International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:4, No:6, 2010

Application of Advanced Oxidation Processes to Mefenamic Acid Elimination

Olga Gimeno*, Javier Rivas, Angel Encinas, Fernando Beltran

***Abstract*—**The elimimation of mefenamic acid has been carried out by photolysis, ozonation, adsorption onto activated carbon (AC) and combinations of the previous single systems (O_3+AC and O_3+UV). The results obtained indicate that mefenamic acid is not photo-reactive, showing a relatively low quantum yield of the order of 6 x 10^{-4} mol $Einstein^{-1}$. Application of ozone to mefenamic aqueous solutions instantaneously eliminates the pharmaceutical, achieving simultaneously a 40% of mineralization. Addition of AC to the ozonation process does not enhance the process, moreover, mineralization is completely inhibited if compared to results obtained by single ozonation. The combination of ozone and UV radiation led to the best results in terms of mineralization (60% after 120 min).

***Keywords*—**Photolysis, mefenamic acid, ozone, activated carbon.

I. INTRODUCTION

WATER treatment technologies are catalogued as those processes intended to produce water suitable for a predetermined end-use. Generation of drinking water, industrial processing water, etc. are the final goals to be achieved [1]. An efficient water treatment technology should be capable of eliminating not only the main contaminants but also intermediates generated (if any) during its application. In this sense, oxidation based processes are recently increasing their complexity to show a higher mineralization efficacy [2]. Ozone oxidation, photocatalysis and activated carbon are integrated into binary or tertiary combinations to search for synergistic effects [3].

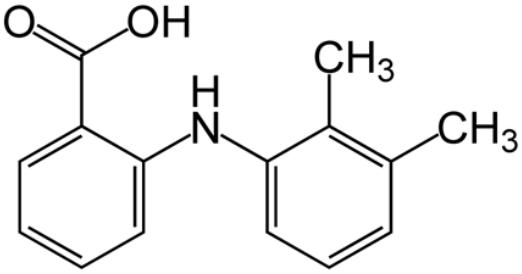

Fig. 1. Mefenamic acid chemical structure

In this work, a potential endocrine disruptor (mefenamic acid) has been used as a model compound to check for the suitability of combined processes in the removal of organic carbon from its aqueous solutions. Mefenamic acid is a non-steroidal anti-inflammatory drug used to treat pain, including menstrual pain [4]. It is typically prescribed for oral administration. The chemical structure of this compound is shown in Fig. 1.

II. MATERIALS AND PROCEDURE

Mefenamic acid was purchased from Aldrich and used as received. Activated carbon was Hydraffin with a surface area of 980 m^2 g^{-1}. A deeper characterization of this AC can be found elsewhere [5]

Experiments were carried out in a 0.8 L glass annular jacketed photochemical reactor. Water pumped from a thermostatic bath circulated through the reactor jacket to ensure a constant temperature inside the reactor. The reactor walls were insulated to avoid release of radiation and/or heat outside. The mefenamic aqueous solution was vigorously stirred to maintain the homogeneous distribution of the solid slurry in the presence of activated carbon.

A 15 W Heraeus low pressure mercury vapor lamp introduced in a quartz well was used for experiments carried out by using UV-C radiation (254 nm).

Total organic carbon (TOC) was determined by a Shimazdu TOC 5000A analyser by directly injecting the aqueous solution. Peroxides were monitored by iodometric titration. Mefenamic acid concentration was quantified by high-performance liquid chromatography (Agilent Technologies, series 1100) equipped with a Chromasil C-18 column.

III. RESULTS AND DISCUSSION

A. Photolysis of mefenamic acid

An initial series of mefenamic acid photolysis experiments was conducted in the absence of other oxidants or photocatalysts. Fig. 2 shows the results obtained in terms of normalized ranitidine evolution with time. As observed, mefenamic acid hardly reacts under UV-C radiation at pH 7. The low photo-reactivity of this pharmaceutical was already reported at pH 10. Thus, Rivas and co-workers [6] reported a moderate extinction coefficient (ε =5500 $M^{-1}cm^{-1}$) but a low quantum yield (ϕ = 5.5 x 10^{-3} mol $Einstein^{-1}$). The extinction coefficient at pH 7 is 4633 $M^{-1}cm^{-1}$ [7]. A rough approximation to the quantum yield value can be obtained by applying the conservation mass balance to a discontinuous

