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pH EFFECT ON DECOLORIZATION OF RAW TEXTILE WASTEWATER POLLUTED WITH REACTIVE DYES BY ADVANCED OXIDATION WITH UV/H₂O₂

The effectiveness of the advanced oxidation process (UV/H₂O₂) in decolorizing real textile wastewater polluted with commercial reactive dyes – Reactive Yellow 84 and Reactive Red 141 – was investigated. All the experiments were performed in a lab-scale reactor with the original high pH of the wastewater. The dyeing wastewater was decolorized in 5 hours. After its acidification to pH 3 the decolorization process was more efficient. Full decolorization was then achieved in 2 hours and the decrease in COD exceeded 70%. The reaction rate constants obtained were as follows: at pH 11.4, 0.0065 min⁻¹; at pH 7, 0.0044 min⁻¹, and at pH 3, 0.019 min⁻¹, which testified to pH importance for UV/H₂O₂ oxidation process.

1. INTRODUCTION

Reactive dyes, though being environmentally hazardous and possibly carcinogenic, are used extensively due to their excellent wash fastness. The amount of cotton dyes is 50% of all dyes consumption in the world (BLACKBURN et al. 2002). Reactive dyeing has been the most common method for cotton dyeing in the past years (RAJKUMAR et al. 2006, ROESSLER et al. 2003). The use of reactive dyes is steadily increasing because of their simple dyeing procedure and good stability during washing process (KUSIC et al. 2006). Reactive dyes bind not only to fabric but also react with water, because of wash fastness (BLACKBURN et al. 2002). Therefore, 30–50% of the reactive dyes applied in the textile industry are washed out after the dyeing process (BLACKBURN et al. 2002, OLIVER et al. 1999, KURBUS et al. 2003). When reactive dyeing wastewater is discharged without appropriate treatment to the conventional public treatment plants, 90% of dyes present in the wastewater pass to the surface waters (OLIVER et al. 1999).

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According to OLIVER et al. (1999) and MURUGANANDHAM et al. (2006) reactive dyes are toxic and carcinogenic to aquatic environments, and in surface waters inhibit light penetration and minimize photosynthesis. Reactive dyes are characterized as hard biologically degradable substances, and biological treatment methods for dyeing wastewater could be employed partly, but not as a main treatment process (OLIVER et al. 1999, AZBAR et al. 2004, ALATON et al. 2001). Therefore much attention is given to physical and chemical treatment methods that have been successfully tested for neutralization of reactive dyeing wastewaters (OLIVER et al. 1999, KURBUS et al. 2003, MURUGANANDHAM et al. 2006, AZBAR et al. 2004, ALATON et al. 2001).

Some of the methods, e.g. Fenton's method and conventional filtration methods, are not suitable for textile wastewater treatment from sustainability point of view, because toxic sludge is produced resulting in sludge disposal problems (NTAMPEGLIOTIS et al. 2006, GULTEKIN et al. 2004, ARSLAN et al. 2000). Considerable attention has been paid to Advanced Oxidation Processes (AOP) in the past decade. The main mechanism of AOP is based on active hydroxide radical ($\bullet\text{OH}$) formation. Radicals are formed under UV light employing hydrogen peroxide (H_2O_2), ozone (O_3), and in some cases a photo-catalyst: titanium dioxide (TiO_2) (FELIS et al. 2008, MURUGANANDHAM et al. 2006, ALATON et al. 2002). UV/ H_2O_2 method application on textile wastewater has some undefined issues, such as the optimal pH. The pH range can strongly affect the decolorization efficiency and reaction rate. Several opinions of pH importance and optimal value are stated in literature (OLIVER et al. 1999, GULTEKIN et al. 2004, ALATON et al. 2002), where the optimal process pH value varies from 11 to 3.

