Article

HYDROGEN PEROXIDE PHOTOLYSIS WITH DIFFERENT UV LIGHT SOURCES INCLUDING A NEW UV-LED LIGHT SOURCE

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ABSTRACT

Hydrogen peroxide 0.1% was photolyzed using 17W low pressure mercury arc lamp and 125 W high pressure mercury arc lamp. The decomposition kinetics was followed through the pseudofirst order kinetics and different conditions of temperature and pH were explored. H_2O_2 0.1% was also photolyzed at 360 nm through a new UV-LED 3W light source using a flow reactor. The kinetics rate constant achieved with the UV-LED photolysis is at least one order of magnitude lower than that achieved with the low pressure mercury arc lamp. Other drawbacks of the UV-LED photolysis were evidenced.

Keywords: Hydrogen peroxide, photolysis, UV-Hg light sources, UV-LED light source.

1. INTRODUCTION

Hydrogen peroxide is considered an environmentally safe reagent since its decomposition leads, in general, to the formation of water and oxygen [1]. The main industrial use of hydrogen peroxide are as oxidizing agent and as disinfectant and sterilant alone or in the form of peracids (e.g. peracetic acid) [1]. Hydrogen peroxide is one of the preferred reagent in wastewater treatment and in the advanced oxidation processes (AOPs) [1].

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After industrial use, the resulting diluted solutions of H_2O_2 should be decomposed before being disposed. A number of catalysts are known as effective decomposition agents of diluted hydrogen peroxide. The undisputed most effective catalyst is the enzyme catalase which is widespread in nature being present in animals, plants and lower organisms. The most common catalase enzyme used industrially is from bovine liver, having the incredibly high H_2O_2 decomposition rate constant of 3.2×10^5 s^{-1} [2,3]. Another highly selective catalyst capable to decompose H_2O_2 is Pt sol with a rate constant of 7.1×10^2 s^{-1} [2]. According to Jones [1] palladium is even more effective than platinum. Another very important and practical catalyst for diluted H_2O_2 decomposition is MnO_2 which however is several orders of magnitudes slower than catalase. In fact, k values of 1.5×10^{-4} s^{-1} were measured at pH =3 till 9.7×10^{-4} s^{-1} at pH = 10 for the diluted hydrogen peroxide decomposition on manganese dioxide [4,5]. It was also put in evidence that some stabilizer normally added to H_2O_2 like for example pyrophosphates may reduce the catalytic activity of pyrolusite (MnO_2) [6]. Also ferric ions and iron oxide catalyze the decomposition of H_2O_2 and the maximum rate constant reported was 2.7×10^{-3} s^{-1} [7,8].

Other examples of H_2O_2 decomposition catalysts (without the claim of being comprehensive) are iron-cobalt oxides [9], certain rare earth perovskites [10], copper (II) ions [11], water-ceramic interfaces [12]. A special mention should be deserved on the H_2O_2 decomposition on activated carbon with rate constants in the range comprised between 6×10^{-4} and 3×10^{-2} s^{-1} [13,14].

The decomposition of H_2O_2 leads, under certain circumstances, not only to common molecular oxygen but also to the reactive singlet oxygen as underlined in a rather comprehensive work [15]. Therefore care must be taken in the disposal of the generated oxygen.

The main drawbacks in H_2O_2 decomposition using a catalyst like those mentioned above are linked to the necessity to remove the the catalyst once it reaches exhaustion and its substitution. Additionally, some of the mentioned catalyst can leach and release ions into the treated water, so that hydrogen peroxide is destroyed but the resulting water results polluted by undesired transition metals ions. Furthermore, certain catalysts like catalase must be dissolved into hydrogen peroxide to display in full their potential, posing again the problem of catalyst removal from the solution.

An alternative way to decompose diluted H_2O_2 involves the use of a UV light source [16]. The process of H_2O_2 decomposition can be generally described by the simple reaction scheme $H_2O_2 \rightarrow 2$ •OH, but in reality is much more complex and characterized by a quantum yields approximately ≈ 1.0-1.5 in a wide range of wavelengths used for irradiation spanning from 193 nm to the canonical 254 nm to the UV-A represented by 308 and 354 nm [16-27]. Special variants in the photolysis of H_2O_2 involve the photocatalytic decomposition process where the UV irradiation is conducted in presence of a suspension of titanium dioxide [23], or the use of highly energetic vacuum UV radiation [24].