---

*Corresponding author address: Department of Chemical Engineering and Physical Chemistry of the University of Extremadura. 06071 Badajoz SPAIN. (phone: 00-34-924-289300; fax: 00-34-289385; e-mail: fjrivas@ unex.es).

bath photochemical reactor [8]. Thus, the following pseudoempirical equation can be used:

$$-\frac{dC_i(t)}{dt} = \varphi_i \frac{\varepsilon_i C_i(t)}{A_{254nm}(t)} I_o \left[1-\exp\left(-2.303\ L\ A_{254nm}(t)\right)\right] \quad (1)$$

where φ_i and ε_i are the quantum yield and molar absorptivity at 254 nm of compound i, respectively. $A_{254nm}(t)$ accounts for the absorption of UV light of all the species present in solution. The incident radiation intensity per volume $I_o = 3.0 \times 10^{-6}$ Einstein L^{-1} s^{-1} and radiation pathlength in the reactor L = 2.5 cm were calculated by actinometry experiments. At the sight of mefenamic acid evolution profile (very low conversion), it can be considered that the absorption of radiation is manly due to the parent compound (intermediate light absorption can be neglected), i.e. $\varepsilon_i C_i(t) \approx A_{254nm}(t)$. Under these circumstances, analytical integration of the kinetic equation leads to (the subscript "o" indicates time zero):

$$C_{i_o} - C_i(t) - \frac{1}{\xi}\ln\left[\frac{1-\exp\left(-\xi\times C_{i_o}\right)}{1-\exp\left(-\xi\times C_i(t)\right)}\right] = \varphi_i\times I_o\times t \quad (2)$$

Where $\xi = 2{,}303\times\varepsilon_i\times L$ (3)

A plot of the left member in Eq. 2 versus time should lead to a straight line of slope: $\varphi_i\times I_o$. From the slope a value for the quantum yield in the proximity of 6.0×10^{-4} mol Einstein^{-1} ($R^2 = 0.985$) could be calculated, i.e. ten times lower than the value reported at pH 10 [6].

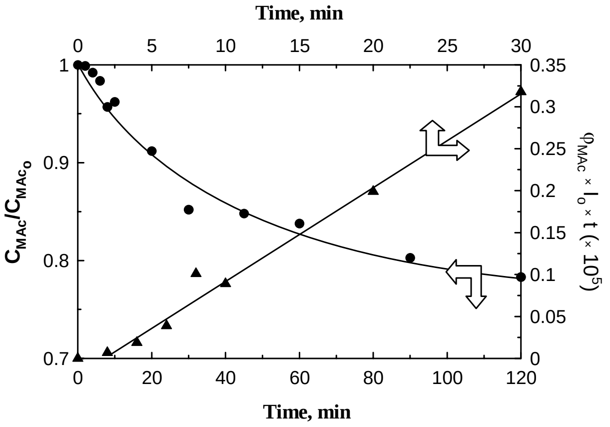

Fig. 2. Photolysis of mefenamic acid (5×10^{-5} M). Quantum yield determination.

B. The combination ozone + activated carbon.

Ozone is a powerful oxidant capable of efficiently degrade a number of chemicals, especially those substances showing double or triple bonds in their structure or aromatic character. However, some chemicals are recalcitrant to the ozone action and accumulate in the water bulk. A typical example is the intermediates generated after ozone application to reactive substances. Thus, small acids, alcohols and, in general, small oxygenated species tend to build up in water so the mineralization level achieved is normally low in simple ozonation processes [9].

Mefenamic acid ozonation is shown in figure 3. As observed, this pharmaceutical immediately reacts with ozone disappearing in less than 4 minutes at the operating conditions used in this study. However, as pointed out before, total organic carbon (TOC) conversion does not follow a similar trend. Hence, TOC removal is just 40% after 120 minutes of treatment. Mefenamic acid reacts instantaneously so dissolved ozone accumulates in water once this compound and first intermediates have been oxidized. Thereafter, slow reactions take place and dissolved ozone can be easily detected. It is also noteworthy the generation of hydrogen peroxide, typical of the ozonation of aromatic compounds [10].

