Comparison of the hydroxyl oxidative effect in the UV/H$_2$O$_2$ and in the ozonation systems to degrade the dye rhodamine 6G

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Abstract

The aim of the present work is to deepen the study of two different advanced oxidation processes: H$_2$O$_2$/UV where UV light is used to generate radicalary species from H$_2$O$_2$ and ozonation that uses ozone as oxidant and radical generator agent. The importance of radical oxidation pathway during pollutant degradation in both systems will be studied. As pollutant model, a dye used in textile industries, rhodamine 6G, known because of its resistance to conventional oxidation treatments was selected. Different radical activities were analyzed in the case of H$_2$O$_2$/UV varying the molar dosage from 0 to 400 mol H$_2$O$_2$/mol R6G. In the ozonation process, the radical activity was modified with pH between 2 and 9.5. In both cases, the oxidation due to the radical HO$^\bullet$ is accompanied of other oxidative mechanisms: photolytic in the case of H$_2$O$_2$/UV and molecular in the ozonation. The contribution of the photolytic mechanism was always lower than 20% using molar dosages above 20 H$_2$O$_2$/mol R6G. On the other hand, in the ozonation, the contribution of the molecular mechanism varied between 100% (pH=2) and 0% (pH=9.5) so that an equilibrium in the contribution of both mechanisms was found at pH = 7.

Keywords: ozonation, radicalary mechanism, dyes, hydrogen peroxide, UV photolysis

1. Introduction

The Rhodamine 6G dye (Rh6G) presents an aromatic structure with two changing amino groups depending on the pH of the reaction environment giving rise to different molecular species with different electric charge and therefore with own behaviors against oxidation. These kind of aromatic structured dyes are satisfactory treated and decolorized using several advanced oxidation processes, but the efficiency on dye degradation depends mainly on the generation of free radicals as hydroxyl radical HO$^\bullet$ (Catalkaya and Kargi 2007), that is why in this study two different oxidation processes are selected in order to compare their efficiency in terms of radical generation capacity. Hydroxyl radical is highly reactive and nonselective that can oxidize and decompose numerous toxic compounds into CO$_2$ and water (Garcia-Montaño et al., 2008) but, these radicals can be generated in very different ways. Their activity will be determinant in their later industrial applications (Bierbaum 2014; Ghatak 2014). Different radical generation ways may have influence into compounds degradation, that is why we have choose for this study two different advanced oxidation processes where, oxidant agent or radical generation substances are added at the beginning of oxidation treatment, H2O2 system, or continuously during the ozonation treatment, in order to determinate how that radical generation strategy influence into radicalary oxidation pathway.In this study, we will analyze how two different hydroxyl radical generation ways, using two different advanced oxidation processes, contribute to the global oxidation pathway for the R6G dye degradation. During H$_2$O$_2$/UV treatment dye oxidation follows a photolytic-radicalary oxidation and when ozonation treatment is applied the oxidation runs following a molecular-radicalary pathway. In both systems radicalary oxidation pathway seems to play an important role into the whole dye degradation, meanwhile, photolytic and molecular contribution are less effectives.Radicalary oxidation pathway is mainly related to oxidant agent or concentration of the radical generator source (Long and Jin , 2012), being in the present study H$_2$O$_2$ and ozone concentration for each treatment system. The comparison between photo-radicalary and molecular-radicalary oxidation systems will leads us to analyze how treatment operational parameters, such us, oxidant-pollutant molar relation or pH will affect to the capacity of the radical oxidation system, and, at the same time, to set up a comparison so we can select for each system their respective operational conditions which lead to the most efficient radicalary activity.

