Photo-degradation of 5 – Fluorouracil. Comparative Study on the Efficiencies of UV/H_2O_2, UV/TiO_2, UV/H_2O_2/TiO_2 Processes

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Degradation experiments on 5-Fluorouracil synthetic solutions were performed using three types of advanced oxidation systems: UV/H_2O_2, UV/TiO_2 and UV/H_2O_2/TiO_2. Optimum parameters for all three systems were established and 5-Fluorouracil degradation efficiencies were calculated, for all systems being more than 97%. The results showed that the combined UV/H_2O_2/TiO_2 system is offering shortest irradiation time, the possibility to recover and reuse the photo catalyst as well as the possibility to use solar radiation. Obtained results proved also that advanced oxidation processes represent a viable option for degradation of hazardous pollutants that cannot be removed properly via conventional wastewater treatment processes.
***Keywords**: 5-Fluorouracil, TiO_2, H_2O_2, degradation efficiency*

5-Fluorouracil (5FU) is one of the most common drugs used in cancer treatment worldwide [1].

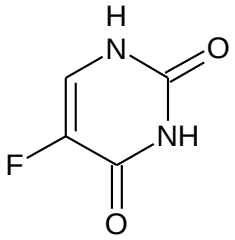

Fig. 1. 5-Fluorouracil (5FU) structure

Due to its non-selective action it affects not only cancerous but healthy cells, presenting an carcinogenic, genotoxic, mutagenic and teratogenic potential [2]. Moreover about 15% of the administered 5FU is leaving the human body with no transformation ending within the sewerage network [3]. Recent studies demonstrated that this type of pollutant cannot be removed within the wastewater treatment plants [4]. Even if cytostatic residues concentrations within the sewerage system of hospitals are low,varying from micrograms to hundreds of micrograms, its removal through conventional wastewater treatment processes is not possible asking for application of more performant processes [5], [6]. Therefore, 5FU degradation experiments were performed in order to determine the optimum parameters for the following systems: UV/H_2O_2, UV/TiO_2 and UV/H_2O_2/TiO_2.

EXPERIMENTAL PART

Degradation experiments were performed using a Heraeus UV reactor with the following characteristics: UV lamp - TQ150-Z3 type, cooling jacket, reaction vessel from quartz, volume = 400 cm^3, equipped with a magnetic recirculation pump. Determination of 5FU concentration was carried out using an Agilent 7890A gas chromatograph coupled with an Agilent 240MS ionic trap spectrometer [7]. Synthetic solutions were prepared using 5FU supplied from Sigma-Aldrich.

All samples were bubbled with air (50 L/h) prior to irradiation in order to avoid electrons – holes recombination.

All experiments were at least duplicated in order to assure their repeatability.

Fig. 2. Experimental installation

RESULTS AND DISCUSSIONS

UV/H_2O_2 system

From the main parameters that are influencing the degradation processes the following were investigated: H_2O_2 dose and irradiation time.

Effect of H_2O_2 dose

In order to set up optimum H_2O_2 dose, 5FU degradation experiments were performed for an initial 5FU concentration $[5FU]_0$ = 13.35 mg/L = 1.03 x 10^{-4} M for an irradiation time of 30 minutes and H_2O_2 doses within the interval $[5FU]_0/[H_2O_2]$ = 1:3 – 1:28.

Obtained experimental results are presented within Table 1 and Figure 3.

Table 1. 5FU degradation efficiency in UV/H_2O_2 system
[5FU]0 = 13.35 mg/L=1.03 x 10-4 M; irradiation time = 30 min

$[H_2O_2]/[5FU]_0$	**[5FU] mg/L**	**[5FU] M**	**-ln([5FU]/ $[5FU]_0$)**	**k s^{-1}**	**Eficienta %**
3	1.65	1.27 x 10^{-5}	2.09	1.16 x 10^{-3}	87.64%
11	1.32	1.02 x 10^{-5}	2.31	1.29 x 10^{-3}	90.11%
17	**1.11**	**8.54 x 10^{-6}**	**2.49**	**1.34 x 10^{-3}**	**91.69%**
22	1.45	1.12 x 10^{-5}	2.22	1.23 x 10^{-3}	89.14%
28	1.53	1.18 x 10^{-5}	2.17	1.20 x 10^{-3}	88.54%

