DEGRADATION OF 2,4-D IN WATER EMPLOYING HYDROGEN PEROXIDE AND UV RADIATION

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Abstract. This paper reports the photooxidation of 2,4-dichlorophenoxyacetic acid (2,4-D) in aqueous solution employing hydrogen peroxide and ultraviolet radiation. The experimental work was performed in a batch, well-stirred tank reactor irradiated from its bottom. Herbicide degradation initial rates more than thirty times faster than those obtained employing only UV radiation were found. Two important aspects of the of the 2,4-D photodegradation reaction enhanced by H_2O_2 were studied: (i) effect on the rate of the H_2O_2/2,4-D initial molar ratio and (ii) effect on the rate of the irradiation power and, particularly, the characteristics of the wavelength distribution of the lamp output emission.

1. Introduction

Increasing concern for protecting the environment has led to growing efforts in the application of Advanced Oxidation Technologies for the treatment of air and water. Among them, the use of UV irradiation combined with the presence of different oxidants is a typical example. The objective is to produce the *in situ* generation of OH• radicals to oxidize organic contaminants. In the past we have studied the degradation of a widely spread water contaminant, the 2,4-dichlorophenoxiacetic acid (2,4-D) under the following conditions: (1) employing UV alone (Cabrera et al., 1997) and (2) employing UV + Hydrogen Peroxide (HP) (Alfano et al., 2001.a). Two important technical questions were not addressed in those studies: (1) the existence of an optimal initial concentration ratio for the system HP/2,4-D, including the existence of a single value for this relationship and (2) the selection of the most appropriate radiation source as far as the spectral characteristics of its output power (wavelengths of emission). The change in the HP concentration may have two different and opposite effects (Stefan et al., 1996): (i) at low HP concentration, radiation absorption may be too low and so will be the OH• radical generation and (ii) at high concentration HP acts as a radical trapping agent, thus competing with the pollutant degradation path and rendering lower degradation rates. Thus, an optimal concentration ratio should be expected. An additional question is related to the potential uniqueness of this optimal ratio and its relationship with the reaction stoichiometry. The second aspect that must be also analyzed is the effect of the spectral distribution of the radiation source emission (Hager, 1990). The main alternatives may be defined as follows: (i) low pressure

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mercury lamps (Germicidal type) with substantial emission at 253.7 nm and (ii) medium or high pressure mercury lamps with a much broader range of emission, usually from 220 nm to sometimes even more than 800 nm. In the first case, absorption by HP is not too high, leading to rather low reaction rates. But usually, in a properly designed reactor, more than 90% the energy produced by the lamp will be used in the degradation reaction. Conversely, the second group of lamps will have emission in a region of much higher radiation absorption by the HP (λ < 250 nm) producing higher degradation rates. This beneficial effect is achieved with a relatively high consumption of energy because of radiation emission in wavelengths above 300 nm, where neither absorption by HP nor direct photolysis will occur. A third group of lamps is also possible: there exist Excimer UV lamps with almost monochromatic emission at 222 nm but they are rather expensive and not regularly produced in large sizes.

2. Objectives

To determine the existence of an optimum hydrogen peroxide/contaminant concentration ratio for the UV degradation of 2,4-D and decide if this value is unique.

To quantify the efficiency of irradiating the hydrogen peroxide/contaminant mixture with radiation below 250 nm.

3. Experimental

The reaction was studied in a well-stirred, batch reactor irradiated from the bottom with a tubular lamp. The UV lamp is placed at the focal axis of a cylindrical reflector of parabolic cross section (see Cabrera et al., 1997). We have used three different types of lamps: two of them were of the germicidal type having nominal input powers of 15 and 40 W with almost monochromatic output at 254 nm and producing a per unit length emission of 0.08 W/cm and 0.6 W/cm of output power respectively. The third lamp was a medium pressure, Mercury arc type with 360 W of nominal input power. The output power of this lamp in the entire range of emission is 4W/cm and below 254 nm just 0.23 W/cm.