Most of the AOP studies refer to artificially polluted water containing one dye or a group of dyes (INCE et al. 2002, GALINDO et al. 1998, KUSVURAN et al. 2005). Only very few cases on successful AOP application on real textile industry wastewater treatment are published (OLIVER et al. 1999, SHU et al. 2006). Real textile wastewater treatment is complicated because of extremely varying composition and high pH and COD values. Substantial amount of chemicals like NaCl, Na_2SO_4 , NaOH, Na_2CO_3 and surfactants are added to the dyeing process, to improve the reactivity of the dyes. Chemicals added have extra load to wastewater pollution and are also responsible for a high COD and pH level of the wastewater (KURBUS et al. 2003). Also, these chemicals are used to keep a pH constant during the dyeing process, necessary to improve the reactive dye bonding to the fabric. The anions Cl^- and CO_3^{2-} are both stated as $\bullet\text{OH}$ radical scavengers and remain after the dyeing bath in the wastewater. The presence of scavengers has a great negative influence for UV/ H_2O_2 – AOP performance (OLIVER et al. 1999, MURUGANANDHAM et al. 2006, AZBAR et al. 2004, ALATON et al. 2001, SHU et al. 2006, GALINDO et al. 1998).

The purpose of the study is to determine the applicability of UV/ H_2O_2 advanced oxidation method for the removal of reactive dye from reactive dyeing raw wastewater and to define the influencing factors.

To gain more information about the UV/H₂O₂ method, the pH influence was investigated in this work. Two types of textile reactive dyeing raw wastewaters obtained from industry were examined in the lab – scale UV/H₂O₂ reactor. For investigation of the pH impact on UV/H₂O₂ – AOP kinetics, the pH dependency on the decolorization reaction rate was examined. Oxidation performance was investigated by applying an ordinary UV/H₂O₂ method at original textile reactive dyeing wastewater pH, which is ~11. Based on the buffer capacity of the wastewater, two lower pH values were chosen to perform an oxidation experiment in the UV/H₂O₂ reactor.

2. MATERIALS AND METHODS

2.1. MATERIALS

Hydrogen peroxide 30% (w/w) from Merck, Germany was used. Raw textile wastewater was obtained in The Netherlands from a small scale textile industry, which dyes cotton yarn and pieces of cotton fabric. The production rate is approx. 500 tons of dyed yarn per year, and 60 000 m³ of wastewater is produced per year. The wastewater (composition presented in Table 1) was taken from the reactive dyeing equipment prior to the rinsing stage. Two different colors reactive dyeing wastewater samples for the investigation of the UV/H₂O₂ – AOP performance were used: red color that contains 86% of reactive red 141 Color Index, 1976 (further in the text TYPE 1), and yellow color that contains 92% of reactive yellow 84 Color Index, 1976 (further in the text TYPE 2). The wastewater samples were stored in plastic impenetrable tanks that were kept at +4 °C. Each experiment was repeated at least 3 times. The average of the values obtained was taken; data confidence interval is 97%.

Table 1

Dyeing wastewater average composition

Waste-water samples	Waste-water type	pH level	COD (mgO ₂ /dm ³)	Cl ⁻ (mg/dm ³)	Dye concentration in sample (mg/dm ³)	Wavelength (nm)	Absorption units (Abs)
1.	RR141	11.09	8664	51360	55.6	418	0.35
2.	RY84	11.23	10120	42468	62.3	430	0.42

2.2. EQUIPMENT SETUP

A schematic representation of the experimental lab – scale UV/H₂O₂ reactor is presented in Figure 1. A reaction vessel of 800 ml, made of quartz glass, was placed

