# Comparison of flutamide degradation via UV/TiO$_2$, UV/H$_2$O$_2$ and UV/H$_2$O$_2$/TiO$_2$ systems

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*Abstract*
*Synthetic solutions of flutamide were subject to degradation using three advanced oxidation systems, namely UV/TiO$_2$, UV/H$_2$O$_2$ and UV/H$_2$O$_2$/TiO$_2$. Optimum conditions and degradation kinetics has been established for all three systems. The experimental results showed that all three systems can be successfully used for flutamide degradation with efficiencies higher than 99% and that advanced oxidation processes are showing good potential for degradation of organic pollutants that cannot be suitable removed/degraded using conventional wastewater treatment processes.*
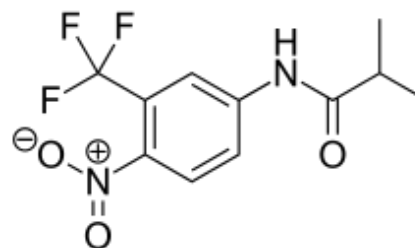
*Keywords: flutamide, TiO$_2$, H$_2$O$_2$, AOPs, kinetic*

## INTRODUCTION

Flutamide (FT) is a nonsteroidal androgen drug used in cancer treatment but also in transgender hormone therapy and hair and skin conditions. Even if based on available studies at European level [1-2] both the frequency (1%) and concentrations (µg/L) of FT within wastewater treatment plants effluents are rather low, it proved to be resistant to both chemical oxidation using ClO$_2$ [3] and ozone treatment [4]. A possible explanation to this behaviour is FT structure, which contains electron withdrawing fluoro groups. FT has been indicated also as an endocrine disruptor [5].

There is limited information available within the literature related to the use of advanced oxidation processes for FT degradation, available studies are mainly focussing on FT photochemistry in various media [6].



**Fig. 1.** Flutamide (FT) structure

In the last years there are available some studies focussing on FT degradation via solar photo-Fenton [7-8] and heterogeneous photo Fenton coupled with ozone treatment [9]. Preliminary data on FT degradation via TiO$_2$ assisted photo catalyse are also available [10].

## EXPERIMENTAL PART

FT degradation experiments were performed with a UV reactor (Heraeus type) equipped with a TQ 150-Z3 medium pressure mercury lamp. Used reagents were FT (Sigma), TiO$_2$ (Merck), 30% H$_2$O$_2$ solution (Fluka). FT synthetic solutions were prepared using FT (purity $\geq$ 99%) produced by Sigma – Aldrich and ultrapure water generated by a Milli-Q Integral 15 system (Merck Millipore). FT concentration was monitored by HPLC technique and F$^-$, NH$_4^+$, NO$_3^-$, NO$_2^-$ concentration were determined via ion chromatography.

## RESULTS AND DISCUSSION

*UV/TiO2 system*

Previously reported work confirmed that FT degradation using UV/TiO2 system take place with efficiencies above 95%, in optimum operating conditions [10].

Experiments were resumed in order to refine optimum parameters for FT degradation. Synthetic solution with an initial concentration $[FT]0 = 8.08$ mg/L $= 2.93$ x $10^{-5}$ M was used and titanium dioxide dose was kept at $[TiO2] = 100$ mg/L within all experiments. FT degradation efficiencies were determined at various irradiation time together with mineralization efficiencies for organic F and N, experimental results are presented within table 1.

**Table 1.** FT degradation via $UV/TiO_2$ system
$[FT]_0 = 8.08$ x $10^{-5}$ M, $[TiO_2] = 100$ mg/L

| Time min | [FT] mg/L | η [FT] % | [F] mg/L | η [F] % | [N] mg/L | η [N] % |
|---|---|---|---|---|---|---|
| 0 | 8.08 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 30 | 3.67 | 54.58 | 0.09 | 5.39 | 0.06 | 7.32 |
| 60 | 0.80 | 90.10 | 0.27 | 16.18 | 0.22 | 26.84 |
| 120 | 0.20 | 97.52 | 0.53 | 31.76 | 0.53 | 64.66 |
| 180 | 0.05 | 99.38 | 0.71 | 42.55 | 0.68 | 82.96 |
| 240 | 0.02 | 99.75 | 0.72 | 43.15 | 0.71 | 86.62 |

Prolonging of irradiation time proved to have a positive effect upon FT degradation efficiency, which reached more than 99% after 180 minutes of irradiation.

