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STUDY ON THE PHOTOCATALYTIC DEGRADATION OF DICLOFENAC AND SULCOTRIONE IN SOME LAKE WATER SUBSTRATES IN HANOI

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Abstract

Diclofenac (DFS, a pharmaceutical product) and sulcotrione (SCE, a new herbicide replaced on altrazine) has been investigated degradation by the photocatalyst (TiO_2/UV) on the TiO_2-PC500 Millennium paper. DFS (50 μM) and SCE (20 μM) were added in the lake water substrates in Hanoi (West lake, Dong Da lake, Bay Mau lake, Hoan Kiem lake) and distilled water. The cycling prototype pilot has 6L volume with an immersed pump whose flow is adjustable between 500 and 2.000 $mL.min^{-1}$. After 3 irradiated hours, amount of degraded DFS obtained 70%, in the West lake, Dong Da lake, Bay Mau lake is 50% and Hoan Kiem lake is only 24%. The degradation results of SCE in the Dong Da lake and Hoan Kiem lake is the less after 3 irradiated hours (about 12%). However, elimination effect of SCE in the distilled water is higher than DFS, about 75%.

Some physico-chemic characters of lake such as : pH, TOC, CO_3^{2-},... were evaluated. The influence of TOC and CO_3^{2-} presences to the degradation effect was explained in this paper.

Keywords : *Diclofenac, PC500-Millennium, Photocatalyst (TiO_2/UV), Sulcotrione.*

1. Introduction

Diclofenac and sulcotrione (figure 1) were studied in this present work. DFS is a non-steroidal anti-inflammatory drug (NSAIDs) with anti-inflammatory, analgesic and antipyretic properties, was developed in the late 1970s and approved for clinical use in treating several rheumatic diseases (rheumatoid arthritis, osteoarthritis, and ankylosing spondylitis) [**10**]. During the different processes of production, utilization and excretion, DFS is discharged thus causes an environmental pollution. The most important problem may arise from contamination of the aquatic compartment. Actually, diclofenac has been frequently detected in surface water with concentration up to 1.2 $\mu g.L^{-1}$ [**3**; **11**] and in STP effluents with concentration up to 6 $\mu g.L^{-1}$. SCE which is used in Europe is a new herbicide replaced on altrazine [**1**; **9**]. Therefore, there is a little study on this compound. In some documents abroad, its concentration presents although in the surface water about 10-25 ng/L [**2**].

Figure 1: Structure of diclofenac (A) and sulcotrione (B)

Photocatalysis is one of the Advanced Oxidation Processes (AOPs) which is based on the generation of the highly reactive hydroxyl radicals able to degrade organic pollutants resistant to biological and/or classical physicochemical processes. Hydroxyl radical $^{\circ}OH$ is a very powerful oxidant (oxidation potential 2.80 eV at pH=0), [**4**].They mostly react with organic molecules with second order rate constants in the range 10^{7}-10^{10} $M^{-1}.s^{-1}$. The formation $^{\circ}OH$ radicals on the TiO_2 surface have been extensively described in literature [**8**].

We focused on the degradation of DFS and SCE in the surface water in Hanoi by heterogeneous photocatalysis using the TiO_2 commercially available photocatalyst PC500-Millennium coated on the paper. The experiments were carried out on the pilot prototype under UV light or solar light, experiment scale.

2. Materials and equipments

a. *Material*

- Diclofenac natri salt 99,9 % was from Sigma-Aldrich
- Sulcotrione 99,9 % was from Sigma-Aldrich
- Metanol and Acetonnitril were from Carlo Erba : mobile phase HPLC grade
- H_3PO_4 85 % was from Carlo Erba, buffer for HPLC
- TiO_2-PC500 Millennium paper was from Ahlström Paper Group amount of TiO_2 about 18 g/m^2.

b. *Equipment for analyse and UV-365nm light*

- HPLC Shimadzu LC-10ADvp
- TOC Shimadzu TOC-V_{CPH}
- Sylvania Blue Light Black (BLB) – 6 W light with a 365 nm maximum wave-length.

c. *Reactor*

The stainless pilot (figure 2) includes a recevoir of 6 L with a immersed pump whose flow is adjustable between 400 and 2.000 $mL.min^{-1}$. The solution arrives at the supporting reactor of the paper covered with TiO_2. On the surface of the reactor, two partitions were assembled to stabilize the water volume. This volume under the irradiation is evaluated to 680 ml. This pilot can be closed by a lid under which three emitting lamps UV are fixed mainly at 365nm.