into a stainless steel hexagonal reflector with 6 UV – C light lamps (type – low pressure lamps maximum emission at 253.7 nm, 15 W each, length of lamp 0.41 m; Philips, The Netherlands). UV lamps were situated in a circular arrangement as shown in Figure 1 (A-A). The irradiation power in the reactor was calculated according formulas proposed by MASSCHELEIN (2002). Temperature was maintained constant at $20\text{ }^{\circ}\text{C} \pm 2$ as it influences the reaction kinetics (NTAMPEGLIOTIS et al. 2006). pH was monitored throughout the experiment with a pH meter – MT28-280-001 (pH electrode WTW Sen Tix 21, The Netherlands). For continuous monitoring of the dye concentration, the reactor was connected to a peristaltic pump (Watson–Marlow 302, The Netherlands) pumping the wastewater through the UV/Vis spectrophotometer cuvette. The spectrophotometric color intensity (absorption) was measured with Varian Cary 3E UV-Vis Spectrophotometer (Varian B.V., The Netherlands). The absorption measured was in range below 1 absorption units (Abs). Therefore, dilution was not performed and change in color intensity could be measured online. Spectrophotometer was connected to a computer and data was recorded at 1–10 minutes time intervals.

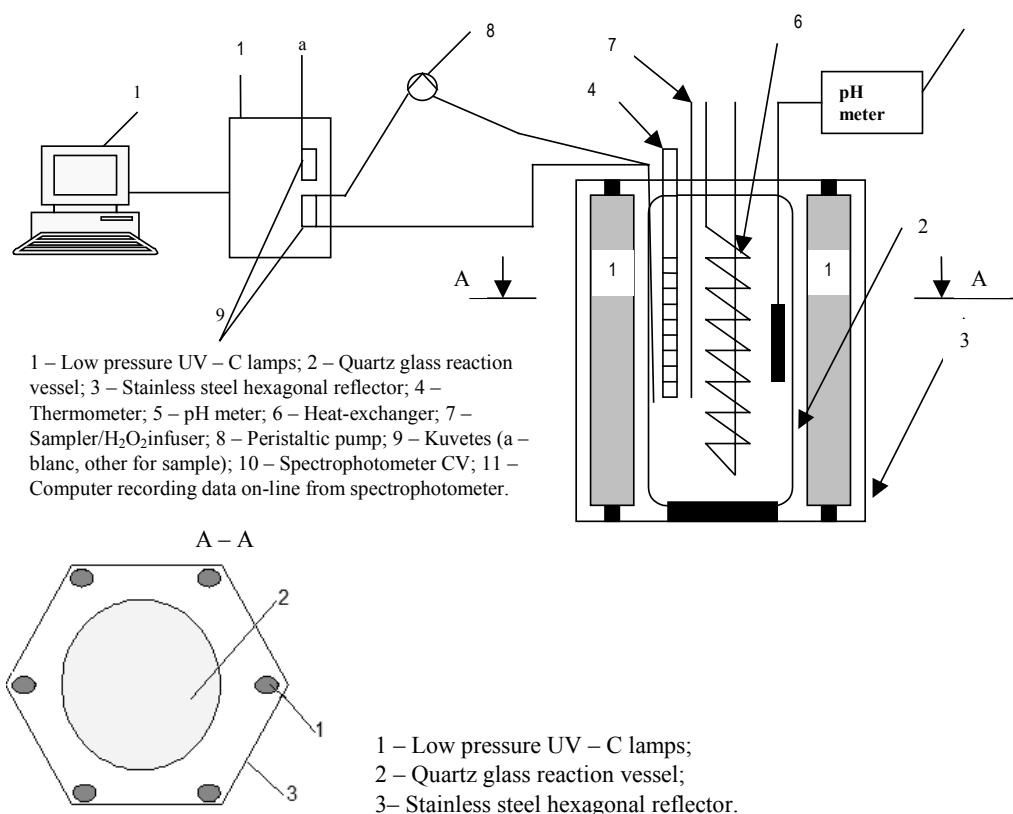


Fig. 1. Schematic representation of experimental lab- scale UV/H₂O₂ reactor

The reactor was filled with 800 ml of wastewater and 5 ml of 30% H₂O₂ solution was added. The solution was irradiated until a steady value of absorption was observed with the spectrophotometer. The wastewater during the decolorization process was mixed hydraulically in 15 minutes time intervals in order to get better light penetration in the depth of the reaction vessel. During mixing, there was no contact with oxygen.