4. Results and Discussion

4.1. Effect of the hydrogen peroxide concentration

The degradation reaction with UV and hydrogen peroxide is not fast. To reduce the reaction time, these studies were performed using the monochromatic, 40 W, Heraeus Germicidal lamp. Figure 1 portraits experimental results corresponding to initial photo-degradation reaction rates as a function of the initial molar concentration ratio r = H_2O_2/2,4-D for two initial pollutant concentrations: 30 and 90 ppm. It can be clearly seen that rates increase with r and that for values of r between 25 and slightly over 30 the maximum initial reaction rate is reached. During the course of the reaction, equally toxic reaction intermediates were observed such as 2,4 dichlorophenol and chlorohydroquinone (Alfano et al., 2001.a). Thus, it is convenient to add an additional variable to control, from a practical standpoint, the pollution abatement.

Total Organic Carbon (TOC) has been chosen as an indicator. Figure 2 shows the results of the TOC conversion (after a reaction time t = 4 h) vs. the initial molar ratio of H_2O_2/2,4-D, for two different initial concentrations of the water pollutant. These results indicate that there not exists a single value for this optimal ratio. Moreover, it was observed

that this optimal initial concentration ratio increases with the increase in pollutant concentration. In other words, there is no direct and simple relationship between the stoichiometric demand of OH• radicals and this optimal ratio.
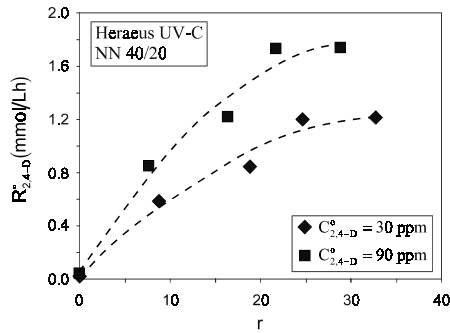

Fig. 1. Initial reaction rate of 2,4-D vs. H_2O_2/2,4-D initial molar ratio (r).
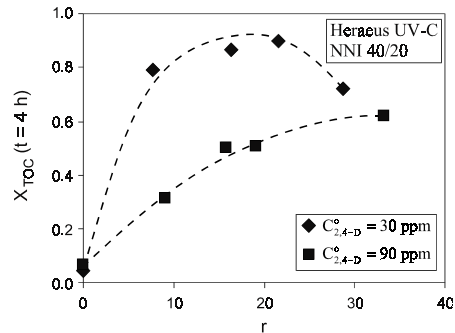
Fig. 2. TOC conversion vs. H_2O_2/2,4-D initial molar ratio (r).

4.2. Effects of the lamp spectral emission characteristics

Results with three different UV lamps are reported in this section Figure 3(a) shows results of 2,4-D concentration vs. time for a molar ratio of r = 8, an initial 2,4-D concentration of 30 ppm and for the three employed lamps. With the 360 W polychromatic lamp the time needed to reach a significant reduction of the pollutant concentration is greatly shortened. For example: (i) half of one hour for the 360 W lamp, (ii) 2 hours for the 40 W lamp, and (iii) 4 hours with the 15 W lamp. It is fair to note that the 15 W lamp (0.08 W/cm) is not totally used because only 15.8 cm are inside the reflector that is used to irradiate the reactor. *i.e.* approximately only 5 W of its nominal input power are really being used in the illuminating system. Figure 3 (b) shows an important increase in the required time and this result is directly related to the initial pollutant concentration (90 ppm for this case).
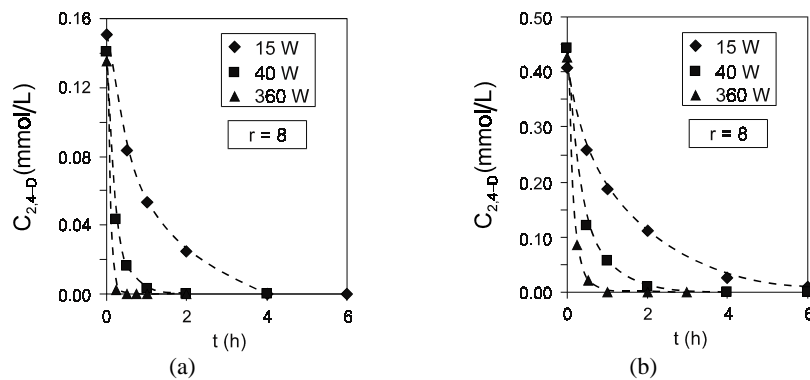