This paper is dedicated to a comparison of different UV light sources in the decomposition of diluted H_2O_2.

2. EXPERIMENTAL

2.1. Materials and Equipment

Hydrogen peroxide 35% was supplied from Evonik. Sulfuric acid, potassium iodide and ammonium molybdate were obtained from Sigma-Aldrich.

For the UV irradiations use was made of 17W low pressure mercury lamp from Helios Italquartz having an almost monochromatic emission at 254 nm. The lamp was inserted into a cylindrical quartz sheath having a length 18 cm. The sheath was then inserted into a Durhan glass reactor filled with 200 nm of diluted H_2O_2.

The UV irradiation with a medium pressure mercury lamp was performed with 125 W lamp with water jacketed quartz sheath (18 cm length) and dedicated glass reactor. Also this lamp was from Helios Italquartz with main emissions at 365 nm and in the visible, with minor lines at 222-265 nm. For a detailed description of the photochemical apparatus used and the mercury lamp main emission see ref. [28].

The UV-LED irradiation was performed using 3W LED (=light emitting diode) with main emission at 360 nm. The led was characterized by a Shimadzu UV 1670 spectrophotometer and as shown in Fig.1 the diode main emission occurs as a monochromatic line at about 360 nm, in the UV-A region. However, this line is accompanied by a broader and intense emission at 204 nm (in the UV-C region) which has saturated the spectrophotometer detector. It is not sure if the line at 204 nm is due to an artifact since the current UV-LED lamps are known to irradiate only at about 360 nm.

Figure 1: Emission lines from the light emitting diode as recorded in the UV-VIS spectrometer. The main emission is located at 359 nm as a narrow line. However, there is also another emission at 204 nm which appears even more intense (the signal is saturated) and broader than the emission at 359 nm. The emission above 750 nm is near infrared emission and goes beyond 800 nm
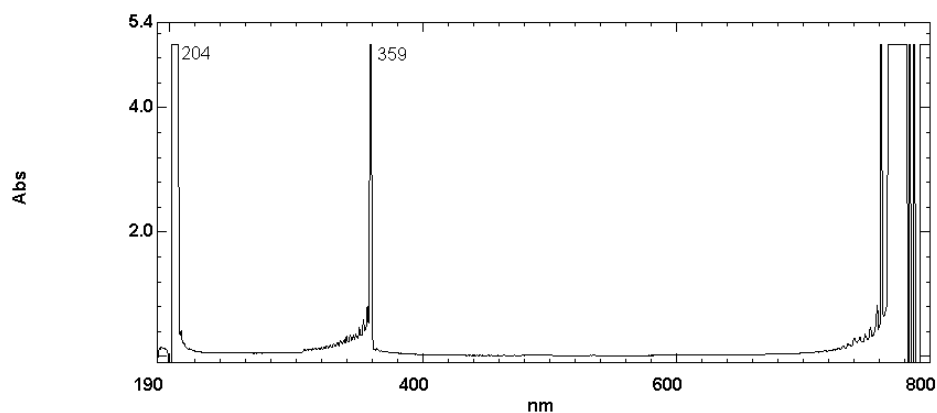

Fig. 2 shows the home-made UV-LED reactor made in polycarbonate and with the light source mounted at the top. The diluted hydrogen peroxide solution was circulated into the reactor using an external peristaltic pump.

Figure 2: UV-LED reactor. The lamp is at the top of the reactor and the H_2O_2 solution is circulated through the reactor with inlet at the bottom and outlet at the top
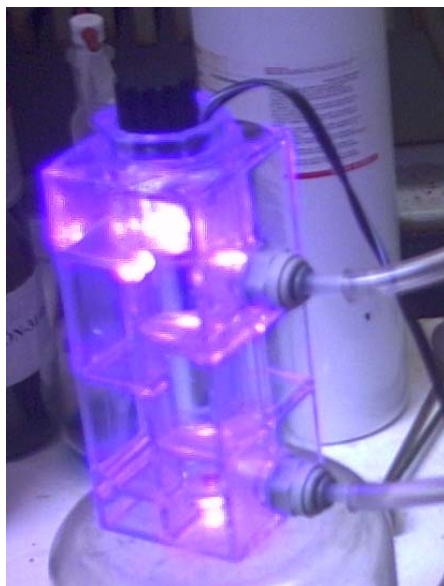

2.2. Experimental Method/Model

Stock solutions of approximately 0.1% H_2O_2 were prepared by sampling 1.5 ml of H_2O_2 35% and diluting with distilled water to a final volume of 500 ml.

