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KrCl and XeCl excilamps and LP-Hg lamp for UV and UV/H_2O_2 decolourization of dyes in water

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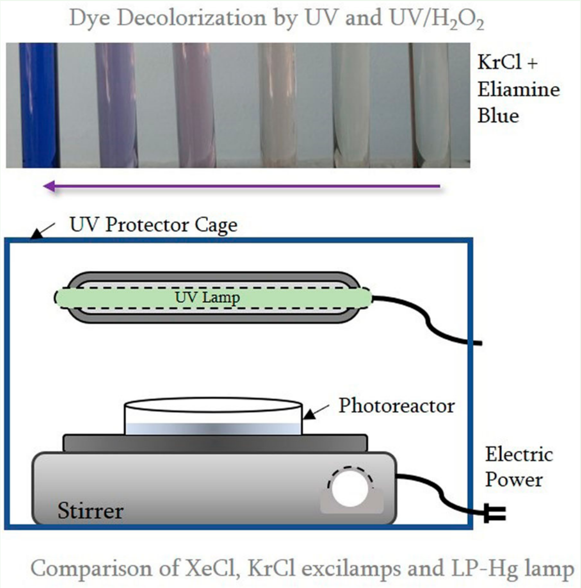
ABSTRACT

In the present study, the decolourization efficiencies of LP-Hg lamp, XeCl and KrCl excilamps at the same power density were compared for the decolourization of dyes in water by UV and UV/H_2O_2 processes in a batch reactor. Laboratory prototypes of XeCl and KrCl excilamps and a commercial LP-Hg lamp were studied as UV sources. Methylene Blue and Eliamine Blue dyes were used as model pollutants. The effect of the initial concentrations of dye and H_2O_2 in the TOC removal and kinetic parameters were also studied. The ratio of dye decolourization to the electric power consumption of the KrCl excilamp and LP-Hg lamp for the decolourization of Methylene Blue and Eliamine Blue were evaluated. As a result, the KrCl excilamp showed significantly higher decolourization efficiencies than LP-Hg lamp and XeCl excilamp, but the dye removal rate was significantly slower for Methylene Blue than for Eliamine Blue with this lamp. The KrCl lamp can be an alternative to conventional LP-Hg lamp for the decolourization of dyes by photodegradation, but it depends on the type of dye treated. The addition of H_2O_2 in a concentration between 0.05 and 0.09%v/v increases significantly the efficiency of the decolourization of Methylene Blue, and further increase does not lead to a higher increase in conversion. The experimental data were fitted to the one phase decay kinetic model with good agreement and the kinetic parameters were reported.



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Photolysis; AOPs; mercury-free lamps; Methylene Blue; power consumption

1. Introduction

It has been estimated that between 450,000 and 700,000 tons of dyes are produced annually worldwide, and around 1–15% of them are discharged to the environment in industrial effluents [1–3]. Wastewater containing dyes are generally characterized by intense colour, high organic content, low BOD/COD ratios (<0.1) and high volumetric flows [1,4–7]. The removal

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of dyes from wastewater has been a major environmental concern, because they cause negative impacts in aquatic ecosystems due to intense colouration [7], toxic effects [4–7] and insufficient oxygen concentration levels [1,8]. Conventional water treatments do not fully degrade dyes due to their recalcitrant nature [2,9]. Thus, it is necessary to develop cost-effective wastewater treatment technologies for dye decolourization and mineralization to accomplish the environmental regulations related to wastewater discharge which are becoming stricter, to reuse industrial effluents, to achieve lower production costs and more sustainable processes.

UV and UV/H_2O_2 processes have been tested for the dye decolourization in water [10]. In these processes, strong oxidizing species, like hydroxyl radicals (HO•), react with organic matter leading firstly to decolourization by degrading the chromophoric structure of the dye (responsible of the water colouration) [11], and secondly to mineralization to CO_2, H_2O and inorganic ions [3,7]. These hydroxyl radicals can be generated by UV irradiation and reactions involving strong oxidizers, such as hydrogen peroxide (H_2O_2). UV mercury lamps are usually used in the photodegradation of pollutants in water because of their low cost and effectiveness. However, these traditional UV lamps contain mercury compounds that are harmful to environment and human health if released to the environment during production, breakage and/or disposal of the lamps [11,12]. Moreover, new governmental regulations (Minamata Convention on Mercury) will ban the manufacture, import or export of mercury-added products, including electrical and electronic equipment like UV mercury lamps, in many countries [13]. Therefore, the development of mercury-free UV radiation sources and their validation in the UV and UV/H_2O_2 processes for water treatment is required [14,15].

Excilamps are attractive alternatives to the commonly used LP-Hg and MP-Hg lamps due to the absence of mercury in lamp bulbs (except for HgX excilamps), the long lifetime, the high flexibility in lamp geometry, the mild operation temperatures, the narrow band emission and the high UV intensities [6,14,16,17]. Contrary to traditional UV mercury lamps, excilamps emit radiation in a narrow band of high intensity in the UV and VUV regions of the electromagnetic spectrum [17,18]. Excilamps may enhance the efficiency of photochemical processes, because 80% or more of the total radiant flux is concentrated in a narrow emission band. Moreover, if the emission wavelengths matches those of the absorption spectrum of the pollutants bond breakage is facilitated [17,19]. Excilamps are of interest for the UV and UV/H_2O_2 degradation of pollutants in water, such as dyes, because most of the absorbed radiation is in the range emitted by these lamps [19].

Excilamps have been reported previously for the degradation of dyes in water by UV and UV/H_2O_2 processes [20–28]. Some of these studies compared the decolourization efficiency of different excilamps (KrCl, Xe_2, XeBr and Cl_2) [20,21,25,26]. It has been determined that KrCl and Xe_2 excilamps are the most promising excilamps for dye decolourization, achieving higher decolourization efficiency in shorter reaction times [26,28]. Although XeCl excilamps have been reported for the removal of organic pollutants in water [29], to our knowledge this UV source has not been reported in the literature for dye decolourization in water.

Moreover, to determine the feasibility of excilamps in industrial applications it is important to compare their decolourization efficiencies to the efficiencies of MP-Hg and LP-Hg lamps, which are currently applied in industry. Oppenländer [21] reported that KrCl and Xe_2 excilamps showed similar efficiencies compared to an MP-Hg lamp. Also, Xe_2 excilamp was reported to be 6.5 times more efficient than LP-Hg lamp for Rhodamine B decolourization [30]. Electric power consumption in photoprocess represents the most important parameter for their implementation in water treatment. Thus, it is important not only to consider the decolourization efficiency but also the ratio of pollutant removal to the electric power consumption to compare different UV sources.