Fig. 3. 2,4-D concentration vs. time for r = 8 and three different UV lamps.
(a) $C_{2,4-D}^o$ = 30 ppm, and (b) $C_{2,4-D}^o$ = 90 ppm

Had we used the TOC measurements in the plots, the observed differences would have been much more pronounced. For the 15 W lamp, after 6 hs. the TOC decrease is still unacceptable. Good improvement is obtained with the 40 W lamp but the most noticeable result is obtained employing radiation below 254 nm. In this case, after 2 hs the TOC drops to an almost negligible value (4 hs for 2,4-D initial concentration of 90 ppm.). However, it should be noted that complete mineralization is not always required. Sometimes, after an initial oxidation, a less expensive treatment (*e.g.* biological purification) can be applied. Clearly, absorption by hydrogen peroxide below 250 nm becomes significant and yields a better use of the inputted energy.

The initial degradation rates of 2,4 D are presented in Fig. 4 (a) and (b) for the three lamps, two initial concentrations and two different molar ratios: r = 0 (direct photolysis) and r = 8 (H_2O_2 enhancement). In all cases, a noticeable increment in the degradation rate (between 6 to 32 times) is observed when H_2O_2 is added. Even better yields are obtained employing radiation below 250 nm. After comparing the 360 W lamp (between 220 and 300 nm, 0.92 W/cm) with the 40 W lamp (0.6 W/cm), the initial rate increases up to 4 times for the UV-HP combined process and up to 18 times when direct photolysis alone is used.
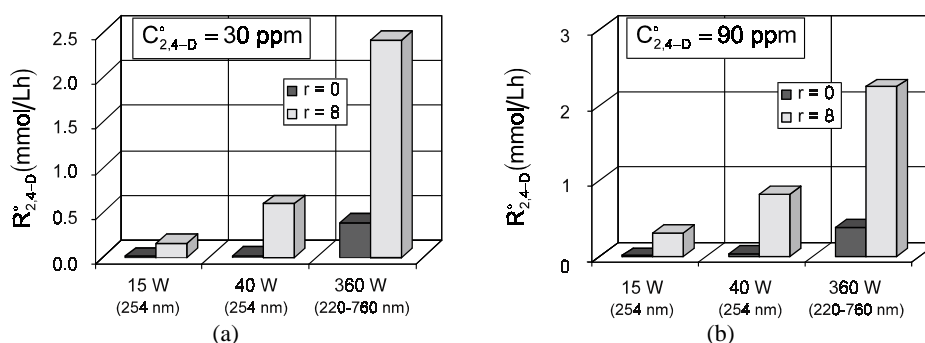
Fig. 4. Initial reaction rate of 2,4-D for three different UV lamps and r = 0 and 8.
(a) $C^o_{2,4-D}$ = 30 ppm, and (b) $C^o_{2,4-D}$ = 90 ppm.

Figure 5 (a) and (b) shows a similar representation but the dependent variable is the TOC conversion. Using the 360 W (only 3.14 W from 220 to 250 nm, 3.95 W at 254 nm and 6.87 W from 260 to 300 nm), for r = 8 the following results are obtained: (i) an increase from 3.0 to 3.5 times when moving from the 40 W lamp [Approx. 12 (15.8/20) ≈ 9.5 effective W at 254 nm] and (ii) an increase from 6.9 to 7.8 times with respect to the 15 W [Approx. 3.5 (15.8/44) ≈ 1.3 effective W at 254 nm].

The lamp with emission below 250 nm is the only one that achieved a 90 % TOC conversion after 2 hs (starting from 30 ppm of initial 2,4-D concentration) and after 4 hs (for 90 ppm of initial 2,4-D). It should be noted that the change in the output energy of the 360 W in the range of 220 to 300 nm with respect to the 40 W lamp is just 16 % higher. Thus, the observed beneficial effect is produced by the existence of a rather small emission at lower wavelengths (below 250 nm) where absorption by the HP becomes much more important.
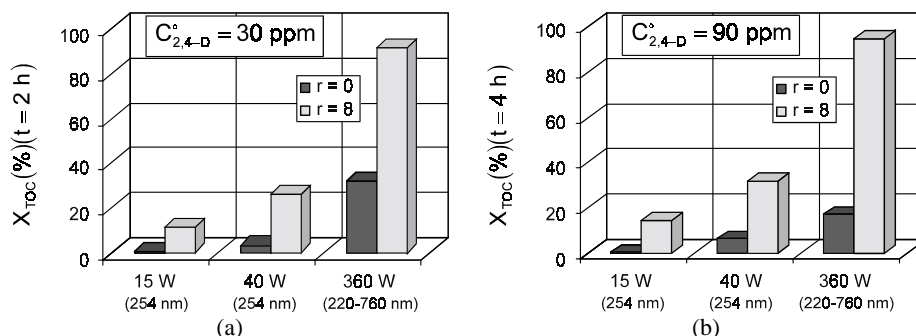
Fig. 5. TOC conversion for three different UV lamps and r = 0 and 8.
(a) $C^o_{2,4-D}$ = 30 ppm, and (b) $C^o_{2,4-D}$ = 90 ppm.

