

REMOVAL OF REACTIVE BLACK 5 FROM TEXTILE WASTEWATER BY OZONE AND PHOTO-FENTON – INFLUENCE OF INDUSTRIAL MATRIX EFFECTS

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Abstract— Textile waste water containing dyes, surfactants, salts and other contaminants represent a challenge for the selection and design of treatment processes due to the stability of some of its components. Advanced oxidation processes (AOPs) are attractive alternatives to partially or totally degrade dyes and other persistent pollutants using relatively compact devices to perform water treatment. To test the efficiency of these technologies it is necessary to count with laboratory made solutions that can match the characteristics of a typical textile waste waters effluent. In this work the application of two AOP, ozonation and photo-Fenton, to the treatment of textile effluents are compared, using a specially design model solution. The effect of typical textile wastewater composition on the treatment efficiency is discussed. Higher decoloration efficiencies were obtained with both AOPs tested in this work, being slightly higher with ozonation. TOC was only partially removed, being more efficient photo-Fenton than ozonation.

Keywords— Ozone, photo Fenton, Textile Wastewater, Dye, Reactive Black 5

I. INTRODUCTION

Industrial processes developed in textile factories generates important volumes of wastewater that should be treated before its discharge to surface water bodies. Some of those liquids are colored, and rich in salts, additives and several organic and inorganic compounds (Bilińska *et al.*, 2016; Ulson de Souza *et al.*, 2009; Bisschops and Spanjers, 2003; O’Niell *et al.*, 1999). Textile processes involve several operations required to transform the raw material into commercial fabrics. Some operations, like washing, bleaching, mercerizing, dyeing and functional finishing are usually developed by wet processes, producing wastewaters with different characteristics (Paździor *et al.*, 2019; Bisschops and Spanjers, 2003).

Most of the dyes added to the dyeing baths are incorporated to the fabrics, but a no negligible part remains in the spent bath, and consequently in the wastewaters. The

fraction of dye incorporated to fabrics (called “Exhaust” of dyeing bath) depends of the dye itself, the bath formulation, and the operative conditions. According to a survey developed between years 2013 and 2016 on cotton processing factories in Buenos Aires, for Reactive Black 5 (RB5), typical exhaust rounds 80%. Consequently, 20% of the dye remains in the solution discarded with the wastewaters. This value coincides with Arslan-Alaton *et al.* (2002).

Textile dyes are intrinsically designed to resist sunlight and biodegradation along the time, once they are on the fabrics. Therefore, those compounds are usually recalcitrant to the conventional wastewater treatment methods (Zuorro *et al.*, 2013; Arslan-Alaton *et al.*, 2008; Forgacs *et al.*, 2004; Bisschops and Spanjers, 2003). The combination of dyes with high salinity and the presence of additives result in wastewater streams with low biodegradability ratio (BOD/COD) with adverse effect to conventional biological wastewater treatment facilities. For these reasons it is necessary the development of new technologies in order to treat those liquids. (Bilińska *et al.*, 2016; Forgacs *et al.*, 2004).

Advanced Oxidation Processes (AOPs) are promising alternative for treating colored and recalcitrant wastewaters like the produced in textile industries. (Bilińska *et al.*, 2015; Anjaneyulu *et al.*, 2005) These technologies involve in-situ generation of strong oxidant species like hydroxile radicals (HO•) (Rosenfeldt *et al.*, 2006; Legrini *et al.*, 1993; Glaze *et al.*, 1987). Two AOPs were selected for comparative proposes on this work. 1) photo Fenton (phF) processes, based on the catalytic decomposition of H₂O₂ in presence of Fe(II) or Fe(III) under UVA illumination (365-420 nm), and 2) Ozonation (Oz), based on incorporation of ozone on the system. Pollutants dissolved on the system may be oxidized through two main pathways, direct reaction with ozone and reaction with HO• radicals generated by ozone decomposition via chain reaction (Rosenfeldt *et al.*, 2006; Hoigné and Bader, 1983). The main reaction pathway depends on

pH, concentration of initiators, promoters and scavengers in the reacting medium (Lovato *et al.*, 2009; Arslan-Alaton *et al.*, 2002).