In this study, the decolourization efficiencies of LP-Hg lamp, XeCl and KrCl excilamps at the same power density are compared for the decolourization of dyes in water by UV and UV/H_2O_2 processes. Methylene Blue and Eliamine Blue dyes are used as model pollutants. The effect of the initial concentrations of dye, the initial H_2O_2 concentration and the UV source in dye removal, TOC removal and kinetic parameters are studied. The ratio of dye removal to the electric power consumption of the KrCl excilamp prototype to a commercial LP-Hg lamp for the decolourization of Methylene Blue and Eliamine Blue is evaluated.

2. Experimental

2.1. Materials and methods

Methylene Blue (Merck, $C_{16}H_{18}ClN_3S\ xH_2O$, Mw = 319.86 g/mol) and Eliamine Blue (46 L – 250% 57147 donated by an industrial partner) dyes were used as model pollutants. Solutions of known concentrations (ranging from 17 to 72 mg/L) were prepared by dissolving the appropriate amount of dye powder in milli-q water and were used as model waters for the experiments. Hydrogen Peroxide (Merck, 30% w/w, ρ = 1.05 g/ml) was used for UV/H_2O_2 experiments. All the chemicals were used without further purification.

2.2. Photoreactor

The reaction system consisted of a 106 ml batch reactor (9.5 cm diameter × 1.5 cm height, glass) equipped with a magnetic stirrer (Scilogex), irradiated from the top using a UV lamp (Figure 1.). The photoreactor was equipped with three different UV lamps: KrCl exciplex lamp (222 nm), XeCl exciplex lamp (308 nm) and LP-Hg lamp (254 nm). A commercial VIQUA LP-Hg lamp with cylindrical configuration (reference S287RL) was purchased. This UV lamp was fed by a BA-ICE-S ballast at a fixed operating point that was purchased to the same manufacturer. The XeCl and KrCl excilamps used in this study are laboratory prototypes recently developed [31–33]. These excilamps had a dielectric barrier discharge with axisymmetrical configuration, filled with KrCl or XeCl mixtures. Both lamps were driven by a rectangular shape current-mode power supply with bidirectional current pulses of 3 µs of duration, an amplitude of 150 mA, and a frequency of 70 kHz [33]. This power supply could change the instantaneous and average power radiated by the DBD lamp. The UV power density was measured with a Hamamatsu C9536 power metre using a sensor head H9535–222. The obtained values were rectified using the sensitivity curve as a function of the wavelength given by Hamamatsu [34]. The power of the excilamps was adjusted via the power supply during the experiments, to obtain the same power density in the irradiated solution as with the LP-Hg lamp, that was 14 mW/cm^2. The emission spectrum of each lamp was determined by spectrometer (model Thorlabs CCS200/M (200–1000 nm)), used with a CCSB1 cosine corrector.

2.3. Degradation experiments

All the experiments and analyses were performed at room conditions (20°C). During all the experiment the temperature of the reaction volume was maintained within a range of 20 ± 2°C. To do this the UV lamps were refrigerated by intense air convection, the distance between the lamp and the solution was at least 8 cm, the solution was mixed intensely, and the irradiation exposure times were minimized to a maximum of 60 min.

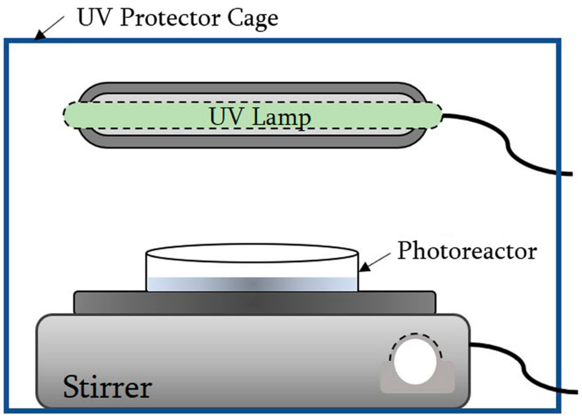

Figure 1. Scheme of the experimental set-up for dye decolourization by UV and UV/H_2O_2.

2.3.1. Blank tests

Experiments without irradiation from UV lamps were performed to determine if Eliamine Blue and Methylene Blue solutions of different initial concentrations (18, 42 and 72 mg/L) degraded at room conditions in the reaction system. For these experiments, 25 ml of a dye solution of different initial concentrations of Methylene Blue and Eliamine Blue were placed in the reactor for 60 min (maximum time of UV and UV/H_2O_2 experiments) under magnetic stirring (100 rpm) without UV irradiation from lamps. The dye concentration was measured initially and after 60 min to determine if the dyes degraded.

The same experiments were performed adding H_2O_2 to the solution containing the dye, to obtain a concentration of H_2O_2 of 0.05%v/v, to determine if H_2O_2 could significantly remove Eliamine Blue and Methylene Blue without UV irradiation from the lamps.

2.3.2. Direct UV photodegradation experiments

UV photodegradation experiments were carried out to determine the variation of the Eliamine Blue and Methylene Blue concentration in time due to UV radiation. For each experiment, 25 ml of a dye solution were irradiated a certain time using one of the UV lamps, during the experiments the solution was stirred (100 rpm) to assure homogenization. After a certain reaction time, the lamp was turned off and the solution was immediately analysed (as indicated in Section 2.4); i.e: the total reaction volume did not change during the experiments (no aliquots were withdrawn) and each exposure time corresponds to an individual experiment. In the experiments the dye (Methylene Blue or Eliamine Blue), the initial concentrations of the dye (C_o: 18, 42 and 72 mg/L), the type of lamp (KrCl and XeCl excilamps and LP-Hg traditional) and the irradiation times (0, 5, 10, 20, 30, 40 and 60 min) were varied.

2.3.3. UV/H_2O_2 experiments

Experiments were carried out to determine the variation of the Methylene Blue concentration in time due to UV radiation with different concentrations of H_2O_2 (0–0.17%v/v). For each experiment, 25 ml of a Methylene Blue solution (C_o:18 mg/L) were irradiated with UV light in the presence of H_2O_2. During all the experiments, magnetic stirring (100 rpm) was maintained to homogenize the solution. After a certain reaction time, the lamp was turned off and the solution was immediately analysed (as indicated in Section 2.4). i.e. the total reaction volume did not change during the experiments (no aliquots were withdrawn) and each exposure time corresponds to an individual experiment. The initial concentrations of H_2O_2 ($C_{o,H2O2}$: 0, 0.05, 0.09 and 0.17%v/v), the type of lamp (KrCl and XeCl excilamps and Hg-lamp traditional) and the irradiation times (0, 5, 10, 20, 30, 40 and 60 min) were varied.

