonate radicals becomes the major route of its transformation [21]. Moreover, Mazellier et al. showed that although carbonate radical is about 1,000 times less reactive than hydroxyl radical, it can be a significant source of contaminate transformation and an additional pathway which include that carbonate radical must be taken into account in both natural sunlight water and wastewater treatments [22]. Therefore, it is expected that carbonate and bicarbonate anions present in UV/H2O2 treatment systems might have dual roles: either retard the decolorization rate due to well-known scavenging of •OH radicals or enhance the decolorization rate through the formation of carbonate radicals. In order to investigate the

effect of carbonate and bicarbonate on decolorization rate, RO16 dye solutions with different concentrations of these anions (10, 50 and 100 mmol L⁻¹) were irradiated, while keeping the remaining variables constant. The effect of carbonate and bicarbonate was investigated at pH values where these anions are prevalent, which are 8.0 and 11.0, respectively. As it can be seen from the results presented in Fig. 2, the increase in the bicarbonate concentration from 10 up to 50 mmol L⁻¹ did not have a measurable effect on decolorization efficiency, while with the further increase of bicarbonate concentration up to 100 mmol L⁻¹, decolorization efficiency decreased for about 10%.



Figure 2. Effect of carbonate and bicarbonate on decolorisation of RO16 azo dye with UV/H₂O₂ process. $c_0(RO16) = 50.0 \text{ mg } \text{L}^{-1}$, $c_0(\text{H}_2\text{O}_2) = 25.0 \text{ mmol } \text{L}^{-1}$, a) pH 11.0 ± 0.2, b) pH 8.0 ± 0.2, UV light intensity was 730 µW cm⁻², the temperature was 25 ± 0.5 °C.

On the other hand, the influence of carbonate on decolorization efficiency showed a different trend. Initially, a small decrease of decolorization from 88% to 83% was obtained by increasing the carbonate concentration up to 50 mmol L⁻¹. However, when the carbonate concentration was further increased up to 100 mmol L⁻¹, decolorization efficiency was enhanced and reached the value of 93%, which is higher than in the absence of carbonate. A negligible inhibitory effect in the experiments carried out with low concentrations of bicarbonate in comparison to carbonate (10 and 50 mmol L⁻¹) can probably be ascribed to the fact that bicarbonate is 45 times less reactive towards •OH radicals than carbonate and therefore the worst scavenging agent. In other words, the presence of higher concentrations of bicarbonate is required so that the scavenging of •OH radicals becomes pronounced. A significant inhibitory effect in the experiments carried out with a lower investigated concentration of carbonate may be attributed to its better scavenging ability. With equally high concentration of carbonate and bicarbonate used in this study (100 mmol L-1), a higher amount of carbonate radicals was probably produced in the presence of carbonate rather than in the presence of bicarbonate, since the formation of carbonate radicals is favored in the presence of carbonate. Carbonate radicals present at a significant concentration may probably act as a selective photooxidant for this dye, as mentioned above.

It is well known that nitrates which undergo sunlight irradiation can generate hydroxyl radicals, and this reaction is the major source of •OH radicals in natural waters [23, 24]. The overall reaction of nitrate photolysis can be presented by the reaction (11) [25]:

Hydroxyl radicals are produced owing to the rapid protonation of O⁻⁻, which can be formed upon photolysis of nitrite (reactions (12) - (14)) [25]:

$NO_2^- \xrightarrow{hv} [NO_2^-]^*$	(12)
$[\mathrm{NO}_2^-]^* \to \mathrm{NO}^\bullet + \mathrm{O}^{\bullet-} \cdots$	(13)
$O^{\bullet-} + H_2 O \leftrightarrow^{\bullet} OH + OH^{-}, k = 1.7 \times 10^6 M^{-1} s^{-1}, k$	$=1.2 \times 10^{10} \mathrm{M}^{-1} \mathrm{s}^{-1}$.(14)

Furthermore, it is reported that nitrite anions are very efficient 'OH radicals scavengers (k = 1×10^{10} M⁻¹s⁻¹), unlike nitrates which are not so efficient (k < 1.0×10^5 M⁻¹s⁻¹), and hence can negatively affect UV/H₂O₂ treatments, particularly in the nitrate rich water (reactions (15) and (16)).

$NO_2^- + OH \rightarrow NO_2^+ + OH^-, k = 1.0 \times 10^{10} M^{-1} s^{-1}$	15))

$$NO_{3}^{-}+OH \rightarrow NO_{3}^{\bullet}+OH^{-}, k < 1.0 \times 10^{5} M^{-1} s^{-1}.....(16)$$

Decolorisation of RO16 dye by UV/ H_2O_2 process was conducted in the presence of 10, 50, and 100 mmol L⁻¹ of nitrate. As shown in Fig 3. about 98% of 50 mg dm⁻³ RO16 dye was decolorized in the absence of nitrate, while in the presence of 10, 50, and 100 mmol L⁻¹ of the nitrate the obtained percentage of decolorisation after 20 min of irradiation was 98%, 95%, and 85%, respectively.