The linearization of FT degradation by a pseudo-first order kinetic led to the calculation of degradation rate constant, which was found to be equal with 2.72 x $10^{-2}$ $min^{-1}$, based on the following equations:

$$[FT] = [FT]_0 \ e^{-kt} \qquad (1)$$

$$-\ln\left(\frac{[FT]}{[FT]_0}\right) = k \ t \qquad (2)$$

where [FT] is flutamide concentration at a given time t, $[FT]_0$ is flutamide initial concentration, k is FT degradation rate constant and t is irradiation time.

Formation of intermediary transformation products with F and N is proved by the mineralisation efficiencies that are permanently lower than FT degradation efficiency.
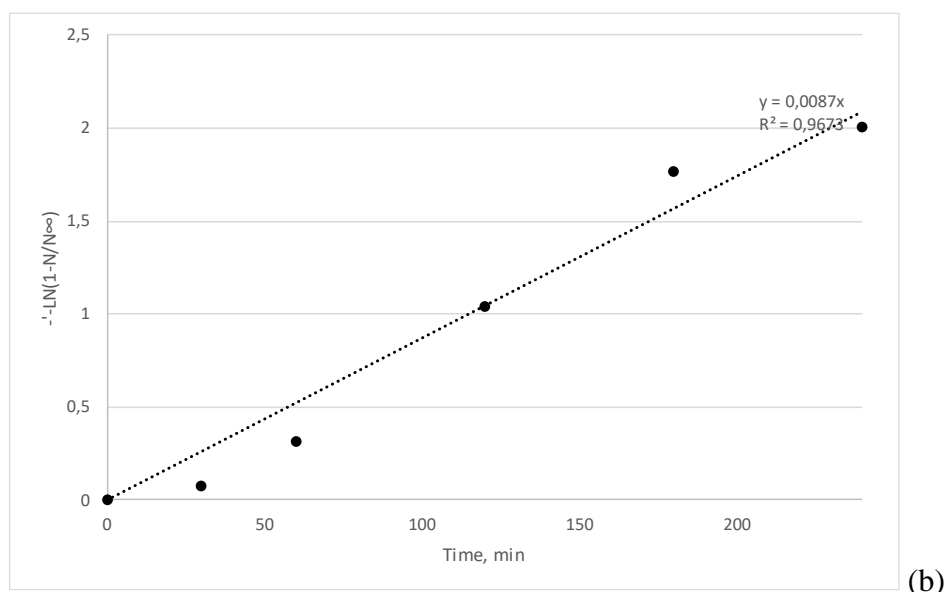


(a)

(b)
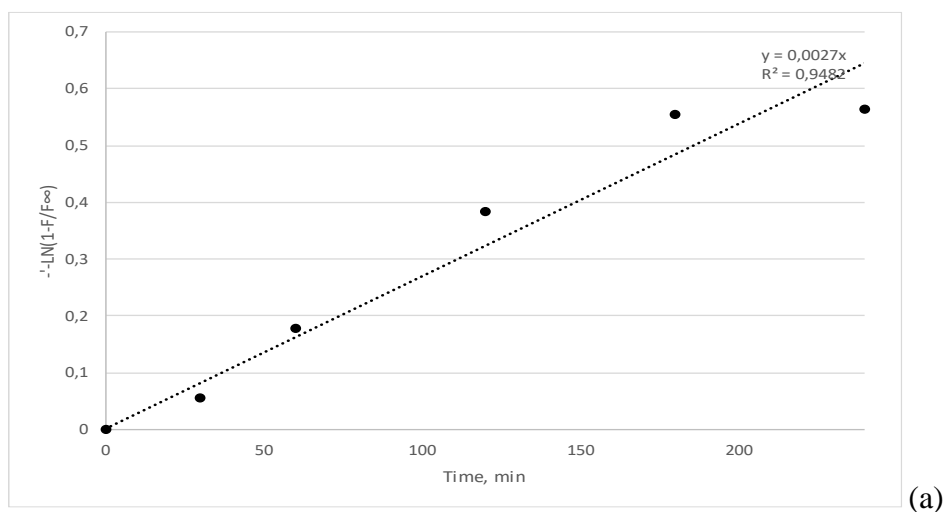
**Fig. 2.** Pseudo-first order kinetic for F (a) and N (b) mineralization
$[FT]_0 = 8.08$ mg/L $= 2.93 \times 10^{-5}$ M, $[TiO_2] = 100$ mg/L