These technologies are still relatively new on the market, and require to be carefully studied to set the optimal conditions for each case. Therefore, several research papers compare and analyze the optimal conditions for new wastewater purification techniques. Some of these works, studied the treatment of solution obtained by dissolution of dyes in water (Cataño *et al.*, 2012; Gutowska *et al.*; 2007; Sarayu *et al.*, 2007; Wang *et al.*, 2003). This simplified condition, ignores the effect of salts and additives present on real samples on the effectiveness of the treatments. Some authors have demonstrated the impact of the presence of salts and additives on the final treatment results (Bilińska *et al.*, 2015; Colindres *et al.*, 2010; Arslan-Alaton and Balcioglu, 2000). Other authors, assayed the treatment of real wastewaters (Somensi *et al.*, 2010; Sundrarajan *et al.*, 2007; Constapel *et al.*, 2009; Arslan-Alaton and Balcioglu, 2000). Although this alternative seems more realistic, it does not allow to compare results because the real wastewaters are very variable and it is impossible to repeat an experiment with the same raw liquid properties. Each industry uses different raw materials and formulation for dyeing baths. Moreover the industrial wastewater treatment facilities, usually receive a mixture of liquids coming from all the operations developed on the factory. Most of the articles published in the specialized literature developed with real wastewaters, does not specify all the sources (industrial operations) of this wastewater (Bisschops and Spanjers, 2003). Textile operations, like dyeing, are usually developed on batch mode. Each combination of fabrics and desired color require different conditions, and consequently different bath formulations. Therefore, the wastewater properties vary significantly, even along a working day (Paździor *et al.*, 2019; Hanela *et al.*, 2018; Savin and Butnaru, 2008). Those situations hinder the possibility of duplicate a raw wastewater sample, even on the same factory (Hanela *et al.*, 2018).

Some authors (Arslan-Alaton and Balcioglu, 2000; Constapel *et al.*, 2009; Alvares *et al.*, 2001; Ince and Tezcanlı, 2001) employed procedures to “hydrolyze” the dyes, by mixing with some salts and/or alkalis on similar proportions used on industrial processes and heat prior the treatment experiments. This is an intermediate approach between the last mentioned but does not consider the effect of all the additives used on the process and the effect of the contact with fabrics dyed.

On a previous work (Hanela *et al.*, 2018), the authors presented a methodology to reproduce, at bench scale, the dyeing process of cotton fiber with RB5 based on typical operative conditions found at local dyeing industries. The process reproduces several steps, in order to develop scouring of raw cotton fabrics, and its dyeing using industrial grade materials. The wastewater generated by the nine steps of dyeing process, were mixed giving the Model Textile Wastewater (MTW) used in this work as

raw liquid, to compare efficiency of two treatment methods. The MTW is representative of real industrial wastewater, under controlled conditions, and it could be reproduced several times for comparative proposes.

II. METHODS

A. Materials

RB5 solutions were prepared using Remazol Black B 133 (Reactive Black), Dystar, batch #90260, with 70-85% purity according supplier data sheet. This product is industrial quality, from a recognized international brand, and its purity is higher than several analytical grade dyes, available on the market. Analytical grade reagents (Merck, J.T. Baker, Anedra) were used for salts, alkalis and acids. Water used for solution and bath preparations was deionized (conductivity < 8.5 $\mu\text{S}/\text{cm}$). Surfactant, softeners and additives employed for MTW elaboration were commercial products, and raw 100% cotton fabric was used.

B. Elaboration of Model Textile Wastewater (MTW)

Although each company employs proper recipes for the dyeing bath composition, the authors gather information from a survey of industries, textile additives suppliers and specialist on textile industry in Argentina to develop a “typical” process for dyeing cotton with RB5. The different operations involved in the dyeing process were carried out in metallic pots of 3-4 L volume. A clean 100 g cotton fabric (on 2 cm x 10 cm strips) per each liter of bath solution was used as substrate for dyeing. The system was stirred manually and the liquids were decanted and collected after each operation to compose the final compensated MTW. The system was heated with heating plates to follow the temperature settings of the recipe. The process may be divided on three steps: Scouring, Dyeing and Rinsing.

Scouring is the process while impurities proper of raw cotton, as oils, fats, waxes, minerals and plant matter are removed by caustic solutions and surfactants (Bisschops and Spanjers, 2003). This step prepares the raw fabrics for an optimal dyeing, but is not part of the dyeing process. Then, the wastewaters generated at that stage were not considered on this work. On dyeing stage, the fabrics were soaked on dyeing bath and the system followed a temperature program while dye, salts and additives were incorporated step by step. Each liter of dyeing bath contained 100 g of scoured fabrics, 80 g of NaCl, 5 g of RB5, 3 g of Na_2CO_3 , 1 g of NaOH, 1 g of surfactant (Tensia NG3) and 1 g of surfactant (Heptol NWS). Spent bath was decanted and collected. After dyeing, fabrics were rinsed several times in order to remove the excess of dye and additives from the final product. Some rinsing solutions contains additives as surfactants, acetic acid and softeners. After each rinse, the liquids were decanted, and collected to compose the MTW. Textile was squeezed and the next rinse was developed with the same liquid volume employed for dyeing bath. Detailed process was presented on a previous work (Hanela *et al.*, 2018) and is summarized on Table 1. MTW was obtained by mixing the spent dyeing bath, with liquids drained from the rin-