Figure 3. Effect of nitrate on decolorisation of RO16 azo dye with UV/H₂O₂ process. $co(RO16) = 50.0 \text{ mg L}^{-1}$, $co(H_2O_2) = 25.0 \text{ mmol L}^{-1}$, pH 8.0 ± 0.2, UV light intensity was 730 µW cm⁻², temperature was 25 ± 0.5 °C.

Furthermore, it was found that the apparent rate constant stayed almost unchangeable with increasing the nitrate concentration to 10 mmol L⁻¹ (0.235 min⁻¹), decayed to 0.195 min⁻¹ as the concentration of nitrate increased to 50 mmol L⁻¹, while a significant decay to 0.133 min⁻¹ was observed with the increase in the nitrate concentration up to 100 mmol L⁻¹. It is evident that the presence of nitrate inhibited decolorisation of RO16, whereas the inhibition was favored at higher concentrations, which is probably due to the fact that nitrate mostly acted as ·OH scavenger under the investigated experimental conditions. Moreover, even though nitrate has a very low molar absorption at 254 nm (3 M⁻¹cm⁻¹), these anions can act as "an inner filter" to some extent, reducing the fraction of UV light absorbed by hydrogen peroxide and hence inhibit the degradation of the target compound during UV/H2O2 treatments. Bedzca et. al. reported that the presence of nitrate had a neutral impact on n-butylparaben degradation in UV/H₂O₂ system: they neither consumed 'OH radicals nor their photolysis led to the increase of •OH radicals [26]. On the contrary, Jacobs et. al. showed that the presence of nitrate enhanced photodegradation of caffeine under solar simulated conditions and emphasized the role of nitrate as a photosensitizer [27]. Moreover, in the paper published by Kalsoom et. al., a slight increase in the percentage of Remazol Turquoise Blue in the presence of nitrate was achieved [28].

A negative effect of chloride on the AOPs through scavenging of •OH radicals has been reported by many authors [29]. Gultekin *at. al.* reported that the degradation of azo dye C.I. Reactive Red 141 noticeably declined in the presence of chloride up to 1250 mmol L⁻¹, while a further increased chloride concentration up to 2,500 mmol L⁻¹ had no influence on the degradation [30]. Some authors have emphasized a positive impact of chloride. Grebel *et. al.* investigated the effect of halide ions on the degradation of organic contaminants, and reported that •OH scavenging by halides converted nonselective •OH radicals to selective radical reactive halogen species (RHS), wherein the electron rich compounds are particularly vulnerable to their attack [31]. Wang *et. al.* investigated the role of chloride ions on bleaching of azo dye in the cobalt/peroxymonosulfate (Co/PMS) system and point out that a significant decrease of the decolorisation rate was observed by the addition of chloride at concentrations from 0.05 mmol L⁻¹ to 10 mmol L⁻¹, while a further addition of chloride in the concentration higher than 50 mmol L⁻¹ accelerated dye decolorisation [32]. The effect of chloride on decolorisation efficiency of RO16 dye was studied at three initial chloride concentrations (10, 50 and 100 mmol L⁻¹) and the results are presented in Fig. 4.



Figure 4. Effect of chloride on decolorisation of RO16 azo dye with UV/H₂O₂ process. $c_0(RO16) = 50.0 \text{ mg L}^{-1}$, $c_0(H_2O_2) = 25.0 \text{ mmol L}^{-1}$, pH 7.0 ± 0.2, UV light intensity was 730 µW cm⁻², temperature was 25 ± 0.5 °C.

It was found that the presence of chloride led to the decrease of the decolorisation rate from 0.224 min⁻¹ (without chloride) to 0.161 min⁻¹, 0.117 min⁻¹, and 0.109 min⁻¹ with concentrations 10, 50, and 100 mmol L⁻¹, respectively. It can be noticed that although the increase in chloride concentrations up to 50 mmol L⁻¹ noticeably reduced the apparent rate constant, with the further two-fold increase of the chloride concentration only a slight drop of k_{app} was observed. During photochemical reactions, chloride can be transformed into hypochlorite radical (CIHO⁻⁻), chlorine atom (CI⁻) and dichloride anion radical (CI₂⁻⁻) as it is presented by the following equations (17) – (22) [33]:

Cl ⁻ +•OH → [ClOH] ^{-•} , $k_{+} = 4.3 \times 10^{9} M^{-1} s^{-1}$, $k_{-} = 6.1 \times 10^{9} M^{-1} s^{-1}$ (17)
$CIOH^{\bullet-} + H^{+} \leftrightarrow CI^{\bullet} + H_{2}O, k_{+} = 2.1x10^{10} M^{-1}s^{-1}, k_{-} = 2.5x$ $x10^{5} M^{-1}s^{-1}(pKa = 7.2)$ (18)
$Cl^{\bullet} + Cl^{-} \leftrightarrow Cl_{2}^{\bullet-}, k_{+} = 2.1 \times 10^{10} M^{-1} s^{-1}, k_{-} = 1.1 \times 10^{5} M^{-1} s^{-1} (19)$
$Cl_{2}^{\bullet-} + HO_{2}^{\bullet} \rightarrow H^{+} + 2Cl^{-} + O_{2}, k = 1 \times 10^{9} M^{-1} s^{-1}$ (20)
$Cl^{\bullet} + H_2O_2 \rightarrow H^+ + Cl^- + HO_2^{\bullet}, k = 1x10^9 M^{-1}s^{-1}$ (21)
$Cl_{2}^{\bullet-} + H_{2}O_{2} \rightarrow H^{+} + 2Cl^{-} + HO_{2}^{\bullet}, k = 1.4 \times 10^{5} M^{-1} s^{-1}(22)$