2.4. Sample characterization

Dye concentration in time was measured by UV/Vis spectroscopy (GENESYS) at 294 and 583 nm, for Methylene Blue and Eliamine Blue, respectively. The limit of detection (LOD) for Methylene Blue and Eliamine Blue with this measurement technique are 0.04 and 0.15 mg/L, respectively. To analyse the photodecolourization process, the concentration and the conversion are reported in time. The conversion (X) is defined as:

$$X = \frac{C_o - C}{C_o} \cdot 100, \quad (1)$$

where C is the final concentration of dye after irradiation and C_o is the initial concentration of dye. The conversion normalizes the value of the dye concentration (between 0% and 100%), and in this case, it represents the percentage of the initial concentration of dye degraded in time.

The TOC of the treated samples was measured using a TOC analyser (Shimadzu TOC-VCSH) to determine dye mineralization [3,35].

3. Results and discussion

Methylene blue is a synthetic organic dye that can be classified according to its chemical structure in the group of azindyes [36] and Eliamine Blue is a common dye used in the textile industry (no structure information is provided by the manufacturer). To assess the photochemical potential of a reaction system the absorbance spectrum is required. Figure 2 reports the absorbance spectrum of Methylene Blue and Eliamine Blue solutions.

The absorbance spectrums show two local maxima absorbance peaks centred at 294 and 662 nm for Methylene Blue and 292 and 583 nm for Eliamine Blue (Figure 3). The absorption coefficient of Methylene Blue and Eliamine Blue are $\varepsilon_{294} = 9.5643$ L mg^{-1} cm^{-1} and $\varepsilon_{583} = 45.4354$ L mg^{-1} cm^{-1}. These values were calculated according to the Beer–Lambert law: $A = \varepsilon_\lambda \, \ell \, C$; where: A is the absorbance, ε_λ is the absorption coefficient, ℓ is the pathlength of irradiation (1 cm) and C is the dye concentration (mg/L).

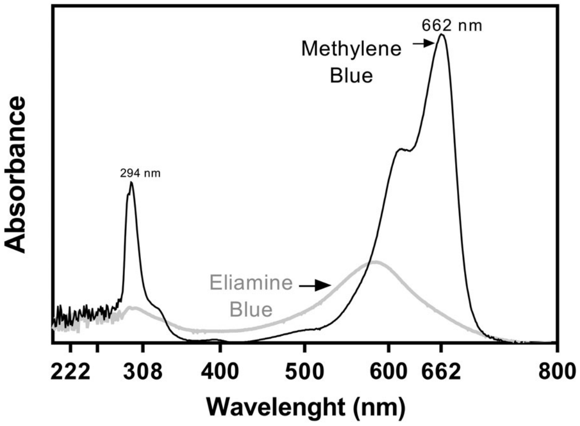

Figure 2. Absorbance spectra of Methylene Blue and Eliamine Blue solutions (C_o: 18 mg/L).

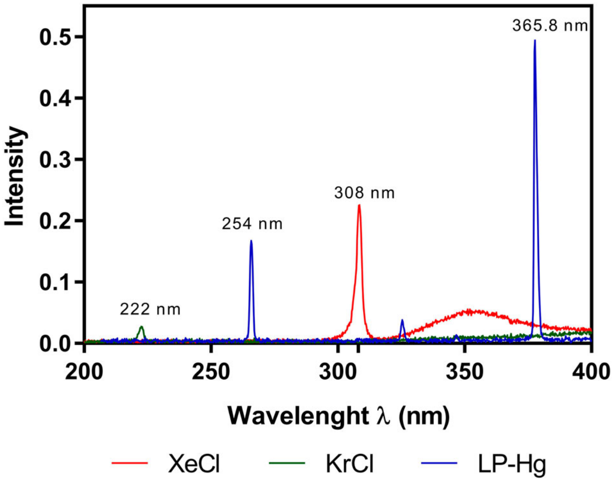

Figure 3. Emission spectra of UV sources used in this study (Integration time: 1500 ms).

Figure 3 shows the emission spectrum of the UV sources used in the present study, different emission characteristics are observed.

The emission spectra of the LP-Hg lamp show three well-defined bands at 254, 313 and 365.5 nm, while the KrCl and XeCl excilamps show a main narrow band at 222 and 308 nm, respectively. The XeCl excilamp shows a broad emission peak after 300 nm. Table 1 shows data of the maxima wavelength of the emission spectrum for each lamp with the corresponding maximum

Table 1. Data at maximum emission wavelength of LP-Hg, KrCl and XeCl lamps used in this study.

UV source	Maximum wavelength (nm)	Max. intensity	FWHM (nm)
LP-Hg	254.1	0.1672	1.4320
	313.4	0.0379	1.6365
	365.8	0.4937	1.4749
KrCl	222.2	0.0274	2.5688
XeCl	308.0	0.2253	2.5498

intensity of each peak and the full width at half maximum (FWHM). According to the supplier, the LP-Hg lamp does not irradiate at 184.9 nm.

3.1. Blank tests results

It was found that in the absence of UV lamp irradiation the dye concentration did not change in time, even when H_2O_2 was added (results not shown). Thus, degradation observed from UV or UV/H_2O_2 experiments are the result of the UV irradiation from the lamps.

3.2. UV photodegradation of Eliamine Blue solutions: effect of the type of UV lamp and the initial concentration of dye

Eliamine Blue solutions with different initial concentrations (18, 42 and 72 mg/L) were irradiated using a KrCl and XeCl excilamps and a traditional LP-Hg lamp without the addition of H_2O_2. The changes in dye concentration and TOC in time were monitored. The variation of the concentration and conversion of Eliamine Blue in time is shown in Figure 4. During all the experiments the power density was kept constant in time (14 mW/cm^2) with all the UV lamps.