2. Methodology

2.1. H$_2$O$_2$/UV system

For the study of the oxidation of R6G through the use of H$_2$O$_2$/UV system, a pilot plant was designed to work at laboratory scale, whose scheme and main elements are shown in Figure 1. Oxidation of synthetic solutions of R6G was carried out. The goal of this work was to analyze the

contribution of radical oxidation pathway to the degradation of pollutant depending on initial H_2O_2 concentration, so the molar ratio between oxidant and pollutant was defined as *MR* (molar ratio: mol H_2O_2/molR6G).
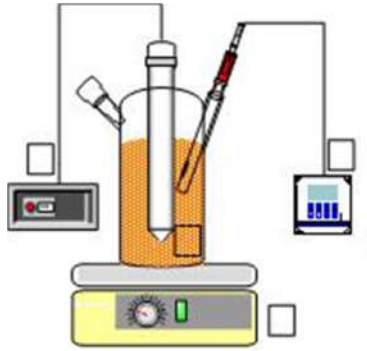
Figure 1. H_2O_2/UV pilot plant scheme. (1) 500 ml glass reactor, (2) Low pressure mercury lamp power 19W, (3) pH meter device, (4) Stirrer.

With that purpose, following the photolytic-radical kinetic model proposed, the overall degradation rate (r_T) radicalary degradation rate (r_R) and photolytic degradation rate (r_{ph}) were calculated using equation (1) (2) and (3).

$$-r_T = -\frac{d[R6G]}{dt} = k^{..}[R6G] = -(r_{ph} + r_R) \tag{1}$$

r_{ph} is photolytic oxidation term expressed as follows:

$$r_{ph} = I_0 \; _{R6G} \; F_{R6G}$$

$$[1-\exp(-2,303 \; L \; \varepsilon_{R6G} \; [R6G] \;)] \tag{2}$$

And r_R is radical oxidation term:

$$r_R = k_{OH} \; [OH^\circ][R6G] \tag{3}$$

Photolytic parameters:

Radiation Intensity: I_o, mol photon L^{-1} s^{-1}

Quantum yield: $\emptyset_{R6G}$ mol R6G/mol photon

R6G absorbed light fraction F_{R6G} and ε_{R6G}

Path length of light L, cm

were experimentally calculated in the original study of this work (Rodriguez C. 2013) and indicated later in the results section.

2.2. Ozonation system

The ozonation of R6G was carried out in the following oxidation plant. The main elements of the plant are the ozone generator and the stainless steel reactor with a volume of 30 L (79 cm high and 11 cm in radius).Gas coming out of the Triogen LAB2B ozone generator, is introduced into the reactor through a venturi installed in the recirculation loop of fluid from the reactor. Besides in the loop, the following measure elements are placed: ozone measurement probe in liquid (Rosemount Analytical model 499AOZ-60), temperature and pH (Rosemount Analytical

model 399 - 09-62). A killer and a KI hydraulic tramp were placed at the bottom of the line in order to destroy remaining ozone in gas stream.
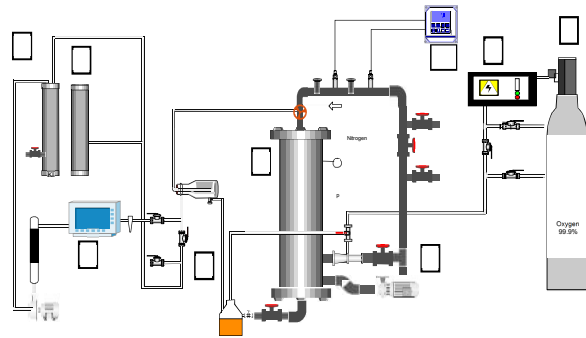
Figure 2. ozone pilot plant scheme. (1) Oxygen feed (2) ozone generator (3) Ozone, pH and temperature analyzer (4) 30 L reactor (5)Recirculating pump (6) Foams recirculating system and samples extraction (7) gas ozone analyzer (8) killer (9) KI hydraulic tramp.