Table 1. Process to produce MTW

Stage	Additives	Temperature	Time
Scouring			
Fabrics soaking	Fabrics (100 g/l) Tensia NG3 (2 g/l) Na ₂ CO ₃ (5 g/l)	Room Temperature (25°C)	
Heating	-----	Ramp to 95°C	45 minutes
Rinsing	Water		
Dyeing			
Fabrics soaking	Scoured fabrics (100 g/l) Tensia NG3 (1 g/l) Heptol NWS (1 g/l)	Room Temperature (25°C)	30 minutes
Salt addition	NaCl (80 g/l)		Instantaneous
Dye	RB5 (5 g/l) - predisolved		Instantaneous
Heating	-----	Ramp to 60°C	60 minutes
Alkaly addition	Na ₂ CO ₃ (1.5 g/l) NaOH (0.5 g/l)		
Mix	-----	60°C	10 minutes
Alkaly addition	Na ₂ CO ₃ (1.5 g/l) NaOH (0.5 g/l)		
Mix-Dyeing		60°C	55 minutes
Rinsing			
Rinse	Water	40-45°C	
Heat Rinse	Water	70°C	
Surfactant Rinse	Heptol NWS (1 g/l)	90°C	
Neutralizing Rinse	Acetic Acid, glacial (0.75 g/l)	60-70°C	
Cold Rinse	Water	Room Temperature (25°C)	
Softening	Comercial softener Vivere (1 g/l) Acetic Acid, glacial (0.5 g/l)	60°C	
Cold Rinse	Water	Room Temperature (25°C)	

Table 2. Characteristics of non treated MTW and RB5 liquids

	Pt-Co index	RB5 (mg/L)	TOC (mg/L)	pH
RB5 (H)	5546	340	82.7	5.45
RB5 (L)	347	20	10.1	6.16
MTW (H)	7465	520	137.9	5.79
MTW (L)	333	24	8.5	5.86

ings. To ensure enough volume and reduce the variations on MTW, the experiments were developed with a mix from three different batches. Characterization of MTW is presented on Table 2.

For comparison proposes, aqueous solutions containing only RB5 were prepared and treated by pH and Oz. Two concentration ranges were studied. High (H): 300 to 500 mg/l of RB5, close to the concentration of RB5 in the MTW, and Low (L): 20 mg/l of RB5, close to the concentrations of RB5 in some individual rinsing wastewater. Solutions of RB5 in water, studied as comparative basis, will be referred as RB5.

Low concentration MTW samples, MTW(L) were elaborated by diluting the obtained MTW 66,6:1000 times for pH experiments and 53:1000 for ozonation experiments. Assays with RB5(L) were performed with 20 mg/l in all the cases and RB5(H) with 300 mg/l for pH and 380 mg/l for Oz experiments.

C. Analytical methods

RB5 concentration was measured by linear correlation with the absorbance at 590 nm, using spectrometers Shimadzu UV-2450 and Hach 9100 calibrated with standard

solution of RB5 in water. Additionally, the Pt/Co color was determined by contrasting the absorbance at 455 nm (yellow color) with the Pt-Co standards. Conductivity and pH were measured using Thermo-Orion Versa Star multi-parametric analyzer. Total Organic Carbon (TOC) was measured using Shimadzu TOC Analyzers (model TOC-5000A and TOC-L).

D. Ozonation

Ozonation experiments were performed on a cylindrical reactor made of borosilicate glass with inner diameter of 11.35 cm and operation level of 42 cm. For each experiment it was charged with 4 liters of the liquid to be treated. A fritted glass diffuser was placed at the bottom of the reactor to allow the continuous injection of ozonized gas. Ozone was produced from pure oxygen (99.5%) with an ozone generator (Ozonogen U.S.pat. # 4,383,976); the ozone mass flow was adjusted by regulating the feed voltage of the ozone generator and verified by iodometric analysis. For comparative MTW and RB5 experiments, ozone mass flow was set on 2.5 g/h. The ozonised gas flow was 1 l/min. Gas pressure at inlet point of reactor was regulated to 0.092 bar. The reactor was sealed on top with 10 cm of gaseous layer above the liquid. Exhaust gases were collected on three washing bottles arranged serially and filled with Potassium Iodide solution to collect and neutralize residual ozone. Experiments were developed without pH adjustment to the liquids.