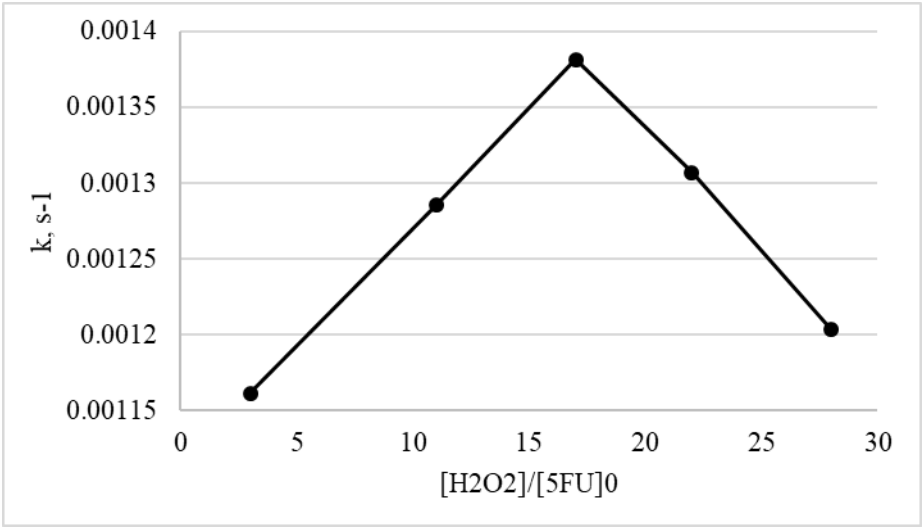

Fig. 3. H_2O_2 dose effect upon the 5FU degradation in UV/H_2O_2 system
[5FU]0 = 13.35 mg/L=1.03 x 10-4 M; irradiation time = 30 min

Results showed that optimum H_2O_2 dose correspond to $[5FU]_0/[H_2O_2]$ = 1:17 which assures a degradation efficiency of 91.69% after 30 minutes of irradiation. Optimum dose was used in all the subsequent experiments for UV/H_2O_2 system.

Effect of irradiation time

In order to establish the optimum irradiation time 5FU degradation experiments were performed for an initial 5FU concentration $[5FU]_0$ = 13.35 mg/L = 1.03 x 10^{-4} M for H_2O_2 dose corresponding to $[5FU]_0/[H_2O_2]$ = 1:17, and irradiation time up to 45 minutes.

Experimental results showed that the increase of irradiation time has a positive impact upon 5FU degradation efficiency. Therefore, the optimum irradiation time was set at 45 minutes, which assured the substrate degradation with a 97.08% efficiency and a residual 5FU concentration of 0.39 mg/L.

