Comparison of flutamide degradation via UV/TiO₂, UV/H₂O₂ and UV/H₂O₂/TiO₂ systems

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Abstract
Synthetic solutions of flutamide were subject to degradation using three advanced oxidation systems, namely UV/TiO₂, UV/H₂O₂ and UV/H₂O₂/TiO₂. 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, TiO₂, H₂O₂, 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 ClO₂ [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].

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), TiO₂ (Merck), 30% H₂O₂ solution (Fluka). FT synthetic solutions were prepared using FT (purity ≥ 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⁻, NH₄⁺, NO₃⁻, NO₂⁻ 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 \([FT]_0 = 8.08 \text{ mg/L} = 2.93 \times 10^{-5} \text{ M} \) was used and titanium dioxide dose was kept at \([\text{TiO}_2] = 100 \text{ mg/L} \) 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.

| Time (min) | \([FT]\) mg/L | \(\eta [FT]\) % | \([F]\) mg/L | \(\eta [F]\) % | \([N]\) mg/L | \(\eta [N]\) % |
|------------|----------------|----------------|-------------|--------------|-------------|--------------|
| 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 \(2.72 \times 10^{-2} \text{ min}^{-1} \), based on the following equations:

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

\[
-ln\left(\frac{[FT]}{[FT]_0}\right) = kt \quad (2)
\]

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.
Mineralization rate constants were calculated from Fig. 2 graphs slopes and values of 2.7 x 10^{-3} min^{-1} for F and respectively 8.7 x 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/TiO₂ system in accordance with the following equations [11]:

\[
 r_0 = -\frac{d[FT]}{dt} = \frac{k_r K_{ads} [FT]_0}{1 + K_{ads} [FT]_0} \tag{3}
\]

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 adsorption-desorption on catalyst surface particles. Equation 3 can be rearranged in the following expression:

\[
 \frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r K_{ads} [FT]_0} \tag{4}
\]

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 adsorption-desorption equilibrium on catalyst surface \( K_{ads} = 9121 \text{ M}^{-1} \) and FT degradation rate constant \( k_r = 2.09 \times 10^{-6} \text{ M min}^{-1} \).
Experimental results proved that FT degradation via TiO₂ assisted photo catalysis 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.

| [H₂O₂]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].

When molar ratio [H₂O₂]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 [H₂O₂]₀ : [FT]₀ of 5:1, led to FT degradation efficiency higher than 99% it was selected as optimum for H₂O₂ dosage.

\[
H₂O₂ \rightarrow 2 \text{HO}^* \quad (5)
\]

Absorption/screening of UV radiation and scavenging of hydroxil radicals:

\[
H₂O₂ + \text{HO}^* \rightarrow \text{HO}_2^* + H_2O \quad (6)
\]

\[
H₂O₂ + \text{HO}_2^* \rightarrow \text{HO}^* + H₂O + O₂ \quad (7)
\]

\[
2 \text{HO}^* \rightarrow H₂O_2 \quad (8)
\]

\[
2 \text{HO}_2^* \rightarrow H₂O_2 + O₂ \quad (9)
\]

\[
\text{HO}^* + \text{HO}_2^* \rightarrow H₂O + O₂ \quad (10)
\]
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.

| [H₂O₂]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 E₀ was used[13], according to equation (11):

\[ E_{EO} = \frac{P \cdot t \cdot 1000}{V \cdot \log_{10}\left(\frac{[FT]_0}{[FT]}\right)} \] (11)

where E₀ 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 time.

Based on E₀ 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.

|          | UV/TiO₂    | UV/H₂O₂   | UV/H₂O₂/TiO₂ |
|----------|------------|-----------|--------------|
| E₀       | 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

| Parameters                        | UV/TiO₂ | UV/H₂O₂ | UV/H₂O₂/TiO₂ |
|-----------------------------------|---------|---------|--------------|
| Optimum parameters                | [TiO₂]₀ = 100 mg/L  
Irradiation time = 240 min | [H₂O₂]₀ : [FT]₀ = 5:1  
Irradiation time = 30 min | [TiO₂]₀ = 100 mg/L  
Irradiation time = 30 min |
| FT degradation efficiency         | 99.75%  | 99.26%  | 99.75%       |
| Main advantages                   | Possibility to reuse the catalyst  
Possibility to use solar radiation | Short degradation time  
Relatively low energy consumption | Combine the advantages of the other two systems  
Lowest electric energy per order |
| Main drawbacks                    | High energy consumption if solar radiation is not used  
Longer degradation time compared to the other two systems | Needs UV radiation  
Hydrogen peroxide cost | Need for an additional step  
for catalyst separation  
Hydrogen peroxide cost |

CONCLUSIONS
Based on obtained experimental results the UV/H₂O₂/TiO₂ system seems to be the suitable option for FT degradation. It combines the main advantages of UV/TiO₂ (low cost, catalyst reuse) and UV/H₂O₂ (short degradation time, low electric energy per order) systems and minimize their disadvantages, which are mainly link to H₂O₂ cost and the need for an additional step for catalyst separation and reuse.

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