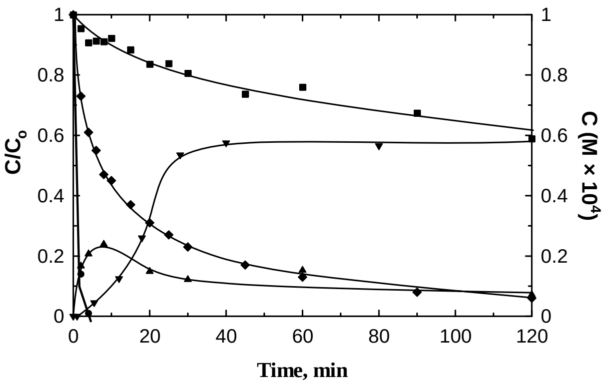

Fig. 3. Ozonation (15 ppm at 30 L h^{-1}) and adsorption (1 g L^{-1} of AC) of mefenamic acid (5×10^{-5} M) at pH 7. ●, normalized mefenamic acid concentration; ■, normalized TOC concentration; ▲, Hydrogen peroxide evolution; ▼; dissolved ozone evolution; ♦ normalized mefenamic acid concentration in the adsorption process.

The adsorption of mefenamic acid onto activated carbon led to the slow elimination of this compound after 120 minutes of contact. Two kinetic models could be applied to the process:

The first order kinetic approach:

$$\ln(q_e - q_t) = \ln(q_e) - \frac{k_1}{2.303} t \quad (4)$$

And the second order kinetic approach:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

Where q_e and q_t are the amounts of mefenamic acid accumulated in the solid (mol g^{-1}) at equilibrium and time t, respectively, t is time in minutes, and the k values stand for the characteristic kinetics of each model.

A plot of the left hand side member of Eq. 3 and 4 led to values of 2.8×10^{-5} and 4.9×10^{-5} mol g^{-1} for q_e when the first and second order models were applied, respectively (see Fig. 4). Values for k_1 and k_2 were 1.54×10^{-2} min^{-1} and 3.2×10^3 g min^{-1} mol^{-1}, respectively. Comparison of experimental and theoretical q_e values and R^2 of the straight lines in Fig. 4 suggest a better modeling of the second order approach.

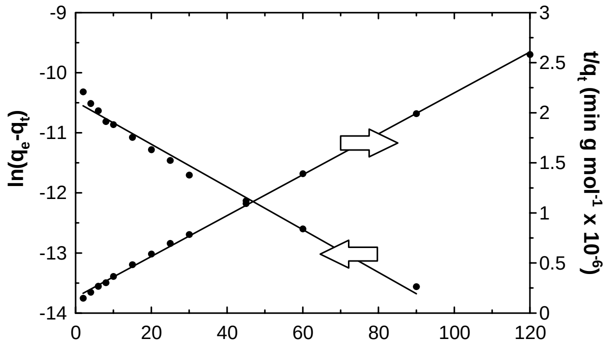

Fig. 4. Adsorption of mefenamic acid (5 x 10^{-5} M). Application of Eqns. 4-5.

Amazingly, the combination ozone+activated carbon led to a deterioration of the efficiency of single processes (Fig. 5). Thus, the ozonation of mefenamic acid in the presence of activated carbon prevented the elimination of TOC. The reason is unclear, although some release of organic material from activated carbon attack by ozone has previously been reported. Additionally, modifications in the activated carbon surface can be achieved by the presence of ozone. For instance, activated carbon can partially lose its adsorption capacity. Finally, it has to be pointed out that the ozonation intermediates are normally more hydrophilic than parent compounds and, as a consequence they have a lower tendency to be adsorbed.

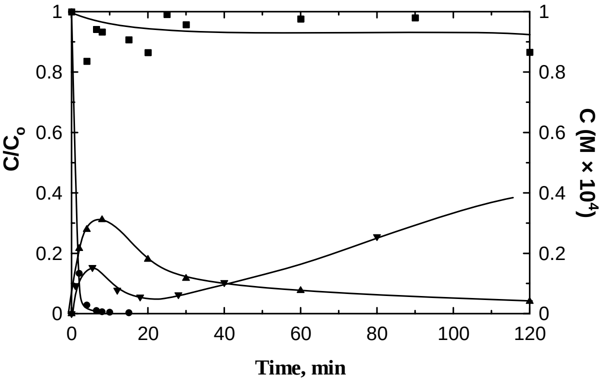

Fig. 5. Ozonation (15 ppm at 30 L h^{-1}) of mefenamic acid (5 x 10^{-5} M) at pH 7 in the presence of activated carbon (1 g L^{-1} of AC). ●, normalized mefenamic acid concentration; ■, normalized TOC concentration; ▲, Hydrogen peroxide evolution; ▼; dissolved ozone evolution.