Conclusions are not the same if we think in terms of the total energy consumption. Figure 6 shows two different ways of defining quantum efficiencies. The first plot is obtained in terms of the absorbed energy. It can be seen that the best yield corresponds to the 360 W lamp, but in terms of the energy consumption this lamp produces de poorest result. This is a consequence of all the unnecessary energy consumed in producing radiation above 300 nm that is totally useless. This result should be a strong stimulus to produce monochromatic, excimer lamps with emission at 220 nm, having larger sizes and lower costs.
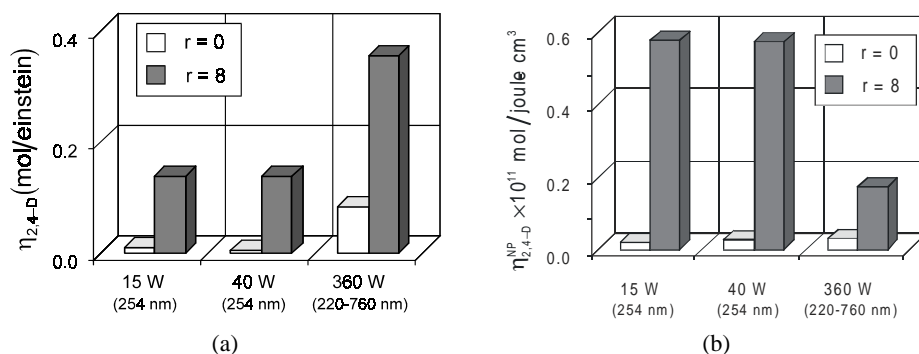

Fig. 6. Quantum and Energy Efficiencies
(a) With respect to the absorbed energy and (b) with respect to the energy consumption

For a mathematical representation of these results, a kinetic model based on a mechanistic sequence for OH• radical generation and interaction with organic substrates has been developed. It includes the existence of direct photolysis and the parallel reaction enhanced by H_2O_2. It represent the concentration evolution of 2,4-D, DCP, CHQ, HP and Humic acids in the whole range of the explored variables. These results have been recently accepted for publication (Alfano et al., 2001.b)

5. Conclusions

- The degradation rate is greatly increased by addition of HP to the process. Even for rather low initial molar ratios of HP/2,4-D (r = 8), the reaction rate increases from 6 to 32 times with respect to the direct photolysis.
- For an initial 2,4-D concentration of 30 ppm the optimal HP/2,4-D concentration ratio is close to 20. This value is about 30 or somewhat larger for an initial 2,4-D concentration of 90 ppm. These results were obtained employing monochromatic light (254 nm) using a lamp with an effective output power of 9.5 W.
- The use of a lamp with emission below 250 nm, with a very slight increase in the output power (13.96 W between 220 and 300 nm as compared with 9.5 W, at 254 nm for the monochromatic lamp) produces an increment in the degradation rate of 2,4-D. It was observed a factor of 4 when HP+UV was used and a factor of 18 with respect to results with UV alone. When these results are expressed in terms of TOC, the increasing effect was traduced in a factor of 3.0 to 3.5 with respect to the 9.6 W output power lamp and a factor of 6.9 to 7.8 with respect to the lamp with an effective output power of 1.3 W.
- Using a value of r = 8, the lamp with emission below 250 nm is the only one that reduces the initial TOC to very low values (90 % conversion). However, this yield is obtained with a lamp that has significant emission above 300 nm (47.44 W) where radiation is almost useless for this process. Energy consumption will be a crucial factor.

Acknowledgment

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