2.3. ANALYTICAL PROCEDURES

Exact H₂O₂ amount consumed during the oxidation was defined by means of determining residual (unreacted) H₂O₂ amount after each experiment by “Nanocolor Peroxid 2” (MACHEREY–NAGEL GmbH & Co, Germany).

The decolorization due to the oxidation was monitored with the UV-Vis spectrophotometer (Carry Varian). The wavelength for measuring the oxidation absorption change was set analytically with the UV-Vis spectrophotometer. The maximal absorption value (Abs) of each wastewater sample was defined by scanning the wastewater sample in the range 200–800 nm. Maximal peaks obtained in the range have been assumed as characteristic values for measurement and were used for UV/H₂O₂ – AOP performance observation. The highest signal measured was used to obtain the highest sensitivity of measurement. The wavelength (nm) at which the peaks for each type of dyes were obtained are given in Table 1.

Dye concentration was estimated from the absorbance unit and are compared and presented as percentage of initial concentration. The initial concentrations of dyes in different wastewater samples were different, therefore initial dye concentrations were taken as 100%, and the demineralised water was used as blank sample (demineralised water conductivity below 0.5 μS/cm at 20 °C) was assumed as 0% of dye concentration.

The buffer capacity titration curves of the wastewater samples were obtained by titrating the wastewater samples with 1 N sulphuric acid and from measured redox potential the pH values were defined graphically. The sulphuric acid was chosen as a strong acid for pH adjustment as it does not scavenge hydroxyl radicals and does not interfere in the spectrophotometric measurement.

The COD of wastewater samples was determined by the Dr Lange COD test, before and after the UV/H₂O₂ method application. The COD decrease was obtained by subtraction from initial measured raw wastewater value the effluent measured value. As in wastewater was present high concentration of Cl⁻ ions and after treatment – H₂O₂. In this case these two compounds interfere with the COD measurement; therefore, the effect on the measurement was quantified according methodology given in the literature (APHA 1995, KANG et al. 1998).

3. RESULTS AND DISCUSSION

3.1. TEXTILE REAL DYEING WASTEWATER DECOLORIZATION

The decolorization under UV/H₂O₂ of two types of raw reactive dyeing wastewater was carried out to define which of the two types of dyes is more receptive to decomposition (Figure 2).

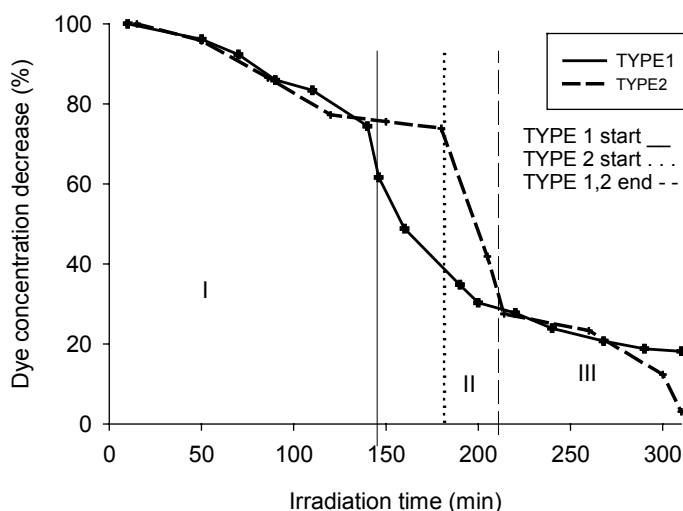


Fig. 2. Real dyeing wastewater decolorization process

Table 2

Real dyeing wastewater decolorization process characteristics

Waste-water type	Average pH during decolorization process	Average H ₂ O ₂ amount used for decolorization (mg/dm ³)	Average COD removal (%)	Average rate constant k' (min ⁻¹)
1	11.33	1531	64	0.00603
2	11.47	2088	75	0.00716