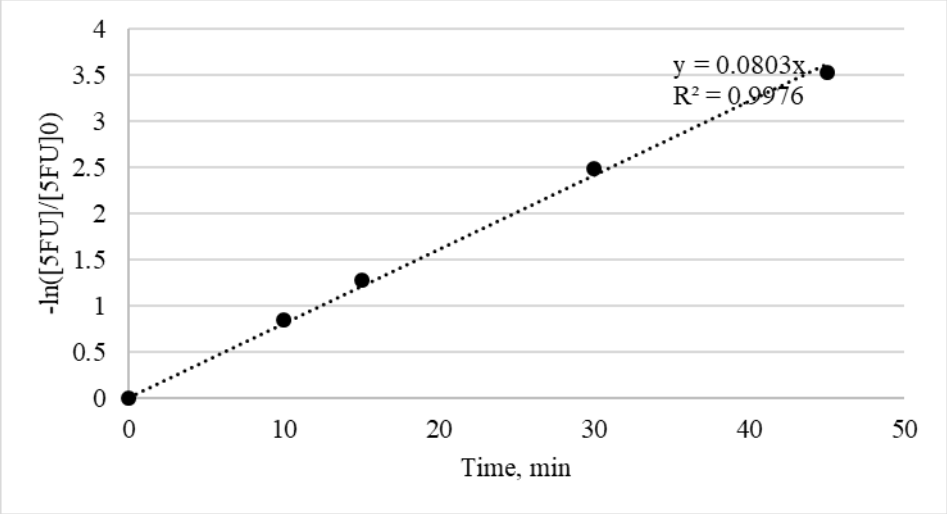

Fig. 4. 5FU degradation kinetic in UV/H_2O_2 system
[5FU]0 = 13.35 mg/L=1.03 x 10-4 M; $[5FU]_0/[H_2O_2]$ = 1:17

UV/TiO_2 system

Previous reported researches on 5FU degradation in UV/TiO_2 system [7] led to the following optimal parameters: pH = 7; photo catalyst dose 100 mg/L; irradiation time 180 minutes. These conditions assured 5FU degradation with an efficiency of more than 99%. Moreover, the processes obey Langmuir – Hinshelwood model proving that degradation process occurs mainly on TiO_2 particle surface.

UV/H_2O_2/TiO_2 system

From the main parameters that are influencing the degradation processes the following were investigated: H_2O_2 dose and irradiation time. All experiments were performed using a synthetic solution with initial concentration $[5FU]_0$ = 13.35 mg/L = 1.03 x 10^{-4} M; photo catalyst concentration $[TiO_2]$ = 100 mg/L at pH = 7 (optimum conditions for UV/TiO_2 system).

Effect of H_2O_2 dose

The oxygen presence plays an important role due to its electron scavenger properties fact that is affecting electrons – holes recombination process. It was demonstrated that oxygen can have both a positive or negative impact upon the pollutant degradation [8].

In order to investigate these parameters; molar ratios $[5FU]_0/[H_2O_2]$ were varied within the domain 1:0.5 – 1:5. Obtained experimental results are presented within Table 2 and Figure 5.

Table 2. 5FU degradation efficiency in UV/H_2O_2/TiO_2 system
[5FU]0 = 13.35 mg/L=1.03 x 10-4 M; $[TiO_2]$ =100 mg/L; irradiation time = 30 min

$[H_2O_2]/[5FU]_0$	[5FU] mg/L	[5FU] M	-ln([5FU]/[5FU]0)	k s^{-1}	Efficiency %
0,5	2,77	2.13 x 10^{-5}	1,57	0,80 x 10^{-3}	79,25%
1	1,73	1,33 x 10^{-5}	2,04	1,13 x 10^{-3}	87,04%
3	1,29	9,92 x 10^{-6}	2,34	1,29 x 10^{-3}	90,34%
5	**1,13**	**8,69 x 10^{-6}**	**2,47**	**1,37 x 10^{-3}**	**91,54%**