C. Photolytic ozonation of mefenamic acid.

Given the poor results obtained when combining ozone and activated carbon, the former was applied in the presence of UV-C radiation. The combination of ozone and radiation involves the existence of two direct routes of degradation plus a radical pathway. The latter is due to the generation of hydroxyl radicals after the homolytic scission of hydrogen peroxide formed by ozone photolysis.

Figure 6 displays the results obtained. As observed, this system achieves the highest efficiency in terms of mineralization. After 120 min almost a 60% of the initial TOC is removed from water. Direct comparison of figures 3 and 6 indicates that for the first 30-40 minutes the single ozonation and the photocatalytic ozonation behave similarly, thereafter, the more recalcitrant compounds are only degraded when ozone is combined with UV radiation

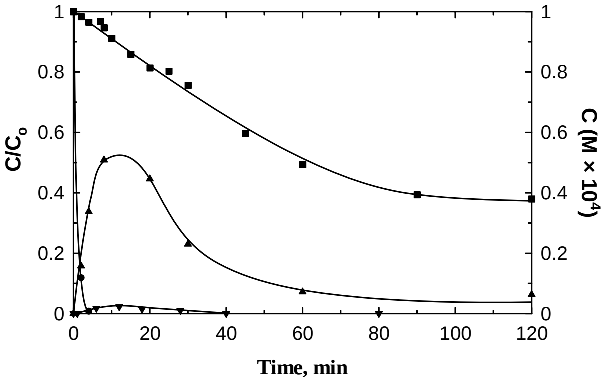

Fig. 6. Ozonation (15 ppm at 30 L h^{-1}) of mefenamic acid (5 x 10^{-5} M) at pH 7 in the presence of UV radiation. ●, normalized mefenamic acid concentration; ■, normalized TOC concentration; ▲, Hydrogen peroxide evolution; ▼; dissolved ozone evolution.

ACKNOWLEDGMENT

The authors thank the economic support received from Junta de Extremadura, the CICYT of Spain and European FEDER Funds through projects CTQ 2009/13459/C05/05 and CSD20060044.

REFERENCES

[1] I. Gültekin, and N.H. Ince, “Synthetic endocrine disruptors in the environment and water remediation by advanced oxidation processes,” *J. of Environ. Manag.*, 85, pp. 816-832, 2007.

[2] S. Esplugas, D.M. Bila, L.G.T. Krause, and M. Dezotti, “Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents,” *J. Hazard. Mat.,* 149, pp. 631-642, 2007.

[3] F.J. Rivas, A. Encinas, B. Acedo, and F.J. Beltrán, “Mineralization of bisphenol A by advanced oxidation processes,” *J. of Chem. Technol. and Biotechnol*., 84, pp. 589-594, 2009.

[4] K. Moribe, R. Kinoshita, K. Higashi, Y. Tozuka, and K. Yamamoto, “Coloration phenomenon of mefenamic acid in mesoporous silica FSM-16,” *Chem. and Pharmac. Bull*., 58, pp. 214-218, 2010.

[5] F.J. Beltrán, P. Pocostales, P. Alvarez, and A. Oropesa, “Diclofenac removal from water with ozone and activated carbon,” J. *Hazard. Mat*., 163, pp. 768-776, 2009.

[6] F.J. Rivas, O. Gimeno, T. Borralho, and M. Carbajo, “UV-C photolysis of endocrine disruptors. The influence of inorganic peroxides,” *J. Hazard. Mat*., 174, pp. 393-397, 2010.

[7] I. Kim, N. Yamashita, and H. Tanaka, “Photodegradation of pharmaceuticals and personal care products during UV and UV/H2O2 treatments,” *Chemosphere*, 77, pp. 518-525, 2009.

[8] F.J. Rivas, F.J. Beltrán, and B. Acedo, “Chemical and photochemical degradation of acenaphthylene. Intermediate identification,” *J. Hazard. Mat*., 75, pp. 89-98, 2000.

[9] S.J. Khan, and H.S. Weinberg, “Characterisation of carbonyl byproducts of drinking water ozonation,” *Wat. Sci. & Technol*., 7, pp. 95-100, 2007.

[10] F.J. Beltrán, I. Giráldez, and J.F. García-Araya, “Kinetics of activated carbon promoted ozonation of polyphenol mixtures in water,” *Ind. Eng. Chem. Res*., 47, pp. 1058-1065, 2008.