Mineralization rate constants were calculated from Fig.2 graphs slopes and values of $2.7 \times 10^{-3}$ $min^{-1}$ for F and respectively $8.7 \times 10^{-3}$ $min^{-1}$ for N mineralization were found.

Langmuir-Hinshelwood kinetic is commonly used to describe heterogeneous catalytic processes and therefore was also used for FT degradation via UV/TiO$_2$ system in accordance with the following equations [11]:

$$r_0 = -\frac{d[FT]}{dt} = \frac{k_r K_{ads} [FT]_0}{1 + K_{ads} [FT]_0} \qquad (3)$$

where $r_0$ is initial FT degradation rate, $[FT]_0$ is flutamide initial concentration, $k_r$ is FT degradation rate constant, $K_{ads}$ is equilibrium constant for FT adsorbtion-desorbtion on catalyst surface particles. Equation 3 can be rearranged in the following expression:

$$\frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r K_{ads}[FT]_0} \qquad (4)$$

Graphic representation of equation 4, shown in Fig. 3, using experimental results after 60 minutes of irradiation was used in order to determine both the constant of FT adsorbtion desorbtion equilibrium on catalyst surface Kads $= 9121$ M$^{-1}$ and FT degradation rate constant kr $= 2.09 \times 10^{-6}$ M min$^{-1}$.
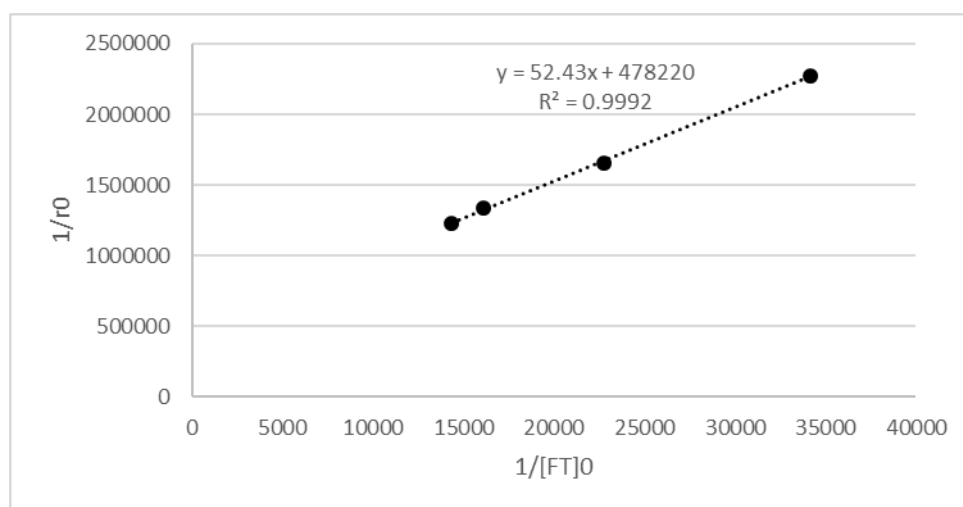


**Fig. 3.** Linearization of Langmuir-Hinshelwood equation for FT degradation via UV/TiO$_2$ system
$[TiO_2] = 100$ mg/L, irradiation time $= 60$ minutes

Experimental results proved that FT degradation via TiO2 assisted photo catalyse is obeying Langmuir-Hinshelwood model showing that FT degradation takes place on catalyst particles surface where radical species generated by UV irradiation are also adsorbed.

*UV/H₂O₂ system*

Experiments were performed using the same synthetic solution of FT used for UV/TiO2 system, with the initial concentration $[FT]0 = 8.08$ mg/L. The main investigated parameter was H2O2 dose, for which $[H2O2]0 : [FT]0$ molar ratios were varied within 0.5:1 to 30:1 domain.