The hydrogen peroxide concentration was determined iodometrically following the method of Kolthoff et al. [29]. The method consists in the addition of 1 g of KI to 25 ml of diluted hydrogen peroxide solution followed by the addition of 10 ml of H_2SO_4 2M and 3-4 drops of a solution of ammonium molybdate as catalyst to accelerate the reaction between KI and H_2O_2. The free iodine liberated is titrated with a 0.05 M solution of $Na_2S_2O_3$.

3. RESULTS AND DISCUSSIONS

3.1 GENERAL ASPECTS OF THE H_2O_2 DECOMPOSITION REACTION

The thermodynamics parameters of H_2O_2 decomposition according to the general reaction:

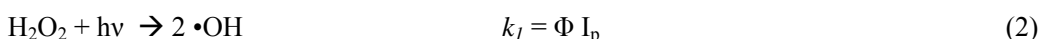$$2 \ H_2O_2 + h\nu \rightarrow [4 \cdot OH] \rightarrow 2 \ H_2O + O_2 \qquad (1)$$
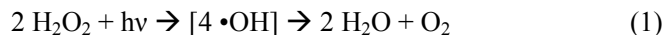
are all favorable. In fact the Gibb's free energy of reaction (1) is largely negative underlining that the reaction is thermodynamically allowed: ΔG_R = -237 kJ/mol. The

enthalpy of reaction (1) is also negative ΔH_R = -190 kJ/mol, showing that the decomposition reaction occurs exothermally.
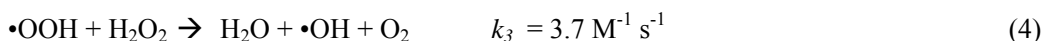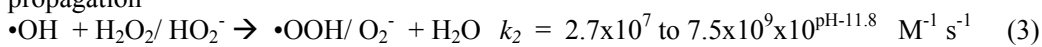
From the photochemical standpoint, as discussed in the introduction, the quantum yield of reaction (1) Φ = 1.0-1.5 Einstein in a wide range of wavelengths. More precisely, it was reported that the H_2O_2 photolysis is effective at any wavelength <380 nm, where H_2O_2 starts to absorb appreciably light [30]. Such quantum yield values around the unity clearly suggest that chain reactions are hindered by an effective termination processes of the $\cdot$OH and $\cdot$OOH radicals.

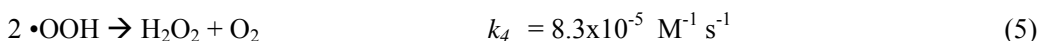A general description of the main reactions occurring in the photolysis of H_2O_2 were reported as follows [31]:
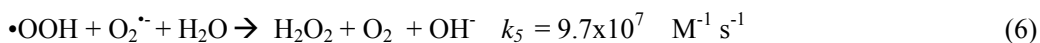
Light absorption initiation

$$H_2O_2 + h\nu \rightarrow 2 \cdot OH \qquad\qquad k_1 = \Phi\, I_p \qquad\qquad (2)$$

propagation

$$\cdot OH + H_2O_2/ HO_2^- \rightarrow \cdot OOH/ O_2^- + H_2O \quad k_2 = 2.7\text{x}10^7 \text{ to } 7.5\text{x}10^9\text{x}10^{pH-11.8} \text{ M}^{-1}\text{ s}^{-1} \quad (3)$$

$$\cdot OOH + H_2O_2 \rightarrow H_2O + \cdot OH + O_2 \qquad k_3 = 3.7 \text{ M}^{-1}\text{ s}^{-1} \qquad\qquad (4)$$

termination

$$2 \cdot OOH \rightarrow H_2O_2 + O_2 \qquad\qquad k_4 = 8.3\text{x}10^{-5} \text{ M}^{-1}\text{ s}^{-1} \qquad\qquad (5)$$

In addition, the disproportionation reaction of of $\cdot$OOH + $O_2^{\cdot-}$ is expected to contribute to H_2O regeneration as shown below:

$$\cdot OOH + O_2^{\cdot-} + H_2O \rightarrow H_2O_2 + O_2 + OH^- \quad k_5 = 9.7\text{x}10^7 \text{ M}^{-1}\text{ s}^{-1} \qquad (6)$$

The above reactions suggest that under determined conditions the photolysis of H_2O_2 could be completely compensated by the termination and disproportionation reactions which are able re-generate hydrogen peroxide.