Decolorization of the wastewater TYPE 1 under UV/H₂O₂ – AOP started with a slow reaction period of 140 minutes. During this period of time 25% of dye residuals in wastewater was decomposed. During the next 60 minutes ~ 50% of dye residuals was decomposed (totally 75% dye decomposition after 200 minutes was achieved). The same tendency could be observed with wastewater TYPE 2. The increase in decolorization begun after 180 minutes, and 75% dye decomposition in wastewater was reached after 240 minutes. Decomposition of dyes present in waste-

waters TYPE 1 and TYPE 2 was initially slow with 140 and 180 minutes lag time respectively (this inefficient stage in the graphical expression is marked as stage I in Figure 2). Apparently, the process starts with oxidation of more easily degradable substances without decolorisation. After stage I has finished, the main fraction of dye residual in both real wastewater samples were decomposed within 100 minutes. This stage is called the useful UV/H₂O₂ – AOP stage and is marked as stage II in Figure 2. After about 220 minutes for both real wastewaters, dye decomposition reactions slowed down, and during 80 minutes of oxidation only 20% of dye residual was removed from the wastewater. This is marked as stage III in Figure 2.

During 3 hours of oxidation, $\geq 60\%$ dye removal was obtained, and after 5 hours 80% of dye removal was obtained. The average amount of H₂O₂ consumed was 1810 mg/dm³ during 5 hours application of UV/H₂O₂ – AOP.

Though the main goal was dye decomposition, also COD was degraded. The COD decrease during 5 hours reached 64% and 75% for TYPE 1 and TYPE 2 respectively (Table 2). The obtained UV/H₂O₂ – AOP application results is similar as described by AZBAR et al. 2004, ALATON et al. 2001, ARSLAN et al. 2000, INCE et al. 2002.

3.2. pH INFLUENCE FOR DECOLORIZATION UV/H₂O₂ – AOP

A Na₂CO₃ – NaOH buffer is applied for stabilisation of pH level in the dyeing process in industry. Buffer capacity was tested to examine the pH characteristics of the wastewater. To reduce the original pH of the reactive dyeing textile wastewater (Figure 3) 1N sulphuric acid was added. The pH was reduced in the solution to reach stable pH intervals, as could be observed from the graph presented in Figure 3. These stable pH intervals are at: 11.4–11 (original pH of the wastewater); 7.5–6.5 and pH 3.5–2. At these pH intervals, the influence of pH on the UV/H₂O₂ oxidation process was investigated.

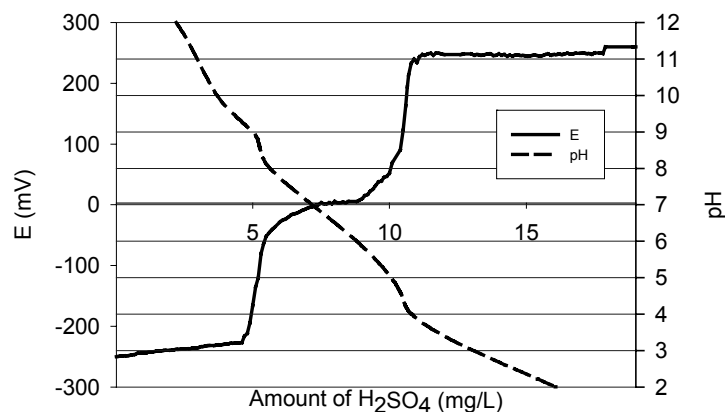


Fig. 3. pH and redox potential as function of sulphuric acid added

According to KUSIC et al. 2006 and MALIK et al. 2004, the pH has a large impact on UV/H₂O₂ – AOP kinetics. Therefore, the pH influence on the kinetics for wastewater TYPE 1 was investigated.