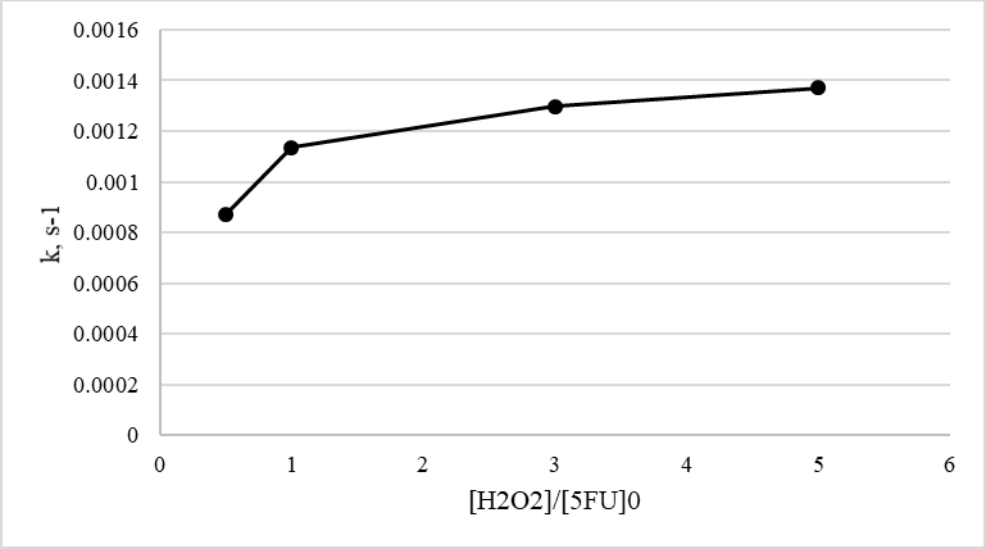

Fig. 5. 5FU degradation kinetic in UV/H_2O_2/TiO_2 system
[5FU]0 = 13.35 mg/L=1.03 x 10-4 M; [TiO_2] =100 mg/L; irradiation time = 30 min

Obtained results proved that optimum H_2O_2 dose corresponds to the [5FU]$_0$/[H_2O_2] ratio of 1:5.

Effect of irradiation time

For the optimum H_2O_2 dose, the influence of irradiation time upon 5FU degradation efficiency was investigated, the results being presented within Figure 6.

The increase of irradiation time has a positive effect upon 5FU degradation efficiency. Optimum irradiation time was set at 45 minutes, assuring the substrate degradation with a 97.37% efficiency and a residual 5FU concentration of 0.139 mg/L.

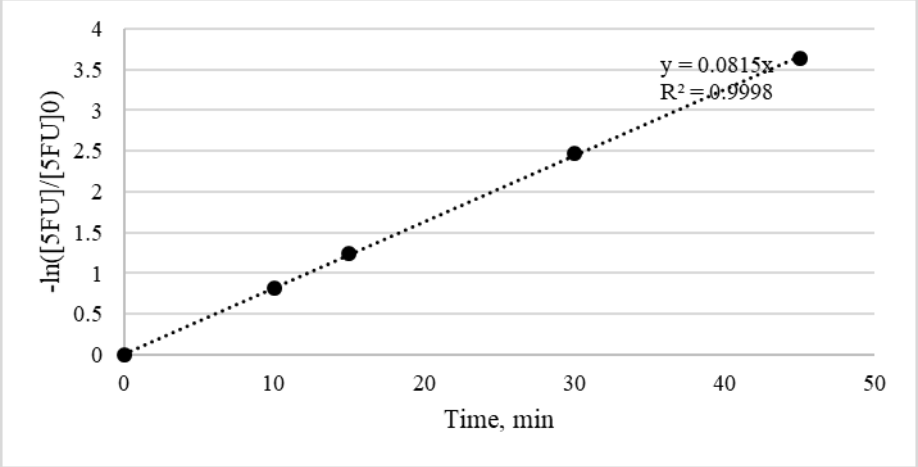

Fig. 6. 5FU degradation kinetic in UV/H_2O_2/TiO_2 system
5FU]0 = 13.35 mg/L=1.03 x 10-4 M; [TiO_2] =100 mg/L; [5FU]$_0$/[H_2O_2] = 1:5

CONCLUSIONS

Optimum parameters for 5FU degradation using UV/H_2O_2, UV/TiO_2, UV/H_2O_2/TiO_2 were established and degradation efficiencies for all three systems were calculated.

A synthesis of these data is presented within Table 3.

UV/H_2O_2/TiO2 system presents the advantage of using solar radiation simultaneously with the shortest irradiation time that leads to energy costs reduction and also to reduction of implementation (compact installations) and operating costs. It also offers the possibility to recover the photo catalyst and reuse it in further treatment cycles.

Table 3. 5FU degradation efficiency using various systems

System	Efficiency
UV/H_2O_2: $[5FU]_0/[H_2O_2]$ = 1:17 Irradiation time = 45 min	97.08%
UV/TiO_2: $[TiO_2]$ = 100 mg/L pH = 7 Irradiation time = 180 min	99.85%
UV/H_2O_2/TiO_2: $[5FU]_0/[H_2O_2]$ = 1:5 $[TiO_2]$ = 100 mg/L pH = 7 Irradiation time = 45 min	97.37%

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