## 3.2 Photolysis of H_2O_2 by low pressure and high pressure mercury lamps

The kinetics of H_2O_2 decomposition is described by a second order kinetics law [31]. However, in first approximation, the use of pseudofirst order kinetics is sufficient to describe the concentration decay of hydrogen peroxide as function of the irradiation time [32], considering also that this study was made on diluted ≈0.1% H_2O_2, a concentration which is closer to the real applied conditions . Consequently, the simple equation:

$$\ln\{[H_2O_2]_t/[H_2O_2]_0\} = kt \qquad\qquad\qquad (7)$$

was used in the determination of the kinetic rate constant k (expressed in s^{-1}) represented by the slope of the experimental data linking the first member of equation 7 with t, the irradiation time in seconds [2,32]. Fig.2 shows an example of this evaluation of the experimental data in the photolysis of 0.1% H_2O_2 in presence of Fe^{3+} ions with a low pressure and a medium-high pressure mercury lamp. Fe^{3+} ions were added 5x10^{-3} M were added in the intention to depress the termination reaction (5) as well as the disproportionation reaction (6). The pseudofirst kinetics rate constants determined from the graph in Fig. 3 show that the low pressure

mercury lamp, although less powerful in light intensity (17 W) gives a higher rate constant for the decomposition of H_2O_2 with $k_{lowP} = -4.57 \times 10^{-4}$ s^{-1} against the high pressure mercury lamp working at 125 W with $k_{hiP} = -3.74 \times 10^{-4}$ s^{-1}.

Figure 3: Pseudofirst order kinetics in the photolysis of 0.1% H_2O_2 with a low pressure mercury lamp (blue diamonds) and with a high pressure mercury lamp (red squares)
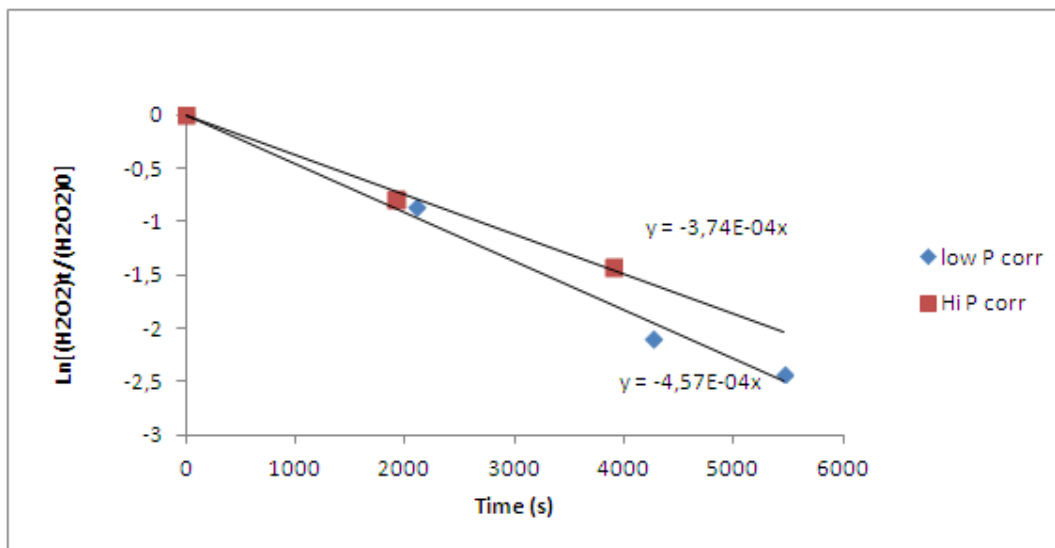
The reason why the low pressure mercury lamp is giving similar photolytic results as the high pressure mercury lamp (although it works at lower power than the high pressure lamp) is due to the fact that all the 17W power is released at 254 nm where H_2O_2 has a molar extinction coefficient of 19.6 L mol^{-1} s^{-1}. Instead, at longer wavelengths, where large part of the irradiation power of a high pressure mercury lamp is released the molar extinction coefficient of H_2O_2 is much lower: e.g. at 300 nm $\varepsilon = 1$ L mol^{-1} s^{-1}, at 320 nm $\varepsilon = 0.22$ L mol^{-1} s^{-1}, at 340 nm $\varepsilon = 0.047$ L mol^{-1} s^{-1}, and at 360 nm $\varepsilon = 0.01$ L mol^{-1} s^{-1}. Thus, with a low pressure mercury lamp, the lower power (17 W) is released exclusively as photons at 254 nm where H_2O_2 has the highest light absorption cross section (in the spectral range considered here). On the other hand the high power of the high pressure mercury lamp (125 W) is dispersed in a wider range of wavelengths including also wavelengths where the absorption cross section of H_2O_2 is negligible and hence is lost without any effect.