The decolourization of Eliamine Blue solutions by UV irradiation depends on the UV lamp used in the photodegradation process. The best UV lamp for Eliamine Blue photodegradation is KrCl followed by the LP-Hg lamp, where the UV irradiation is consumed for the UV photodecolourization of the dye. Almost total decolourization is achieved within 40 min when the KrCl lamp is used, for all initial dye concentrations studied. For this excilamp, between 60% and 80% of the dye conversion occurred in the first 5 min of irradiation, then the photoprocess proceeded at a slower conversion rate until a limit concentration was achieved. For the LP-Hg lamp, between 25% and 50% of dye conversions was achieved at 40 min of irradiation and the solution was not completely decolourized at 40 min. The LP-Hg lamp requires significantly longer irradiation times to obtain the same Eliamine Blue conversion than KrCl excilamp, for all the initial Eliamine Blue concentrations studied. UV photodegradation experiments were also carried out using a XeCl

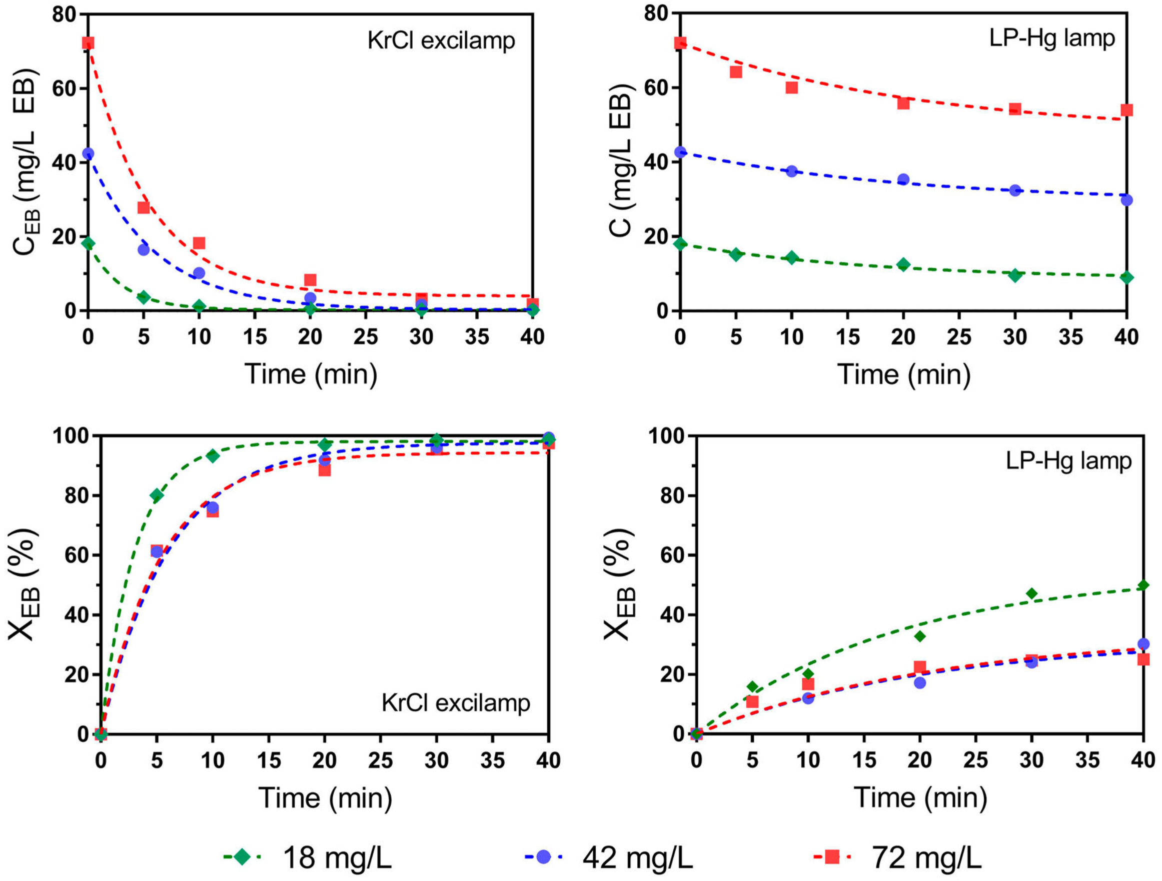

Figure 4. Variation of the Eliamine Blue concentration and conversion in time by UV irradiation: Effect of the initial concentrations of dye (C_o: 18, 42 and 72 mg/L) and the type of lamp (KrCl excilamp and LP-Hg lamp). *Initial conditions:* $C_{o,H2O2}$: 0%, $V_{solution}$: 25 ml, T_{room}: 20°C.

excilamp until 40 min, and no Eliamine Blue removal was observed for the initial concentrations of Eliamine Blue studied (data not shown), indicating that no bond breakage is facilitated at this irradiation wavelength. These results are consistent with previous studies reporting that KrCl lamps have higher removal efficiency for different pollutants in water compared to other excilamps [19,20,26,37,38].

It has been reported that it is desirable that the irradiation wavelength of the UV lamp matches the absorption spectrum of the pollutants, especially at the maximum absorption bands of the dye to facilitate bond breakage [17,19]. However, the KrCl excilamp achieved significantly higher Eliamine Blue conversions than the other UV lamps, but this lamp irradiated at a wavelength farther from the peaks of maximum absorption intensity of Eliamine Blue dye (see Figures 2–4). Moreover, in this case, the emission wavelength of all UV lamps matched absorption bands of Eliamine Blue of similar intensities, so differences in conversion are not attributed to differences in the absorption spectrum of the dye. It is also observed that Eliamine Blue conversion increases when the UV sources irradiate at lower irradiation wavelengths, which correspond to photons with higher radiant energy. In this case, it is probable that the energy of the absorbed photon emitted at this shorter wavelengths exceeded the binding energy of the chemical bonds of the pollutant facilitating bond breakage [39]. This trend is not observed for other dyes, including Methylene Blue (Figure 6) and Congo Red [26], indicating that the degradation depends on the chemical structure of the pollutant and the optimal conditions of the photo decolourization process need to be adjusted when the water composition changes. Thus, it is necessary to design flexible water treatment systems to make them effective for several pollutants.

The initial concentration of Eliamine Blue also affected the conversion. The dye conversion in time varies similarly for solutions with 42 and 72 mg/L of initial concentrations but a significant faster conversion in Eliamine Blue concentration was observed for the lowest concentration (18 mg/L). A higher conversion rate for the lower dye concentration could be related to an easier transmission of the UV light through the solution at 18 mg/L, where there are less molecules to interact with the light [40].

The effect of the type of UV lamp in conversion is stronger compared to the effect of the initial concentration of dye. Thus, selecting the adequate UV lamp according to the type of pollutant is of major importance to increase the efficiency of the process.

In all experiments, no significant changes in the final temperature of the solution were measured, even at 40 min of irradiation. Thus, the effect of temperature in the conversion and kinetic parameters is considered negligible.

Figure 5 shows the variation of the TOC concentration in time for the UV direct photolysis of Eliamine Blue in water.

Decolourization of Eliamine Blue solutions (no matter the initial concentration studied) was achieved using KrCl and LP-Hg lamps (Figure 4). However, TOC removal was not observed during 40 min of UV irradiation even when complete decolourization of the sample was achieved. These results indicate that breakage of the chromophore bond of the Eliamine Blue dye occurred, but the organic matter still remain in solution and further irradiation time is required to obtain total photomineralization [7,41].