RB5 measurement below 30 mg/l was performed on line by absorbance quantification at 590 nm, recirculating

the liquid continuously (70 ml/min) through measuring cell (10 ml) mounted on a spectrometer Hach DR 2100. Information was collected on a PC using a routine programmed on Matlab® software. For kinetic analysis, it was assumed a 50 seconds delay between starting time of the experiments and the absorbance measured on the online spectrometer. This time corresponds to hydraulic delays of ozone to reach the reactor since the generator is turned on (30 seconds), plus the time the bulk reactor liquid takes to reach the measuring cell (20 seconds). This delay was subtracted on the horizontal axis for kinetic analysis.

Concentrations higher than 30 mg/l were sampled, and measured by off-line spectrometer. Immediately after collection of samples, they were mixed 1:1 with quencher solutions in order to stop further oxidation. For direct spectrometry, samples were quenched with acetonitrile and for other parameters, with 0,02M sodium sulfite solution. Additional tests were developed to verify the absence of quencher interferences on measurements. Experiments were performed until constant absorbance at 590 nm, resulting final treatment times of 80 (RB5-H), 20 (RB-L), 120 (MTW-H) and 16 (MTW-L) minutes respectively.

E. Photo Fenton

pH experiments were performed in a 200 mL double jacket batch reactor thermostated at 25 °C by water circulation. The reactor was illuminated from above with an Osram Ultravitalux 300 W solar lamp. pH was adjusted to 3 using sulfuric acid (H₂SO₄). Hydrogen peroxide (H₂O₂) was incorporated in only one dose, being the initial concentration 50 mM or 2.5 mM for the solutions with high or low dye concentration respectively. Iron chloride (III), FeCl₃, (2.5 mM) was added to the system immediately after hydrogen peroxide. H₂O₂ consumption was followed by a spectrophotometric method (Pupo-Nogueira *et al.*, 2005). The experiments were performed until all H₂O₂ was consumed. Controls without FeCl₃ and in the dark were performed.

III. RESULTS AND DISCUSSION

A. Ozonation and photo-Fenton compared results

Both treatments show acceptable decoloration performances, at 455 and 590 nm (Fig. 1). Ozonation reached 100% removal of color in most cases, except for MTW(H) where this value dropped to 98% at 455 nm. Photo Fenton treatment reached 99% color removal for the High concentration range, while exhibit lower values for Low concentration samples. This last result is likely a consequence of the presence of Fe(III) in the solution.

Due to the color developed by Fe(III) in water solutions, and the initial low concentration of the dye in this case, the percentual difference in color between the initial and the final samples are lower than in the case of the solutions with high dye concentration.

Times required to reach Pt/Co index below 100 units on each assay, are summarized on Fig. 2. This value was under 5 minutes for all the Low Concentration solutions with maximum of 5 minutes for pHF applied to MTW(L).

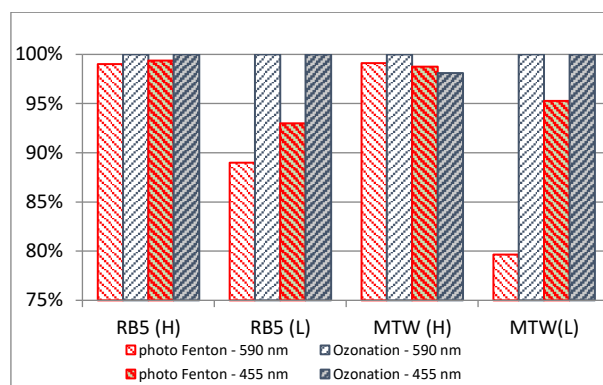


Figure 1: % Color removal for the different systems and treatments.

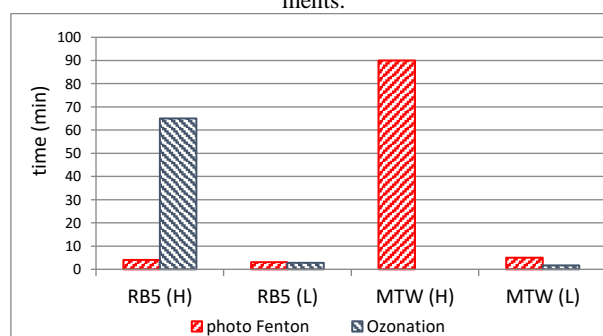


Figure 2: Time required to reach a Pt/Co index color < 100.