In Table 1 are summarized the results of a series of photolysis experiments made on 0.1% hydrogen peroxide and evaluated through the pseudofirst order kinetic law. The data show that the addition of Fe^{3+} ions to 0.1% H_2O_2 does not lead to any decisive improvements in the photolysis rate constants:

$k_{lowP} = -4.57 \times 10^{-4}$ s^{-1} with Fe^{3+}

against

$k_{lowP} = -4.8 \times 10^{-4}$ s^{-1} without Fe^{3+}

and

$k_{hiP} = -3.74 \times 10^{-4}$ s^{-1} with Fe^{3+}

against

k_{hiP} = -5.1x10^{-4} s^{-1} without Fe^{3+}.

Contrary to the expectation, the data show an inhibitory effect of the Fe^{3+} ions in the photolysis of 1% H_2O_2. In the absence of Fe^{3+} ions the photolysis rate constants of the two mercury lamps are practically the same: k_{lowP} = -4.8x10^{-4} s^{-1} against k_{hiP} = -5.1x10^{-4} s^{-1}.

Table 1 shows also the temperature effect and the pH effects in the photolysis of H_2O_2. It is well known that the photochemical reactions are not sensitive to the change of temperature since the mechanism of activation is not affecting the translational kinetic energy of molecules but only and selectively their electronic state. Therefore, it is not a surprise to see that k_{lowP} = -4.8x10^{-4} s^{-1} at 20°C against k_{lowP} = -5.5x10^{-4} s^{-1} at 45°C. For thermally activated reactions it is valid the Arrhenius law which states as general rule of thumb that any reaction rate double by the increase of 10°C in temperature. Thus for thermally activated reactions we must see an increase in the reaction rate by an order of magnitude. Instead in the photochemical reaction under study there was no significant increase in the decomposition rate constant by passing from 20°C to 45°C.

Table 1 shows also the effect of a pH increase from 7 to 10.5-11.0 (at 45°C). The photolysis in alkaline pH conditions causes a significant enhancement of the photolysis rate constant with the low pressure mercury lamp passing from k_{lowP} = -5.5x10^{-4} s^{-1} at neutral pH to k_{lowP} = -1.3x10^{-3} s^{-1} at pH = 11: one order of magnitude faster. This behaviou was expected by the eq. 3 where an increase in the pH leads to an increase in the propagation rate constant step 3.

Another aspect illustrated in Table 1 is the volume effect. The same 17W lamp was used to irradiate 0.1% H_2O_2 in different volumes 2100 ml, 200 ml and 150 ml. Of course the measured rate constant are linked to the irradiated volume: $k_{2100\ ml}$ = -4.9x10^{-5} s^{-1} to normalize such rate constant to a volume of 200 ml the correction factor of 2100/200 = 10.5 should be applied so that 10.5x-4.9x10^{-5} s^{-1} = -5.1x10^{-4} s^{-1} which is almost coincident with the experimental value $k_{200\ ml}$ = -4.8x10^{-4} s^{-1}. Similarly, to normalize the k value measured on 150 ml which was $k_{200\ ml}$ = -6.4x10^{-4} s^{-1}, the correction factor 150/200 = 0.75 should be applied to get 0.75x-6.4x10^{-4} s^{-1} = 4.8x10^{-4} s^{-1} which is exactly coincident with the experimental value $k_{200\ ml}$ = -4.8x10^{-4} s^{-1}.