3.3. Effect of the type of lamp and the H_2O_2 addition in the Methylene Blue UV photodegradation

Figure 6 reports the results of the Methylene Blue conversion in time, when using different lamps in UV and

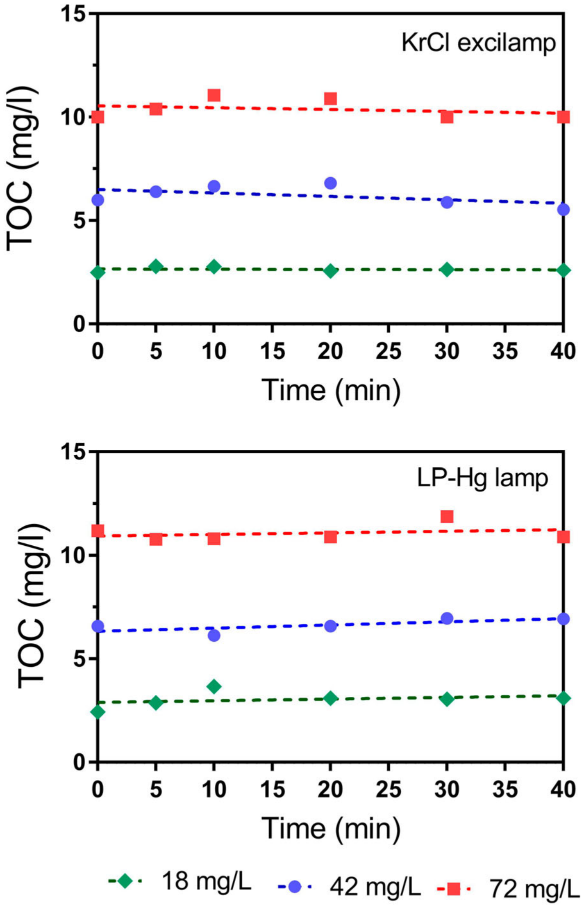

Figure 5. Variation of the TOC concentration vs. time by UV photolysis: Effect of the initial concentrations of dye (C_o) and type of lamp (KrCl lamp and LP-Hg lamp) (No H_2O_2 was added).

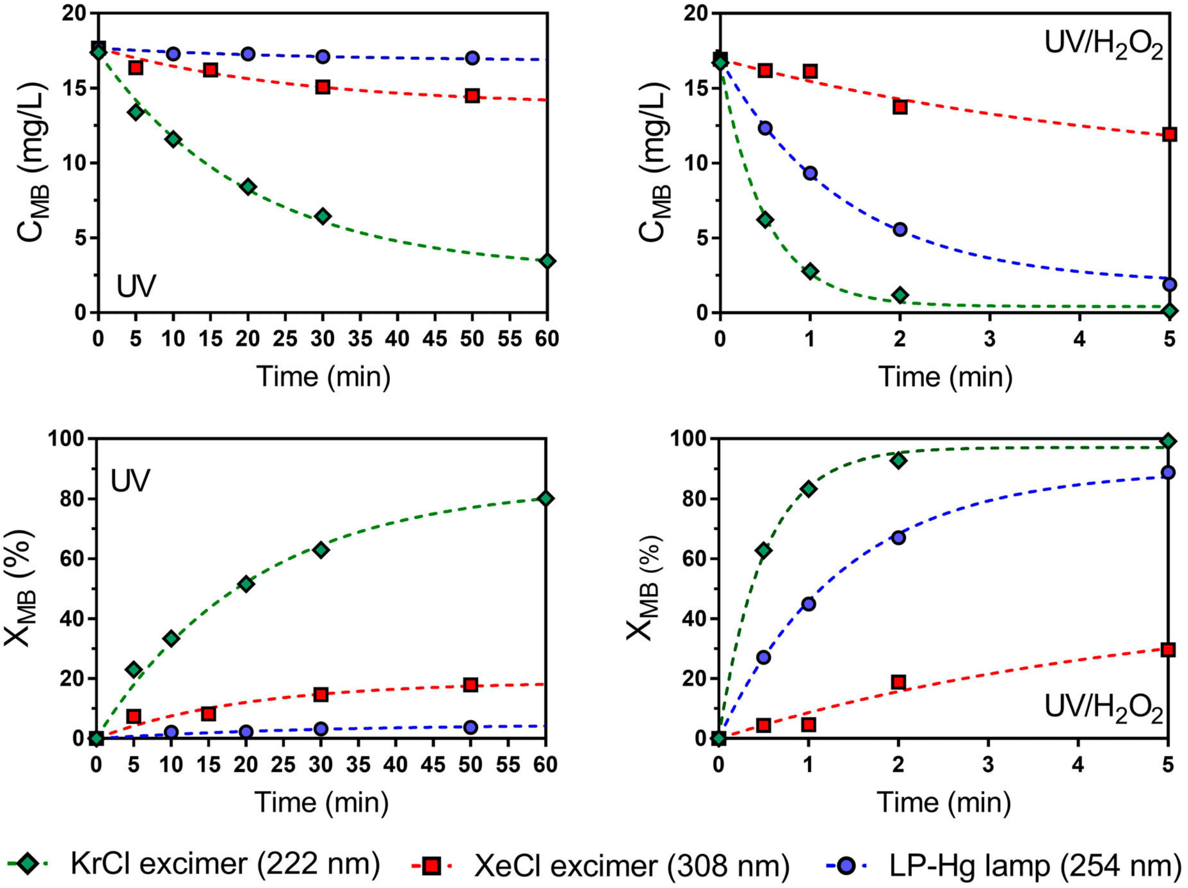

Figure 6. Variation of the Methylene Blue concentration in time: Effect of the type of lamp and H_2O_2 addition (0% for UV process or 0.05%v/v for UV/H_2O_2 process) $C_{o,MB}$: 18 mg/L.

UV/H_2O_2 processes. Significant differences in Methylene Blue conversion are observed over the course of time due to the type of UV lamp and process.

Methylene Blue decolourization strongly depends on the UV lamp used. For the UV process (without H_2O_2), the most effective lamp for the removal of Methylene Blue in solution is KrCl, followed by XeCl and then LP-Hg which did not remove Methylene Blue significantly (4% conversion at 50 min). These results differ partially from the observed for Eliamine Blue at the same reaction conditions.