Organic F mineralisation was also investigated. Irradiation time was kept constant at 30 minutes for all samples. Experimental results are presented within Table 2.

**Table 2.** FT degradation via UV/H₂O₂ system

$[FT]_0 = 8.08$ mg/L $= 2.93$ x $10^{-5}$ M, irradiation time = 30 minutes

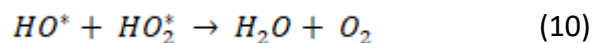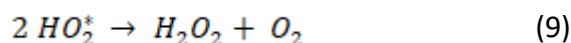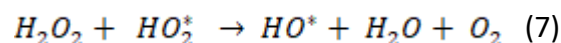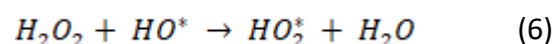| $[H_2O_2]_0 : [FT]_0$ molar ratios | [FT] mg/L | η [FT] % | Increase FT% | [F] mg/L | η [F] % | Increase F% |
|---|---|---|---|---|---|---|
| 0.5:1 | 0.23 | 97.15 | N/A | 0.21 | 12.58 | N/A |
| 2.5:1 | 0.12 | 98.51 | +1.36 | 0.28 | 16.78 | +4.20 |
| 5:1 | 0.06 | 99.26 | +0.75 | 0.33 | 19.78 | +3.00 |
| 15:1 | 0.02 | 99.75 | +0.49 | 0.36 | 21.57 | +1.79 |
| 30:1 | 0.01 | 99.88 | +0.13 | 0.38 | 22.77 | +1.20 |

FT degradation via UV/H₂O₂ system occurs with much better degradation efficiencies compared with UV/TiO₂ system. For the same initial FT concentration, the efficiencies of FT degradation using UV/H₂O₂ system are above 97% (for all applied H₂O₂ doses) after 30 minutes of irradiation in comparison with FT degradation efficiency of only 54.57% via UV/TiO₂ system after the same period of irradiation. F mineralization efficiency are also higher for UV/H₂O₂ system compared with UV/TiO₂ system.

FT degradation efficiency in UV/H₂O₂ system are increasing with the increase of H₂O₂ concentration but the marginal value of the increase become lower. This behaviour can be explained by combination of two opposite processes [12].

Photolysis with generation of hydroxyl radicals that are reacting with FT:

$$H_2O_2 \xrightarrow{UV} 2\ HO^* \qquad (5)$$

Absorbtion/screening of UV radiation and scaveging of hydroxil radicals:

$$H_2O_2 + HO^* \rightarrow HO_2^* + H_2O \qquad (6)$$

$$H_2O_2 + HO_2^* \rightarrow HO^* + H_2O + O_2 \qquad (7)$$

$$2\ HO^* \rightarrow H_2O_2 \qquad (8)$$

$$2\ HO_2^* \rightarrow H_2O_2 + O_2 \qquad (9)$$

$$HO^* + HO_2^* \rightarrow H_2O + O_2 \qquad (10)$$

When molar ratio $[H_2O_2]_0 : [FT]_0$ reaches the value of 5:1 the marginal increases of FT degradation efficiency and organic F mineralization efficiency are decreasing due to hydroxyl radicals scavenging in accordance with reactions (6) - (10).

Therefore taking into consideration the use of a molar ratio $[H_2O_2]_0 : [FT]_0$ of 5:1, led to FT degradation efficiency higher than 99% it was selected as optimum for H₂O₂ dosage.

*UV/H₂O₂/TiO₂ system*

The UV/H2O2 system is representing the rapid alternative but is inducing higher costs compared with UV/TiO2 system, which presents the disadvantage of longer irradiation time. A combination of both processes was envisaged in order to set up the most convenient alternative from the point of view of both irradiation time and reagents costs.

In order to ease the comparison process the same initial FT concentration $[FT]0 = 8.08$ mg/L was used. [TiO2] was kept at 100 mg/L (optimum dose for UV/TiO2 system) and H2O2 doses were varied in accordance with the following molar ratios $[H2O2] : [FT]0 = 0.1:1$ , 0.2:1 and 0.3:1. Irradiation time was maintained for all experiments at 30 minutes. Obtained results are presented within Table 3.