3.3 Photolysis of H_2O_2 by UV-LED reactor

UV-LED lamps are a great novelty in photochemistry. The limitation of the UV-LED sources at present are linked to the relatively low power emitted by each lamp (3W) and by the fact that the main emission of the UV-LED lamp occurs at about 360 nm (see Fig.1), in the UV-A spectral range which is photochemically less useful than the eventual emission in the UV-B and UV-C spectral range. Despite these limitations, we have used a UV-LED lamp (see Fig. 2) in the photolysis of 1% H_2O_2 in comparison to the photolysis with the traditional low pressure and high pressure mercury arc lamps.

The photolysis data are reported in Table 1 and refer to a volume of irradiated solution of 55 ml which is the capacity of the home-made reactor. From the data collected it is evident that the photolysis rate constant of H_2O_2 with the UV-LED lamp is at least one order of magnitude lower than that measured with the traditional mercury arc lamps. However, for a more straight comparison of the experimental results, the kinetics values reported in Table 1

and referred to a volume of 55 ml of solution should be normalized to a standard volume of 200 ml. Hence the volume correction factor is 55/200 = 0.275 and this gives $k_{UV-LED200ml}$ = 0.275x-1.5x10^{-5} = -4.1x10^{-6} s^{-1} or $k_{UV-LED200ml}$ = 0.275x-3.6x10^{-5} = -9.9x10^{-6} s^{-1}. Thus, the UV-LED lamp leads to a 200 ml normalized photolysis rate constant two orders of magnitude lower than that achieved by the traditional mercury arc lamps. The reason of such lower performance of the UV-LED lamp is certainly ascribable not only to the low power of the lamp, but also to the emission in the UV-C where the molar extinction coefficient of H_2O_2 is very low.

**Table 1:** Summary Of The Photolysis Data On H_2O_2 0.028-0.030 M

Entry #	Process	H_2O_2 (ml)	pH	T(°C)	k (s-1)
1	**UV 17W (Low P Hg)**	200	7	20	-4.8x10^{-4}
2	**UV 17W (Low P Hg)**	200	7	**45**	-5.5x10^{-4}
3	**UV 17W (Low P Hg)**	200	10.5	**45**	-1.2x10^{-3}
4	**UV 17W (Low P Hg)**	200	11	**45**	-1.3x10^{-3}
5	**UV 17W (Low P Hg)**	2100	7	20	-4.9x10^{-5}
1	**UV 17W (Low P Hg)**	200	7	20	-4.8x10^{-4}
6	**UV 17W (Low P Hg)**	150	7	20	-6.4x10^{-4}
7	**UV 125W (High P Hg)**	200	7	20	-5.1x10^{-4}
8	**UV 17W (Low P Hg) + Fe^{3+}**	200	8	20	-4.6x10^{-4}
9	**UV 125W (High P Hg) + Fe^{3+}**	200	8	20	-3.7x10^{-4}
10	**UV-LED 360 nm**	55	7	20	-1.5x10^{-5}
11	**UV-LED 360 nm**	55	7	20	-3.6x10^{-5}
12	**UV-LED 360 nm**	55	11.5	20	-6.8x10^{-5}

Taking the $k_{UV-LED200ml}$ = -9.9x10^{-6} s^{-1} as our reference and multiplying that rate constant by 6 UV-LED lamps (3 W each) put in series the new $k'_{UV-LED200ml}$ = 6x 9.9x10^{-6} = 5.9x10^{-5} s^{-1}. This calculation shows that even operating with 18 W of UV-LED lamps the H2O2 photolysis rate constant will be one order of magnitude lower than that achieved using 17W of a low pressure mercury arc lamp.

The photolysis of 0.1% H_2O_2 with any mercury arc lamp proceeds straightforward till the complete disappearance of the peroxide. A curious and quite unexpected phenomenon was observed in the case of the UV-LED photolysis of 0.1% H_2O_2 as shown in Fig. 4. At the beginning the H_2O_2 photolysis proceeds following strictly the pseudofirst order kinetic law

with the k values reported at the bottom of Table 1. However, prolonged photolysis does not lead to the complete decomposition of H_2O_2 but instead leads to the prevalence of the opposite reaction, i.e. formation and accumulation of H_2O_2. The exact reason of this inversion of trend is not fully clear but based on the equations 2-6, it is evident that once reached a minimal critical concentration of H_2O_2 the photolysis and propagation reactions (2-4) are overcome by the termination and disproportionation reactions (5-6) which instead produce H_2O_2 rather than destroying it.