The KrCl excilamp showed the best conversion for both dyes, but conversion was significantly slower for Methylene Blue, that is, 80% Methylene Blue conversion was achieved at 60 min of reaction, while the same conversion level was achieved at 5 min for Eliamine Blue. These results indicate that the KrCl excilamp is suitable for the decolourization of different dyes by direct photolysis, even if the absorption band of the dyes at 222 nm is not intense (Figure 2), but the retention time in the reactor and subsequently the cost of the wastewater treatment may differ greatly. Moreover, at the same reaction conditions, the KrCl excilamp shows higher conversions of different dyes compared to the conventional LP-Hg lamp. This behaviour could be related to the higher radiant energy (Q_λ) of the photons emitted at 222 nm compared to the 254.1 and 308 nm (538.86, 471.53 and 388.40 kJ/mol, respectively). For Eliamine Blue and Methylene Blue, the irradiation wavelengths of KrCl lamp was short enough to exceed the binding energy of their chemical bonds in a higher extent than the other lamps enhancing degradation of pollutants.

For the LP-Hg lamp, Methylene Blue conversion was also significantly slower than Eliamine Blue conversion, that is, 47% of Eliamine Blue conversion at 30 min of reaction was achieved compared to 3% Methylene Blue conversion. Significantly higher irradiation times are needed to decolourize Methylene Blue than Eliamine Blue with the KrCl and LP-Hg lamps. Considering that the absorption bands of both dyes at 222 and 254 nm are similar in intensity (Figure 2), then this behaviour is attributed to a higher stability of the chemical structure of Methylene Blue to UV irradiation.

The effectiveness of the XeCl excilamp depends in the UV absorption spectrum of the dye. In contrast to the results obtained for Eliamine Blue (0% conversion at 40 min), the XeCl excilamp achieved a higher Methylene Blue conversion than the conventional LP-Hg lamp. This behaviour is attributed to the more intense absorption band at 308 nm observed for Methylene Blue than for Eliamine Blue (Figure 2). In this case, the effect of the higher irradiation wavelength of XeCl in conversion is compensated by the higher intensity of the absorption band of the Methylene Blue.

These results indicate that differences in conversion are not only due to differences in the irradiation wavelength of the UV lamps, but also to differences in the absorption intensities of the pollutants at different wavelengths and to the stability of the chemical structure of the pollutant to UV. Considering the results, it can be concluded that not only a high intensity of the absorption bands of the pollutant in the emission wavelength of the lamp is desirable to increase conversion, but also a low emission wavelength. Tuning these parameters will give the highest conversion when same power density of the lamps is considered.

The same experiments with Methylene Blue were carried out with H_2O_2 added at a concentration of 0.05%v/v at the beginning of the reaction. Compared to the UV process, the irradiation time decreases, and the Methylene Blue conversion increases when H_2O_2 is added. This behaviour is due to the generation of hydroxyl radicals by H_2O_2 photolysis, which is a powerful oxidizing agent contributing to the decolourization of the organic matter in the solution [42].

The Methylene Blue decolourization by UV/H_2O_2 process is also strongly dependent on the UV lamp used; The KrCl lamp achieved the highest dye decolourization (99% conversion) at 5 min of reaction, followed by LP-Hg lamp (89% conversion) and subsequently the XeCl lamp (30% conversion). This trend differs from the observed for the direct UV photolysis of Methylene Blue, because for the UV/H_2O_2 process the UV lamp emission should match not only the adsorption band of the dye but also of the H_2O_2. The H_2O_2 adsorption band has a maximum at 220 nm, and in this case, the efficiency of the lamp to convert Methylene Blue depends on matching a higher adsorption intensity of H_2O_2, i.e. 222 nm, followed by 254 and 308 nm. This agrees with previous reports stating that H_2O_2 decompose into two hydroxyl-free radicals mainly at wavelengths lower than 300 nm [36].

The magnitude of the conversion enhancement differs for each type of UV lamp and the most significant enhancement is observed for the LP-Hg lamp of reaction time, followed by KrCl and then XeCl lamp; Comparing at 5 min of reaction time, the Methylene Blue conversion obtained by the UV/H_2O_2 process is approximately 4 times higher for the KrCl lamps and for the XeCl lamp, and 88 times for the LP-Hg lamp than the UV process. The differences in conversion enhancement suggest different reaction mechanisms according to the type of lamp and process. This could be explained by competitive reactions consuming hydroxyl radicals to produce other oxidizing species less effective for dye decolourization and/or to produce H_2O_2 by dimerization [36,40], and this could vary according to the emission wavelength of the lamps.

The addition of H_2O_2 in the treated solution has a stronger effect in Methylene Blue conversion than the type of lamp, thus optimizing the initial H_2O_2 concentration is of major importance to enhance conversion and to reduce costs of chemical dosage.

3.4 Effect of the type of lamp and H_2O_2 initial concentration in the Methylene Blue UV photodegradation

The effect of the type of excilamp and the initial H_2O_2 concentration (0–0.17%v/v) in the Methylene Blue conversion was evaluated at 5 min of reaction time (See Figure 7). TOC removal was not observed for the photodegradation of Methylene Blue at the studied conditions.

Results in Figure 7 show that the optimum H_2O_2 concentration depends in the type of UV lamp used. Within a range of 0–0.17%v/v H_2O_2, the KrCl excilamp achieved higher Methylene Blue conversions than the XeCl excilamp. This is related to: (i) a higher generation of hydroxyl radicals with the KrCl than the XeCl lamp, because the emission wavelength of the KrCl lamp matches nearly the maximum absorption band of H_2O_2 at 220 nm [26] and (ii) to a higher degradation of the Methylene Blue by direct UV photolysis with the KrCl excilamp.

The Methylene Blue conversion increases when H_2O_2 is added to the reaction volume in the studied range, but the increase depends on the H_2O_2 initial

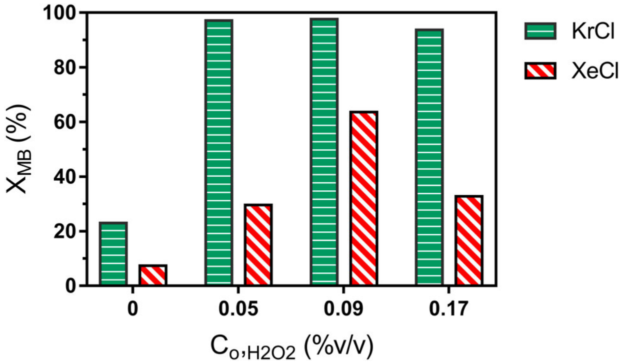

Figure 7. Variation of the Methylene Blue conversion at 5 min of reaction time: Effect of the H_2O_2 initial concentration and type of lamp ($C_{o,MB}$: 18 mg/L).