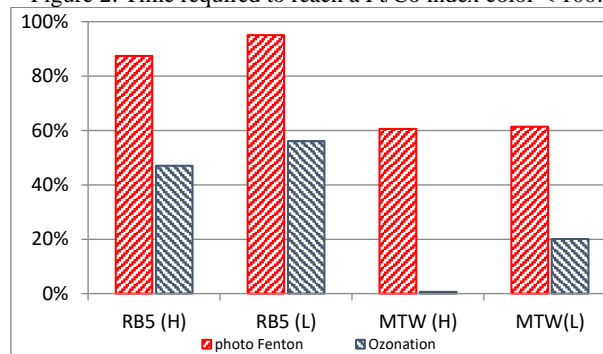


Figure 3: % TOC removal for the different systems and treatments.

On High range solutions ozonation required 65 minutes in case of RB5(H) and only reach a final value of 168 Pt/Co index for MTW(H), reason why it was not included on Fig. 2. Final TOC removals for the experiments are presented on Fig. 3. pHF treatment reached better TOC removals than ozonation. The presence of salts and additives on MTW samples reduced significantly the TOC removal ratios. This observation is correspondent with literature work (Gul and Özcan-Yıldırım, 2009).

B. Ozonation complementary results

Time evolution of RB5 concentration (obtained by measuring color @590 nm) and TOC along ozonation experiments, are presented on Fig. 4. Salts and additives of MTW did not affected the color removal kinetics, but they exhibit a negative effect on TOC removal by ozonation. This effect could be due to the presence of dissolved anions like chloride or carbonate, widely reported in the literature as OH• radical scavengers. (Arslan-Alaton, 2003; Litter, 2005) Ozonation experiments were finished

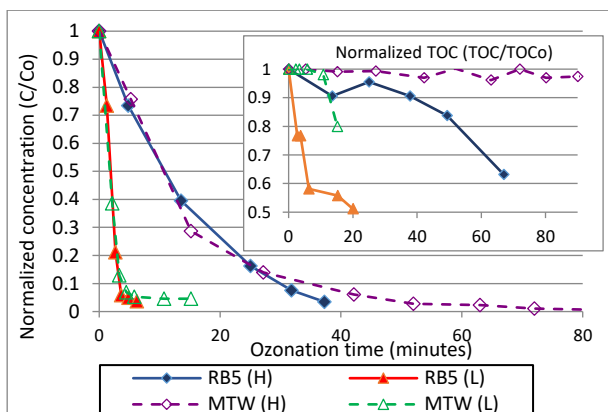


Figure 4: Color and TOC removal along ozonation time (Lines indicate the trend).

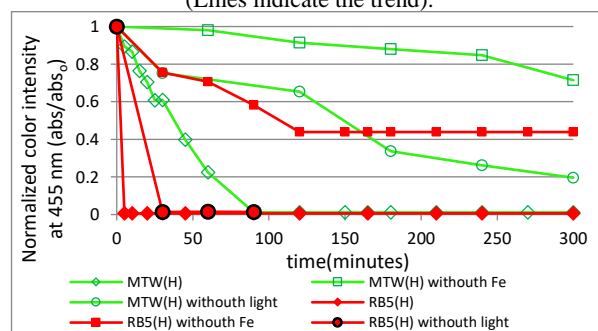


Figure 5: Evolution of color (455 nm) during different pHF experiments using MTW or RB5 solutions. (Lines indicate the trend).

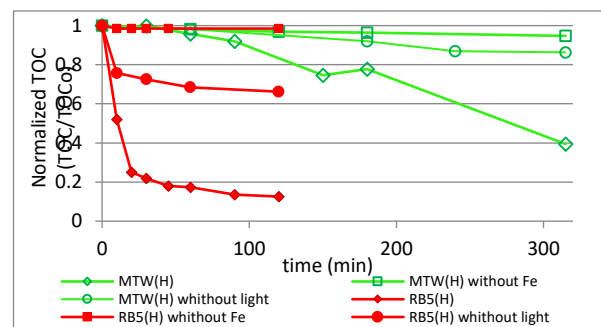


Figure 6: Evolution of TOC during different pHF experiments using MTW or RB5 solutions. (Lines indicate the trend).

once complete decoloration was observed. Therefore, higher TOC removals would be reached for higher ozonation times. This fact should be analyzed on future researching.