The formed chloride atom (Cl[•]), with almost the same magnitude of rate constants with organic pollutants as •OH radicals, is capable of oxidizing organic compounds effectively, whereas a halogen radical anion (Cl₂^{-•}) is less reactive than •OH radicals [34]. However, at low chloride concentrations, the scavenging effect is probably predominant in case of RO16 decolorisation, while in the presence of high chloride concentrations probably more intermediate radicals (CIHO[•], Cl[•], Cl₂^{•-}) are formed which can participate in RO16 decolorisation, thus mitigating a chloride scavenging effect.

The presence of sulfate did not have a noticeable impact on decolorisation of RO16 dye under investigated conditions (results not shown). The decolorisation percentage after 20 min of the irradiation time was slightly changed from 99% to 95%, 93% and 92% by introducing sulfate at the concentrations 10, 50 and 100 mmol L⁻¹, respectively. In addition, a small decline in the decolorisation rate constant from 0.245 min⁻¹ (without sulfate) to 0.227 min⁻¹ was obtained by increasing the sulfate concentration up to 100 mmol L⁻¹. Sulfate reacts with •OH radicals according to the reaction (23) with the rate constant of 3.5×10^5 M⁻¹s⁻¹ and leads to the formation of sulfate radicals:

$SO_4^{2-} + OH \rightarrow SO_4^{-} + OH^{-}, k = 3.5 \times 10^5 M^{-1} s^{-1}$ (23)

Sulfate radicals are strong oxidants with the redox potential of 2.5 - 3.1V, which is similar to the oxidizing power of hydroxyl radicals (1.8 - 2.7 V, pH dependent) [35]. Previous reports have indicated that sulfate radicals based advanced oxidation processes, in which peroxydisulfate and peroxymonosulfate are usually used as oxidants and activated in different ways can be successfully applied for the degradation of water contaminants [36]. It appears that in case of RO16 decolorisation, under the experimental conditions applied, probably two competition reactions for scavenging •OH radicals and the formation of sulfate radicals took place, which led to a negligible change of the decolorisation rate since sulfate radicals together with •OH radicals can participate in the dye decolorisation.

Conclusions –

The effect of organic and inorganic anions typically present in textile dye effluents on decolorisation of azo dye Reactive Orange 16 by UV/H_2O_2 system was investigated in this study. The presence of acetate anions showed a negative impact on the decolorisation rate, which is more prominent at their higher concentrations and at higher initial pH values, at which the presence of deprotonated forms of anions are favored. On the other hand, the effect of inorganic anions on RO16 decolorisation was more specific. Depending on the carbonate concentration, a dual (positive and negative) effect on the dye decolorisation was obtained, whereas bicarbonate showed only a negative impact. A scavenging effect of

nitrate and chloride increased with the increase in their concentration. Although sulfate anions are good scavengers of •OH radicals, they showed a slight impact on RO16 decolorisation efficiency. Therefore, the influence of organic and inorganic anions on AOPs must be taken into consideration during practical applications due to complex photolysis reactions which can take place and a possible formation of number of species which can participate in the target pollutant degradation.

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UTICAJ ANJONA NA DEKOLORIZACIJU TEKSTILNE BOJE REACTIVE ORANGE 16 UV/H₂O₂ PROCESOM

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U ovom radu je ispitan uticaj različitih organskih i neorganskih anjona na dekolorizaciju tekstilne boje Reactive Orange 16 pod dejstvom hidroksilnih radikala. Ispitan je uticaj anjona koji su obično prisutni u otpadnim vodama tekstilne industrije, kao što su hloridni, sulfatni, karbonatni, bikarbonatni i acetatni anjon. Eksperimenti su izvedeni u prisustvu različitih koncentracija anjona i pri različitim početnim pH vrednostima u šaržnom reaktoru, uz izlaganje rastvora UV-C (254 nm) zračenju u prisustvu vodonik-peroksida. Utvrđeno je da na efikasnost uklanjanja boje utiču priroda i koncentracija ispitivanih anjona. Inhibitorni efekat acetatnih anjona raste sa porastom njihove koncentracije i zavisi od toga da li su prisutni u protonovanom ili deprotonovanom obliku. Karbonatni anjon je, u zavisnosti od koncentracije, pokazao i pozitivan i negativan uticaj. Uticaj bikarbonata, nitrata i hlorida je izraženiji pri njihovim većim početnim koncentracijama. Značajan uticaj sulfata na dekolorizaciju boje RO16 nije uočen pri ispitivanim uslovima.

Ključne reči: unapređeni oksidacioni procesi, hidroksilni radikali, karbonatni anjon, acetatni anjon