concentration. Conversion increases until an optimal H_2O_2 concentration of 0.09%v/v for both UV excilamps, probably due to a higher hydroxyl radical production [36]. Further increase of the H_2O_2 initial concentration (0.17%v/v) leads to a decrease in conversion, as previously reported [43,44]. The decrease in conversion could be explained by the promotion of competitive reactions, favoured by a higher H_2O_2 concentration, that consumes hydroxyl radicals to produce other oxidizing species (like $HO_2\bullet$) less effective for dye decolourization and/or to produce H_2O_2 by dimerization [36,40]. Therefore, it is important to determine the optimum H_2O_2 initial concentration to maximize conversion at minimum cost and to avoid an excess that decreases conversion. For the KrCl excilamp, an initial H_2O_2 concentration of 0.05%v/v is enough to increase conversion up to 97% and a further increase in concentration does not lead to significant higher conversions. However, when the XeCl lamp is used a higher H_2O_2 concentration (0.09%) is required, thus the cost of the UV/H_2O_2 is higher due to the lower conversion and higher requirement of H_2O_2 addition. High conversions are not achieved with the XeCl lamp at the studied reaction conditions due to its high irradiation wavelength.

The effect of the H_2O_2 concentration in time in the H_2O_2/UV degradation of Methylene Blue is reported in Figure 8 for the KrCl excilamp. It is observed that at the beginning of the reaction, where dye concentration is high, the conversion increases very fast and then the conversion rate decreases until a constant concentration is achieved. The variations are similar for 0.05 and 0.09% v/v H_2O_2 but a slightly lower rate was observed for 0.17% v/v, specially at the end of the reaction, as previously explained, this indicates an inhibitory effect at high H_2O_2 concentrations.

3.5. Reaction kinetics

The experimental data were fitted to the one phase decay kinetic model developed by Gomez et al. [27], which considers the effect of the initial concentration of substrate in photoprocesses and defines a limit concentration as the final concentration of dye that remains after the photodegradation process.

$$C = (C_o - C_{\text{Lim}})\, e^{-k_r\, t} + C_{\text{Lim}}, \qquad (2)$$

where C_{Lim} is the limit concentration of dye (mg/L); C_o is the initial dye concentration (mg/L); k_r is the rate constant (min^{-1}); t is the time (min)

The fit of the model to the results is shown in Figures 4, 6 and 8 as dotted lines. The kinetic parameters C_{Lim} and k_r where calculated by the Least Squares Method and validated for the UV and UV/H_2O_2 decolourization of Eliamine Blue and Methylene Blue in water. The model shows good agreement to the experimental data.

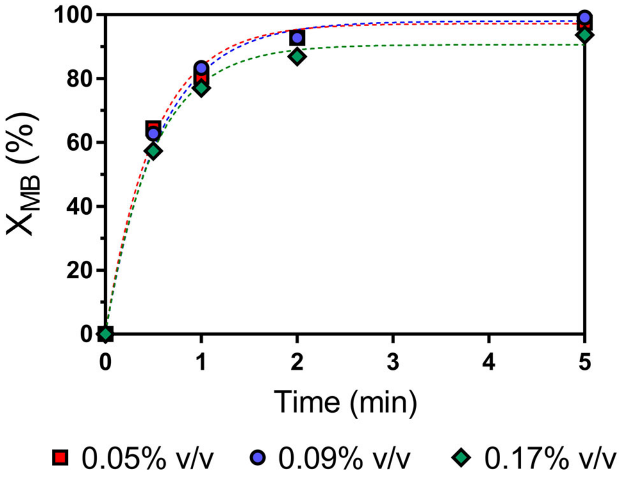

Figure 8. Variation of the Methylene Blue conversion in time using the KrCl excilamp: Effect of the H_2O_2 initial concentration ($C_{o,MB}$: 18 mg/L).

Table 2 reports the kinetic parameters calculated for the decolourization of Eliamine Blue by UV process using KrCl excilamp and LP-Hg lamp, results for XeCl excilamp are not included because this lamp was not effective for Eliamine Blue decolourization.

The kinetic parameters (k_r and C_{Lim}) vary with the initial dye concentration and the UV lamp. The parameter k_r of the KrCl lamp increases up to five times compared to the LP-Hg lamp, confirming that this emission wavelength is better for Eliamine Blue photodecolourization. Moreover, k_r decreases when the initial dye concentration increases from 18 to 42 mg/L, and then a similar rate is obtained with a further increase in concentration. This trend is observed for both UV lamps. A higher rate constant k_r at the lowest initial concentration of Eliamine Blue can be explained by the increase in the UV radiation density per mass of dye in the solution, as previously observed for Methylene Blue [27]. A further increase in Eliamine Blue initial concentration does not lead to a decrease in k_r.

Table 2. Effect of the initial concentration of dye and UV lamp in the kinetic parameters of Eliamine Blue photodegradation by UV direct photolysis.

		KrCl (222 nm)		LP-Hg (254 nm)	
Dye	C_o (mg/L)	k_r (min^{-1})	C_{Lim} (mg/L)	k_r (min^{-1})	C_{Lim} (mg/L)
Eliamine Blue	18	0.326	0.23	0.063	9.00
Eliamine Blue	42	0.166	0.39	0.047	29.00
Eliamine Blue	72	0.166	1.40	0.046	47.53

Significantly higher limit concentrations are obtained for LP-Hg than KrCl lamp, this is related to the irradiation wavelength. The limit concentration C_{Lim} increases linearly with the initial concentration of Eliamine Blue for KrCl and LP-Hg lamps in agreement with the kinetic model.

Table 3 presents the results of the Methylene Blue decolourization by UV and UV/H_2O_2 processes at an initial dye concentration of 18 mg/L.

The k_r parameter for the Methylene Blue varies with the type of lamp and photoprocess. The tendency according to the type of lamp for this parameter are the same trends described for conversion. It is also observed that k_r values for Eliamine Blue are higher than values obtained for Methylene Blue, this is related to differences in the chemical structure of the dyes which should be considered for the design of wastewater treatment plants. Regarding the reaction mechanism, the decolourization of Eliamine Blue and Methylene Blue in water by UV process using KrCl, XeCl or LP-Hg in the absence of H_2O_2 is attributed to direct UV photolysis. In these cases, the degradation by active radicals is less probable because no oxidizing agents were added and because the hydroxyl radicals formation due to H_2O photolysis is negligible at wavelengths greater than 193 nm [22].