C. Photo Fenton complementry results

Figure 5 shows the evolution of Pt/Co color and Fig. 6 the evolution of TOC, normalized with respect to the initial values, for pHF experiments performed with RB5 or MTW in the different ranges of concentration. The results of the control experiments, with or without Fe(III) and/or illumination are also displayed in the figures. Decoloration and TOC diminution were faster for RB5 than for MTW solutions. The kinetics of dye degradation was clearly affected by the presence of salts and other additives in MTW solutions. As was indicated before for ozonation, some species present in the MTW solutions, as chloride and carbonates may act as radicals scavengers. (Santiago *et al.*, 2016; Silva *et al.*, 2016)

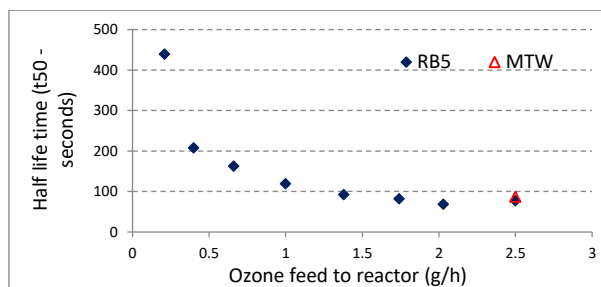


Figure 7: Effect of ozone dose on half life time (t_{50}) for RB5(L) and MTW(L).

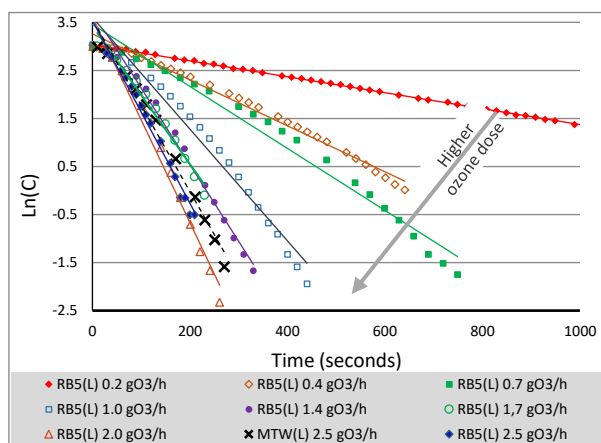


Figure 8. Effect of ozone dose on RB5(L) and MTW(L) treatment

Surfactants and other organic additives may also compete with the dye for the HO^\bullet radicals. In the experiments performed in the dark (Fenton process) dye degradation and TOC diminution were notably lower than in the experiments performed under UVA illumination. These results show the important role of light in the process.

D. Kinetic analysis of ozonation process

Figure 7 shows the times at which RB5 concentrations reach 50% of their initial values (t_{50}) when different ozone flows were fed. It can be seen that above approximately 1.4 g O_3/h t_{50} remained almost constant, indicating that the concentration of dissolved ozone reached a maximum value, probably close to the saturation point.

The kinetics of the ozonation process, besides the chemical reaction between ozone and RB5, is a result of several physical-chemistry phenomena that take place inside the reactor, among them the mixing of the reactants, the formation of the ozone bubbles and the mass transfer to the liquid phase. Thus, the velocity at which RB5 reacts should be a complex function of several variables. However, an inspection of the shape of the curves of RB5 concentration against time, suggests an exponential decay behavior. As a matter of fact, Fig. 8 clearly shows that the kinetic results can be satisfactorily fitted with a simple first-order kinetic law in a wide range of concentrations (until 90 % - 95% conversion) in most of the cases. The slope of the straight lines, that correspond to the pseudo-first order constants, increased when ozone flow was increased. This result suggest that the rate of the

global process was limited by the chemical reaction, being faster the ozone mass transfer to the liquid phase at higher ozone flows, reaching higher ozone concentration steady-state values.

As it was highlighted before, decay speeds observed above 1,4 gO₃/h only exhibits slight differences, close to experiment uncertainty. More studies are in progress to have a better understanding of the phenomena that take place inside the reactor vessel during the ozonation process.

IV. CONCLUSIONS

The results clearly indicate that the presence of salts and additives used in the dyeing bath affect the efficiency of photo-Fenton and ozonation for decoloration and TOC removal on most cases. In this context, it is necessary to use well characterized model solutions containing all the ingredients present in the dyeing baths, to compare the efficiency of different AOPs processes. Decoloration kinetics at 590 nm was the only parameter that was not significantly affected by the presence of salts and additives. Higher efficiencies were obtained for decoloration with both AOPs tested in this work, being slightly higher with ozonation. TOC was only partially removed being more efficient pHF than ozonation. Remaining TOC indicates the presence of partially oxidized compounds and its potential toxicity should be considered before the discharge of treated liquid to the environment. Inherent advantages and limitations, of each technology must be considered for the design of industrial applications. For instance, pHFenton requires a pH adjustment to very low values, while ozonation may present gas-liquid mass transfer limitations. Furthermore, the obtained results verify the applicability of both methods for color and TOC removal on the reported ratios for dye dissolved on water and model liquids.