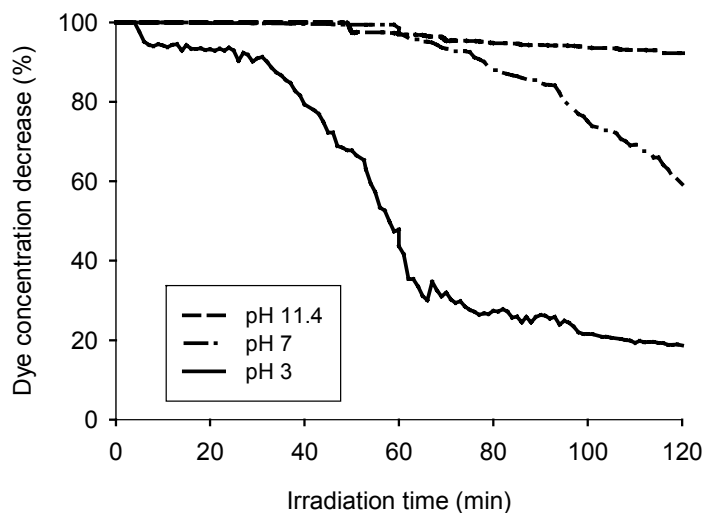


Fig. 4. pH influence on the decolorization rate of textile dyeing wastewater TYPE 1

The slowest decolorization with UV/H₂O₂ – AOP was observed with wastewater when the pH value was 11.4 (original pH level of raw wastewater). After neutralization of wastewater with sulphuric acid to pH 7 the decolorization process was faster and in the acidic environment at pH 3 another large enhancement of the decolorization rate was observed.

The decomposition of the dyes that were present in wastewater TYPE 1 in alkaline environment (pH = 11.4) was rather slow. During 120 minutes of irradiation, the decomposition of the dyes achieved was less than 10% (Figure 4). The calculated average reaction rate constant for the first 120 min was $k' = 0.00073 \text{ [min}^{-1}\text{]}$. The decolorization reaction was supposed to follow pseudo first order kinetics (MASSCHELEIN 2002, YUNG-SHUEN SHEN et al. 2002) but it did not.

During decomposition of the dyes at pH 7, more than 40% of dye concentration was decreased in 120 minutes. The calculated average reaction rate constant $k' = 0.0044 \text{ [min}^{-1}\text{]}$ is 10 times higher at pH 7 than during the decolorization at pH 11.4.

The fastest decolorization reaction rate is observed at pH 3; during 60 minutes of decolorization up to 70% of color was removed. After these 60 minutes, dye decomposition slowed down (stage III), and during the second hour only 10% of color was degraded. At pH 3 the calculated average reaction rate constant $k' = 0.019 \text{ [min}^{-1}\text{]}$ is 4 times larger than at pH 7 and 25 times larger than at pH 11.4. Therefore, it can be concluded that for an efficient decolorization of real wastewater by UV/H₂O₂ – AOP

an acidic environment is optimal. The same conclusion is given by OLIVER et al. 1999, KUSIC et al. 2006 and MALIK et al. 2004. According to OLIVER et al. 1999, KURBUS et al. 2003, KUSVURAN et al. 2005, longer than 60 minutes decolorization is required in order to avoid toxic intermediate compounds formation.

3.3. OXIDATION EXPERIMENTS AT PH 3 FOR TWO TYPES OF REAL DYEING WASTEWATER

In Figure 5 results of the oxidation experiments at pH 3 for TYPE 1 and TYPE 2 wastewater are presented.