Figure 4: UV-LED photolysis of 0.1% H_2O_2: initially the decomposition of hydrogen peroxide is the prevalent reaction, but after a certain photolysis time the reverse reaction appears to be prevalent and the initial concentration of hydrogen peroxide is recovered and even overcome
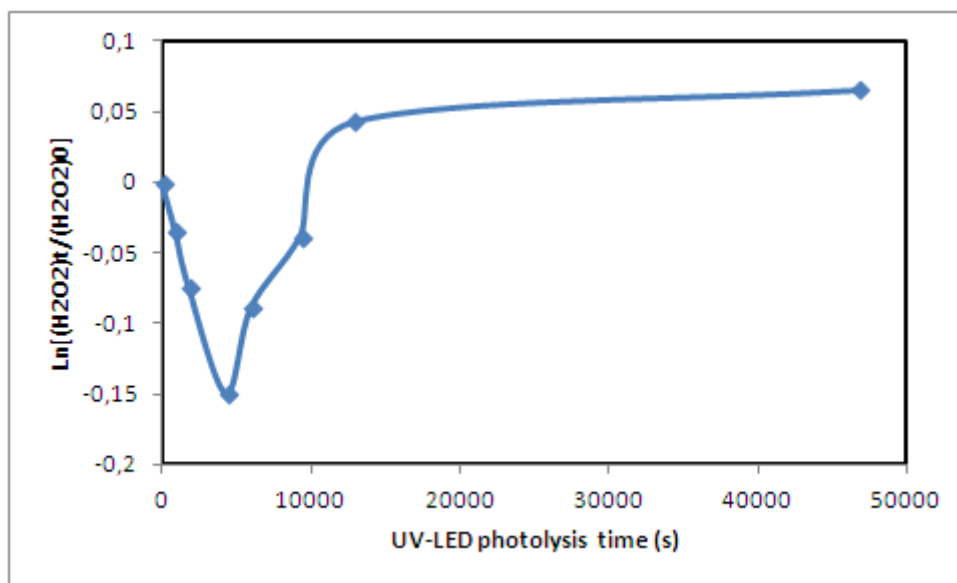
4. CONCLUSIONS

The UV photolysis of 0.1% H_2O_2 was studied under various conditions using three different UV light sources. Traditional mercury arc lamps were used. Low and high pressure mercury arc lamps give almost the same photolysis rate constants although the low pressure mercury lamp was a 17 W lamp while the high pressure mercury lamp was a 125W lamp. The reason of the similar performance resides in the fact that the low pressure mercury lamp emits at 254 nm where H_2O_2 has a high molar extinction coefficient so that all photons emitted by the lamp were used in the photolysis. Conversely the high pressure 125 W lamp emits in a wide ranges of wavelengths and only a fraction of the 125 W energy emitted is used in the photolysis of H_2O_2, for example the light fraction emitted in the UV-A and UV-B spectral range.

The UV photolysis of H_2O_2 is not sensitive to temperature changes, as expected, while instead the phoolysis is considerably enhanced if it is conducted in alkaline H_2O_2 for example

at pH = 11. The addition of Fe^{3+} ions which were expected to enhance photochemical yield did not give any improvement to the photolysis rate constant.

The UV photolysis of H_2O_2 was also performed in a new home-made photochemical reactor using a UV-LED diode emitting at 360 nm with a power of 3W. The photolysis rate constant was found two roders of magnitude lower than that achieved with the traditional mercury arc lamps and calculations show that even by working at 18W, the UV-LED photolysis of H_2O_2 is at least one order of magnitude slower than the photolysis performed with 17 W low pressure mercury lamp.

Another drawback of the UV-LED photolysis of H_2O_2 regards the fact that it does not proceed straightforwardly to the complete decomposition of H_2O_2 as in the case of the irradiation with mercury arc lamps. Instead, once reached a minimal concentration the termination and disporportionation reactions overcome the photolysis and the propagation reactions so that H_2O_2 starts to re-accumulate again. Thus, the complete removal of H_2O_2 cannot be achieved with UV-LED photolysis as instead can be achieved with mercury arc lamp photolysis.

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