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REFERENCES

- Alvares, A.B., Diaper, C. and Parsons, S.A. (2001). "Partial oxidation of hydrolysed and unhydrolysed textile azo dyes by ozone and the effect on biodegradability," *Trans. IChem.E.*, **79**, 103-108.
- Anjaneyulu, Y., Sreedhara Chary, N. and Suman Raj, D.S. (2005). "Decolourization of industrial effluents – available methods and emerging technologies – a review," *Reviews in Env. Science and Bio Technology*, **4**, 245–273.
- Arslan-Alaton, I. and Balcioglu, I.A. (2000). "Effect of common reactive dye auxiliaries on the ozonation of dyehouse effluents containing vinylsulphone and aminochlorotriazine dyes," *Desalination*, **130**, 61-71.
- Arslan-Alaton, I., Balcioglu, I.A. and Bahnemann, D.W. (2002). "Advanced oxidation of a reactive dyebath effluent: comparison of O₃, H₂O₂/UV-C and TiO₂/UV-A processes," *Water Research*, **36**, 1143–1154.
- Arslan-Alaton, I. (2003). "A review of the effects of dye-assisting chemicals on advanced oxidation of reactive dyes in wastewater," *Coloration Technology*, **19**, 345-353.
- Arslan-Alaton, I., Hande Gursoy, B. and Schmidt J.E. (2008). "Advanced oxidation of acid and reactive dyes: Effect of Fenton treatment on aerobic, anoxic and anaerobic processes," *Dyes and Pigments*, **78**, 117-130.
- Bilińska, L., Gmurek, M. and Ledakowicz, S. (2015). "Application of Advanced Oxidation Technologies or Decolorization and Mineralization of Textile Wastewaters," *J. Adv. Oxid. Technol.*, **18**, 185-194.
- Bilińska, L., Gmurek, M. and Ledakowicz, S. (2016). "Comparison between industrial and simulated textile wastewater treatment by AOPs – Biodegradability, toxicity and cost assessment," *Chem. Eng. Journal*, **306**, 550–559.
- Bisschops, I. and Spanjers, H. (2003). "Literature review on textile wastewater characterization," *Environmental Technology*, **24**, 1399-1411.
- Cataño, F.A., Valencia, S.H., Hincapié, E.A., Restrepo, G.M. and Marín, J.M. (2012). "A comparative study between TiO₂ and ZnO photocatalysis: photocatalytic degradation of cibacron yellow FN-2R dye," *Latin American Applied Research*, **42**, 33-38.
- Colindres, P., Yee-Madeira, H. and Reguera, E., (2010). "Removal of Reactive Black 5 from aqueous solution by ozone for water reuse in textile dyeing processes," *Desalination*, **258**, 154-158.
- Constapel, M., Schellentrager, M., Marzinkowski, J.M. and Gab, S. (2009). "Degradation of reactive dyes in wastewater from the textile industry by ozone: Analysis of the products by accurate masses," *Water Research*, **43**, 733-743.
- Forgacs, E., Cserhatia, T. and Oros, G. (2004). "Removal of synthetic dyes from wastewaters: a review," *Environment International*, **37**, 953- 971.
- Glaze, W.H., Kang, J.W. and Chapin, D.H. (1987). "The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation," *Ozone Sci. Eng.*, **9**, 335–352.
- Gül, S. and Özcan-Yıldırım, Ö. (2009). "Degradation of Reactive Red 194 and Reactive Yellow 145 azo dyes by O₃ and H₂O₂/UV-C processes," *Chemical Engineering Journal*, **155**, 684–690.
- Gutowska, A., Kaluzna-Czaplinska, J. and Jozwiak, W.K. (2007). "Degradation mechanism of Reactive Orange 113 dye by H₂O₂/Fe²⁺ and ozone in aqueous solution," *Dyes and Pigments*, **74**, 41-46.
- Hanela, S., Fantoni, S., Romero, E., Díaz, S.N., Cainzos, V., Polla, G., Panebianco, V. and Candal, R. (2018). "Procedimiento de elaboración y caracterización de