Synthetic solutions of Rodamine 6G were carried out using different levels on pH values, so pH was adjusted using NaOH or H_2SO_4 solutions for each experiment. Experiments were carried out in the detailed installation above and the kinetic model, later explained, was used to adjust the experimental results to calculate the overall degradation rate (r_T) and also the radical and photolytic degradation rates for this system and also the molecular and radical contributions.

$$-r_T = -\frac{d[R6G]}{dt} = k_{o_3} \; [R6G][O_3] + 3K_{OOH}[O_3][OH^-] \tag{4}$$

İn this case molecular oxidation term (r_m) was calculated using following equation:

$$r_m = k_{o_3} \; [R6G][O_3] \tag{5}$$

Then, the radical oxidation term (r_R) was calculated by applying the simplification used by other authors (Benitez J.F. *et al*, 1994), so hydroxyl radical concentration can be expressed as a function of pH and k_{OOH}. This kinetic constant is related to the formation of $OOH^\bullet$ radical specie from ozone, and which value was obtained from bibliography data, showing a value of 70 mol^{-1} s^{-1} (Staehelin J. and Hoigne J. 1985).

$$r_R = 3 \; k_{OOH}[O_3][OH^-] \tag{6}$$

3. Results and discussion

UV/H_2O_2 System

Synthetic solutions of 50 mg/L of R6G were treated during one hour in UV/ H_2O_2 system, and several H_2O_2 concentrations were used in each experiment to reach initial values of molar ration *MR* ranged from 0 to 400. Equations (1) (2) and (3) were used to determinate molecular and photolytic participation on overall oxidation process. Photolytic parameters were calculated as before mentioned (Rodriguez C., 2013) resulting in the following values:

Intensity: $I_o = 7,037 \; 10^{-6}$ mol photon L^{-1} s^{-1}

Quantum yield: $\emptyset_{R6G} = 0.0068$ mol R6G/mol photon

Path length of light L= 2.1 cm

R6G absorbed light fraction: $F_{R6G} = \mu_{R6G}/\mu_T$. This fraction of light absorbed by R6G was calculated from molar extinction or absorption coefficients for all the substances present in the reaction medium from bibliographic data (Baxendale J.H. and Wilson A. 1957; Rodriguez C. 2013) Analyzing obtained values for initial degradation rates, shown in Table 1, percentage of each contribution were determinate and represented obtaining Figure 3, were we could conclude that in this kind of systems the concentration of hydroxyl radicals plays and important role. For MR values higher than 20, overall degradation pathway takes place mostly through a radical mechanism which seems to be more effective in R6G degradation due to its less selective and more oxidant character. Is also notorious in Table 1, that at values of molar ratio higher than 20, the radical degradation rate and, as consequence, the overall R6G degradation rate do not improve as expected. This can be explained as a consequence of the saturation of hydroxyl radical species that leads to a less effective oxidation reaction medium. So, the addition of H_2O_2 higher than the initial molar ratio equal to 20 does not show an improvement on system oxidation capacity.

Ozonation System

For the study of this oxidation system also synthetic solutions of 50 mg/L of R6G were treated during one hour, but this time system oxidizing capacity was changed using different initial reaction pH, ranged from 2 to 9.5. As corroborated for many authors (Von Gunten, 2003; Liu 2015) at acid pH ozonation treatment follows mostly a molecular pathway, meanwhile using basic values of pH, oxidation mechanism occurs through a radical pathway which seems to be more effective, because ozone is decomposed onto hydroxyl radicals easily. Molecular and radicalary initial degradation rates were calculated in order to carry out a comparative study only between initial pH influence, because as reaction takes place, pH levels are decreasing due to the presence of acid oxidation intermediates. Besides ozone initial liquid concentration were estimated by adjusting experimental data evolution, since there is an initial period of time were reaction is controlled by mass transfer limitation, as explained in previous researches (Rodriguez C. *et al* 2016)

Table 1. Values of overall, molecular and radical degradation rates for the ozonation system.