**Table 3.** FT degradation via UV/H₂O₂/H₂O₂ system

$[FT]_0 = 8.08$ mg/L $= 2.93$ x $10^{-5}$ M, [TiO₂] = 100 mg/L, irradiation time = 30 minutes

| $[H_2O_2]_0 : [FT]_0$ molar ratio | [FT] mg/L | η [FT] % |
|---|---|---|
| 0.1:1 | 0.41 | 94.93 |
| 0.2:1 | 0.18 | 97.77 |
| 0.3:1 | 0.02 | 99.75 |

Combination of photolysis and photocatalysis (UV/H2O2 and UV/TiO2) led to FT degradation with efficiencies higher than 99% after 30 minutes reaction and with low H2O2 consumption. Optimum conditions for UV/H2O2/TiO2 system established based on the experimental results are: [TiO2] = 100 mg/L, [H2O2]0 : [FT]0 = 0.3:1, irradiation time = 30 minutes.

*Electric energy per order*

In order to assess energy consumptions for all three tested variants, electric energy per order $E_{EO}$ was used[13], according to equation (11):

$$E_{EO} = \frac{P \cdot t \cdot 1000}{60 \cdot V \cdot lg \frac{[FT]_0}{[FT]}} \quad (11)$$

where $E_{EO}$ is electric energy per order expressed in kWh m$^{-3}$ order$^{-1}$, P is the power of UV lamp in kW (0.15 kW), t is the irradiation time in minutes, V is the volume of treated sample in L (0.4 L), $[FT]_0/[FT]$ is the ratio between FT initial concentration and FT concentration at the given t time.

Based on $E_{EO}$ calculated value, presented in the Table 4, it was found that the optimum system for FT degradation from the point of view of energy consumption is represented by the UV/H₂O₂/TiO₂ system.

**Table 4.** Electric energy per order for the studied systems

| | UV/TiO₂ | UV/H₂O₂ | UV/H₂O₂/TiO₂ |
|---|---|---|---|
| $E_{EO}$ | 575.51 kWh m$^{-3}$ order$^{-1}$ | 88.06 kWh m$^{-3}$ order$^{-1}$ | 71.94 kWh m$^{-3}$ order$^{-1}$ |

Optimum operating conditions for FT degradation via UV/TiO2, UV/H2O2, UV/H2O2/TiO2 systems were identified and degradation efficiencies were determined. A short overview of the main results of experimental work are presented within Table 5.

**Table 5.** Comparison of FT degradation via various systems

| | UV/TiO$_2$ | UV/H$_2$O$_2$ | UV/H$_2$O$_2$/TiO$_2$ |
|---|---|---|---|
| Optimum parameters | [TiO$_2$]$_0$ = 100 mg/L<br>Irradiation time = 240 min | [H$_2$O$_2$]$_0$ : [FT]$_0$ = 5:1<br>Irradiation time = 30 min | [TiO$_2$]$_0$ = 100 mg/L<br>[H$_2$O$_2$]$_0$ : [FT]$_0$ = 0,3:1<br>Irradiation time = 30 min |
| FT degradation efficiency | 99.75% | 99.26% | 99.75% |
| Main advantages | Possibility to reuse the catalyst<br>Possibility to use solar radiation | Short degradation time<br>Relatively low energy consumption | Combine the advantages of the other two systems<br>Lowest electric energy per order |
| Main drawbacks | High energy consumption if solar radiation is not used<br>Longer degradation time compared to the other two systems | Needs UV radiation<br>Hydrogen peroxide cost | Need for an additional step for catalyst separation<br>Hydrogen peroxide cost |

## CONCLUSIONS

Based on obtained experimental results the UV/H$_2$O$_2$/TiO$_2$ system seems to be the suitable option for FT degradation. It combines the main advantages of UV/TiO$_2$ (low cost, catalyst reuse) and UV/H$_2$O$_2$ (short degradation time, low electric energy per order) systems and minimize their disadvantages, which are mainly link to H$_2$O$_2$ cost and the need for an additional step for catalyst separation and reuse.

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