For Methylene Blue photodegradation, the kinetic parameter k_r significantly increases (at least one order of magnitude) when H_2O_2 was added compared to experiments without H_2O_2 addition. Thus, the contribution of the reaction rate of hydroxyl radicals to the overall reaction rate of Methylene Blue decolourization is more significant than the reaction rate of UV direct photolysis. The magnitude of the increase in k_r by H_2O_2 addition depends largely on the UV lamp type; The highest increase in k_r is obtained for the KrCl excilamp followed by the LP-Hg and XeCl excilamp (Table 3); This behaviour is related to a higher generation of hydroxyl radicals as follows KrCl > LP-Hg > XeCl because the emission wavelength of the lamps matches more intense absorptions bands of the H_2O_2 (which absorption maximum is at 220 nm) in that order. The increase in the k_r values also leads to lower C_{Lim} values because the photodegradation process is more effective.

Table 3. Effect of the type of UV lamp in the kinetic parameters of the degradation of Methylene Blue by UV and UV/H_2O_2 processes ($C_{o,MB}$: 18 mg/L).

		0% H_2O_2		0.05% H_2O_2	
Dye	UV lamp	k_r (min^{-1})	C_{Lim} (mg/L)	k_r (min^{-1})	C_{Lim} (mg/L)
Methylene Blue	KrCl (222 nm)	0.048	2.70	1.997	0.43
Methylene Blue	XeCl (308 nm)	0.037	13.80	0.202	8.93
Methylene Blue	LP-Hg (254 nm)	0.034	16.80	0.715	1.89

Table 4. Effect of the H_2O_2 initial concentration in the kinetic parameters of Methylene Blue UV degradation with KrCl excilamp.

			KrCl (222 nm)	
Dye	C_o (mg/L)	$C_{o,H2O2}$ (%v/v)	k_r (min^{-1})	C_{Lim} (mg/L)
Methylene Blue	18	0.05	1.997	0.43
Methylene Blue	18	0.09	1.978	0.42
Methylene Blue	18	0.17	1.791	1.10

Table 4 reports the results of the Methylene Blue decolourization by UV/H_2O_2 process at different initial H_2O_2 concentrations. The fit of the model to the results is shown in Figure 8 as dotted lines. Similar rate constant values are obtained for initial H_2O_2 concentrations of 0.05–0.09%v/v, while a further increase leads to a slight decrease in k_r.

3.6. Comparison of the electrical power consumption

The results show that the KrCl excilamp is the most effective lamp for Eliamine Blue and Methylene Blue degradation by UV and UV/H_2O_2 in terms of conversion and reaction time. However, it is also important to consider the electric power consumption of the UV lamps in the process, because it represents an elevated cost for water treatment. In this case, the KrCl excilamp consumes approximately 11 times more electrical power than the LP-Hg lamp (162 W with respect to 14.5 W) to emit the same power density in the irradiated solution as with the LP-Hg lamp, that was 14 mW/cm^2. Figure 9 presents a comparison of the electric power consumption for KrCl excilamp and the conventional LP-Hg to decrease Methylene Blue and Eliamine Blue concentrations in time by UV process.

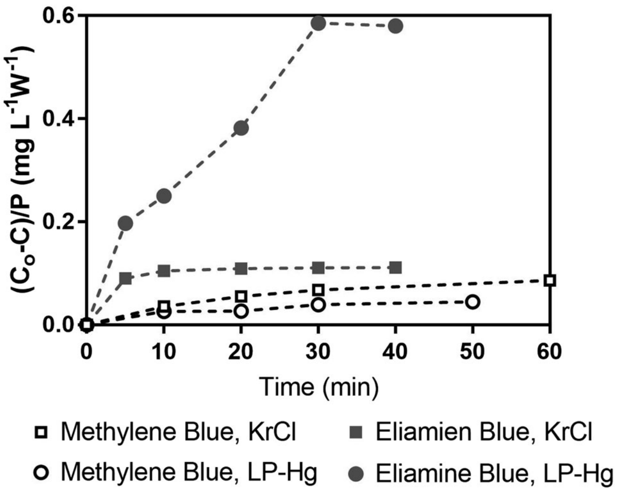

Figure 9. Variation of the Methylene Blue and Eliamine Blue concentration in time by UV process per electric power consumed ($C_{o,dye}$: 18 mg/L).

The optimal process is the one that reduces the most of the initial dye concentration using the minimum electric power, that is, the process that maximizes $(C_o - C)/P$. Results in Figure 9 show that degrading Eliamine Blue is a more efficient process than degrading Methylene Blue because it requires less electric power than Methylene Blue to obtain a higher degradation. Also, the lamp that consumes less electric power per mg of dye decolourized depends on the type of dye. To treat Eliamine Blue the LP-Hg is more efficient while KrCl lamp is more efficient to treat Methylene Blue, and the differences are due to synergies between emission wavelength of the lamp and absorption bands of the dye.

4. Conclusions

XeCl and KrCl excilamps prototypes were compared to a commercial LP-Hg lamp as UV sources for the decolourization of Eliamine Blue and Methylene Blue dyes in water by UV and UV/H_2O_2 processes. The KrCl excilamp showed significantly higher decolourization efficiencies than LP-Hg lamp and XeCl excilamp, but the dye removal rate was significantly slower for Methylene Blue than for Eliamine Blue with this lamp. The effect of the UV source in Eliamine Blue and Methylene Blue conversion is stronger compared to the effect of the initial concentration of dye; thus, selecting the adequate UV lamp according to the type of pollutant is of major importance to increase the efficiency of the process. The addition of H_2O_2 in a concentration between 0.05 and 0.09%v/v increases significantly the efficiency of the decolourization of Methylene Blue, and further increase does not lead to a higher increase in conversion. The optimum H_2O_2 concentration depends on the type of UV lamp used, and the efficiency is specially enhanced for the LP-Hg and KrCl lamp that irradiates UV at more intense band of the H_2O_2. The Eliamine Blue and Methylene Blue degradation by UV and UV/H_2O_2 with the KrCl, XeCl and LP-Hg follows a first order decay kinetic model. At the studied reaction conditions, TOC was not decreased.

Decolourization of Methylene Blue by UV process is a less efficient in terms of conversion and electric power consumption than decolourization of Eliamine Blue. Moreover, the Methylene Blue decolourization per watt consumed is higher for KrCl excilamp than for LP-Hg lamp. On the contrary, LP-Hg lamp is more efficient for Eliamine Blue decolourization per watt consumed. This is due to the higher energy consumption of the KrCl excilamp and differences in the UV absorption spectra of the dyes. The KrCl lamp can be a competitive alternative compared to a conventional LP-Hg lamp for the decolourization of dyes, but it depends on the type of dye treated. The retention time in the reactor and subsequently the cost of the wastewater treatment may differ greatly for the different dyes treated, so flexible reactor designs should be implemented to ensure a wide range of pollutant treatments typical of the textile industry process.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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