| pH	$-r_T$ (M/min)	$-r_M$ (M/min)	$-r_R$ (M/min)
2	6.70E-05	2.40E-07	6.70E-05
5.8	5.00E-05	4.58E-05	4.32E-06
9.5	1.15E-04	1.14E-04	1.54E-06
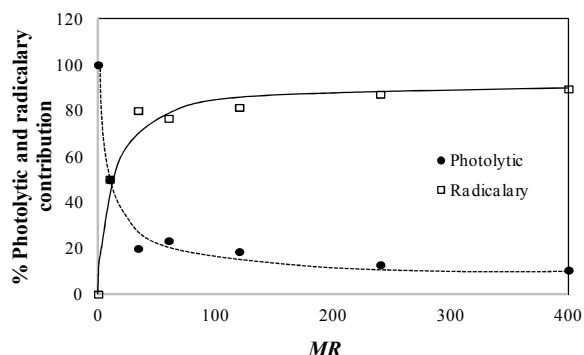
Figure 3. Values of photolytic and radicalary contribution to overall oxidation using an UV/H_2O_2 system

Although oxidizing specie used in these study was the same in both oxidant treatment systems, hydroxyl radical $^{\bullet}$OH, overall reaction medium seems to have high influence on oxidation mechanism, in this case pH values will be determinant on degradation majority pathway. As we can see in results showed in Table 2, as pH increases also the system oxidizing capacity does, reaching higher degradation rate values. Taken into account values on Table 2, percentages of molecular and radical contribution to overall degradation rate were calculated using equations (4) (5) and (6), resulting in Figure 4, were we can conclude that at values of pH near from 5 the contribution of each term to overall R6G degradation is almost 50%.

Table 2. Values of global degradation rate, together with the photolytic and radical rates for the UV/H_2O_2 system

MR (mol H_2O_2/mol R6G)	$-r_T$ (mol/min L)	$-r_{ph}$ (mol/min L)	$-r_R$ (mol/min L)
0	5.93E-08	5.93E-08	-------------
2	7.80E-08	1.91E-09	7.61E-08
10	7.95E-08	1.83E-09	7.77E-08
20	1.51E-07	2.17E-08	1.29E-07
34	1.25E-07	1.16E-08	1.13E-07
60	1.84E-07	7.14E-09	1.77E-07
120	2.27E-07	3.29E-09	2.24E-07
240	2.57E-07	2.07E-09	2.55E-07
400	2.77E-07	1.25E-09	2.76E-07
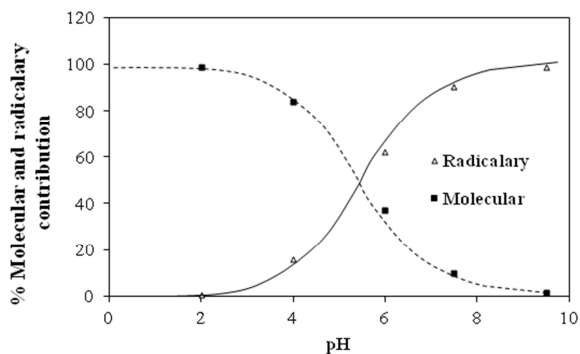
Figure 4. Values of molecular and radicalary contribution to the overall degradation rate using an ozonation system

4. Conclusions

For each used oxidation system there is, in one hand, a principal oxidation pathway, that is the radical one , and, in the other hand, a secondary degradation pathway. These are the photolytic one in the case UV/H$_2$O$_2$ system, and the molecular in the ozonation system. In both cases, this secondary degradation pathway, under certain reaction conditions reach a minor role, this will be at molar ratio higher than 30 in the first treatment system and at pH higher than 8.It is also remarkable that, using UV/H$_2$O$_2$ system under really high molar ratio concentrations of oxidant (MR higher than 240) radical degradation rate is similar to molecular degradation rate for the worse ozonation system conditions (pH = 2), which lead us to conclude that radical contribution to the overall R6G degradation process is favored using an ozonation system, being the ozone a more efficient hydroxyl radical generator agent.

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