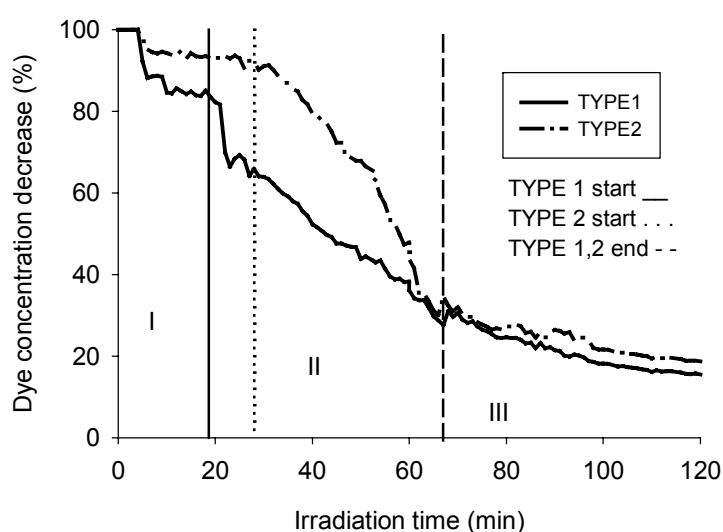


Fig. 5. Textile real wastewater decolorization process at pH = 3

Table 3

Textile raw wastewater decolorization process characteristics at pH = 3

Wastewater type	Average pH during decolorization process	Average H ₂ O ₂ amount used for decolorization (mg/dm ³)	Average COD removal (%)	Average rate constant k' (min ⁻¹)
1	3.06	1246	52	0.0195
2	3.27	1583	61	0.0186

In Figure 5 the same trend in decolorization could be observed as in Figure 3. The decolorization reaction for TYPE 2 showed a lag time (stage I), but when the reaction started, it went fast (stage II). During 30 minutes of decolorization, only 10 % of initial color was removed (stage I). However, over the next 40 minutes, 60% of color

was removed (stage II). Sample TYPE 1 was oxidized equally throughout the oxidation by UV/H₂O₂ – AOP within 100 minutes, and the fast reaction (at stage II) is observed from 22 to 65 minutes. After 100 min for both types of wastewater, decolorization was at a lower reaction rate. Therefore, more time was necessary to decrease the amount of hard degradable substances remaining in the wastewater, which is also noted in the literature (OLIVER et al. 1999).

When UV/H₂O₂ – AOP method was applied in acidic environment (pH = 3) slightly lower amount of H₂O₂ (Table 3 and Table 4) was consumed than in alkaline or neutral environments. Also, a lower decrease in COD was achieved. Apparently, in the acidic environment the oxidation becomes more selective for reactive dye chromophores. Therefore, it is likely that colorless intermediate products are still present in the wastewater after the treatment¹. The COD decrease reached is high when compared to the hydrogen peroxide amount used for the oxidation reaction. It could be explained by complex chain reaction of hydroxyl radicals, hydrogen peroxide itself and UV light photolysis.

Further work on reaction mechanisms should be carried out to reveal the exact background of the H₂O₂ consumption, and the formation of toxic intermediate products.

4. CONCLUSIONS

In this experimental work, decolorization of real wastewater polluted with two types of commercial dyes, was investigated by using UV/H₂O₂ – advanced oxidation process (AOP). Influence of pH on the UV/ H₂O₂ – AOP process performance was investigated and evaluated by means of decolorization and change in reaction rate.

80% of decolorization without pH adjustment (pH 11.4) was achieved during 300 minutes of UV/H₂O₂ – AOP application. The acidification of the reaction medium substantially increased the speed of the reaction at pH 7. The calculated average reaction rate constant is 10 times higher at pH 7 than at pH 11.4. At pH 3 reaction rate constant is 25 times higher than at pH 11.4.

For both wastewaters during 120 minutes decolorization at pH 3, the same effectiveness is reached as in 300 minutes decolorization at pH 11.4. In this respect the amount of reagents needed to decolorize the investigated wastewaters is 22% lower. The shorter decolorization time means a twofold decrease in amount of electricity consumed.

The main conclusion from this work: to achieve the optimal decolorization with UV/H₂O₂ – AOP of reactive dyeing wastewater, a low/acidic pH is recommended.

¹ The intermediate products were not investigated during this work.

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