- un efluente textil sintético para el estudio comparativo de técnicas de tratamiento,” *4 Encuentro de Investigadores en Formación en Recursos Hídricos*, Buenos Aires, Argentina.
- Hoigné, J. and Bader, H. (1983). “Rate Constants of reactions of ozone with organic and inorganic compounds in water,” *Water Research*, **17**, 173-194.
- Ince, N.H. and Tezcanlı, G. (2001). “Reactive dyestuff degradation by combined sonolysis and ozonation,” *Dyes and Pigments*, **49**, 145-153.
- Litter, M. (2005). “Introduction to Photochemical Advanced Oxidation Processes for Water Treatment,” *Hdb Env Chem*, **2**, 325-366.
- Legrini, O., Oliveros, E., and Braun, A.M. (1993). “Photochemical Processes for Water Treatment,” *Chem. Rev.*, **93**, 671-698.
- Lovato, M.E., Martín, C.A. and Cassano, A.E. (2009). “A reaction kinetic model for ozone decomposition in aqueous media valid for neutral and acidic pH,” *Chemical Engineering Journal*, **146**, 486-497.
- O’Neill, C., Hawkes, F.R., Hawkes, D.L., Lourenço, N. D., Pinheiro, H.M. and Dele’ e, W. (1999). “Colour in textile effluents – sources, measurement, discharge consents and simulation: a review,” *J. Chem. Technol. Biotechnol.*, **74**, 1009-1018.
- Paździor, K., Bilińska, L. and Ledakowicz, S. (2019). “A review of the existing and emerging technologies in the combination of AOPs and biological processes in industrial textile wastewater treatment,” *Chem. Eng. Journal*, **376**, 120797.
- Pupo Nogueira, R.F., Oliveira, M.C. and Paterlini, W.C. (2005). “Simple and fast spectrophotometric determination of H₂O₂ in photo-Fenton reactions using metavanadate,” *Talanta*, **66**, 86-91.
- Rosenfeldt, E.J., Linden, K.G., Canonica, S. and von Gunten, U. (2006). “Comparison of the efficiency of •OH radical formation during ozonation and the advanced oxidation processes O₃/H₂O₂ and UV/H₂O₂,” *Water Research*, **40**, 3695-3704.
- Santiago, D.E., Araña, J., González-Díaz, O., Henríquez-Cárdenes, E., Ortega-Méndez, J.A., Pulido-Melián, E., Doña-Rodríguez, J.M. and Pérez-Peña, J. (2016). “Treatment of wastewater containing imazalil by means of Fenton-based processes,” *Desalination and Water Treatment*, **57-30**, 13865-13877.
- Sarayu, K., Swaminathan, K. and Sandhya, S. (2007). “Assesment of degradation of eight commercial reactive azo dyes individually and in mixture in aqueous solution by ozonation,” *Dyes and Pigments*, **75**, 362-368.
- Savin, I.I. and Butnaru, R. (2008). “Wastewater characteristics in textile finishing mills,” *Env. Engineering and Management Journal*, **7**, 859-864.
- Silva, J.O., Silva Vicelma, V.M., Cardoso, L., Machado, A.E.H. and Trovó, A.G. (2016). “Treatment of Sanitary Landfill Leachate by Photo-Fenton Process: Effect of the Matrix Composition,” *J. Braz. Chem. Soc.*, **27**, 2264-2272.
- Somens, C.A., Simionatto, E.L., Bertoli, S.L., Wisniewski Jr, A. and Radetski, C.M. (2010). “Use of ozone in a pilot-scale plant for textile wastewater pre-treatment: Physico-chemical efficiency, degradation by-products identification and environmental toxicity of treated wastewater,” *Journal of Hazardous Materials*, **175**, 235-240.
- Sundrarajan, M., Vishnu, G. and Joseph, K., (2007). “Ozonation of light-shaded exhausted reactive dye bath for reuse,” *Dyes and Pigments*, **75**, 273-278.
- Ulson de Souza, A.A., Petrus, J.C.C., Santos, F.P., Brandão, H.L., Guelli, S.M.A., Souza, U. and Juliano, L.N. (2009). “Color reduction in textile effluents by membranes,” *Latin American Applied Research*, **39**, 47-52.
- Wang, C., Yediler, A., Lienert, D., Wang, Z. and Kettrup, A. (2003). “Ozonation of an azo dye C.I. Remazol Black 5 and toxicological assessment of its oxidation products,” *Chemosphere*, **52**, 1225-1232.
- Zuorro, A., Fidaleo, M., and Lavecchia, R. (2013). “Response surface methodology (RSM) analysis of photodegradation of sulfonated diazo dye Reactive green 19 by UV/H₂O₂ process,” *Journal of Environmental management*, **127**, 28-35.

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