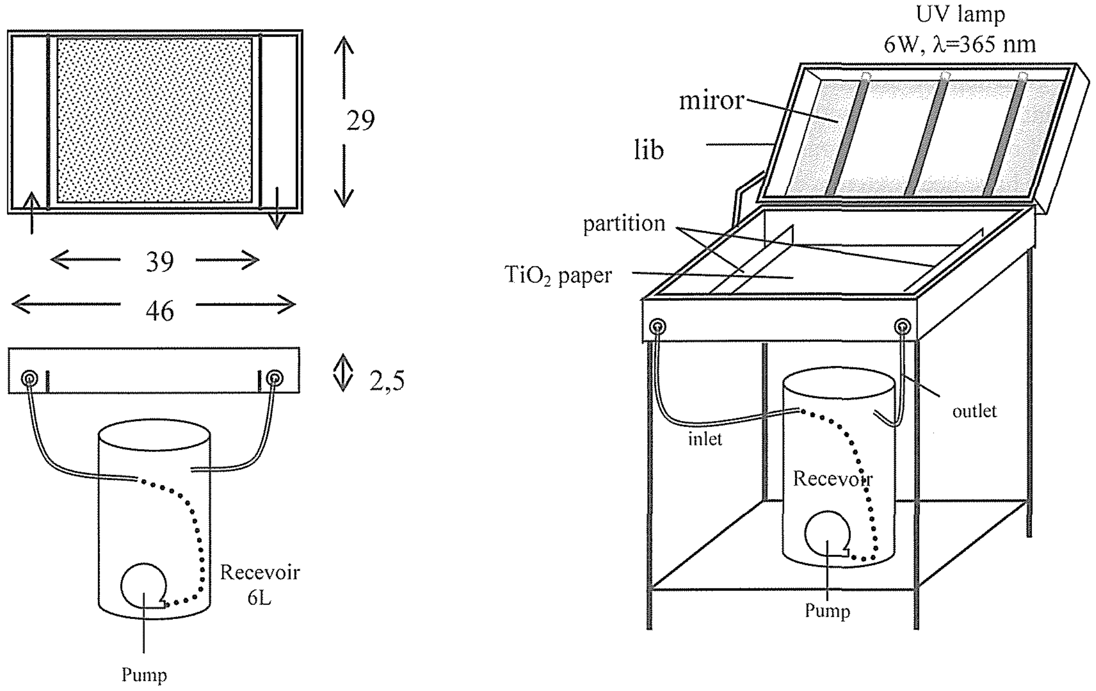

Figure 2 : Prototype pilot

3. Results

3.1. Dark adsorption and UV irradiation

These experiments were purposed to verify the DFS concentration (50 □M) decreased by adsorption on the surface of PC500 TiO_2 paper in the dark and by the UV-365 nm degradation. The results showed that the DFS was negligibility adsorpbed after 3 hours in the dark. With irradiation of 3 UV lamps, DFS concentration was reduced about 9% after 3 experiment hours. The rate constante (k_{app}) has been calculed about 8.5 10^{-6} s^{-1} in this experiment conditions.

3.2. Influence of flow rate

In theory, the flow rate is not purposed an important effect factor in the operation of closed cycle pilot, because it seems that this parameter don't modify degradation affect. However, in this research, we purposed still to study the influence of flow rate in order to assure this argument and evaluate on the other hand the stability of our pilot.

In these experimental series on the influence of flow rate, initial concentrations DFS were always started on 50 μM which must be dissolved in distilled water (pH ≈ 6.5-7.0). The TiO_2 used masses were always 285 mg/L with 38x25 cm calculed area. The flow rate is changeable between 500 and 2000 mL/min (table 1). Figure 3 show that the DFS degradation effects are similar, about 30-35% after 3 experimental hours. These results are according to our primary prediction.

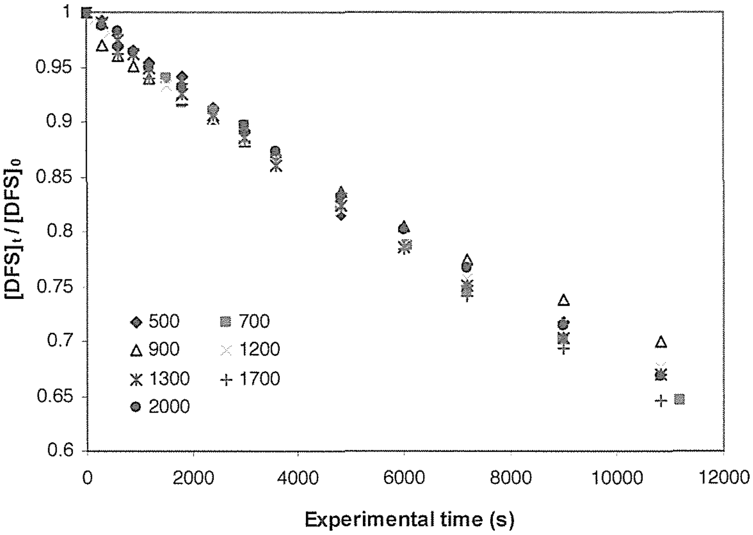

Figure 3: Influence of flow rate on the DFS degradation effect

$([DFS]_0 = 50\ \mu M;\ m^*_{TiO_2} = 285\ mg.L^{-1})$

This non-influence of flow rate could be explained as follows : The time of experiment operating (3 hours) is able to be called t_{exp}. The irradiation time (t_{irr}) on which the degradation effect is depended could be the contact time of DFS on the suface TiO_2 paper. At any flow rate, we can compare between both of time values (t_{irr}/t_{exp}) and this division is always constant which is just equaled the constant value of reaction volume/total volume. It means that 0.68 / 6 L = 0.113. The results from this research has been demonstrated the prediction. The k_{app} constants calculated which symbolize degradation effect are similar. The average k_{app} value is about $8.12\ 10^{-4}\ s^{-1}$.

Table 1 : The k_{app} constants calculated from the experiments with differents flow rate

Q_0 (ml/p)	**500**	**700**	**900**	**1200**	**1300**	**1700**	**2000**
k_{app} (s^{-1})	$8{,}18.10^{-4}$	$8{,}02.10^{-4}$	$8{,}29.10^{-4}$	$8{,}17.10^{-4}$	$8{,}19.10^{-4}$	$8{,}39.10^{-4}$	$7{,}63.10^{-4}$
R^2	0,98	0,99	0,95	0,99	0,99	0,99	0,99

3.3. DFS degradation in lake water

The photocatalytic degradation has been carried out with DFS added (concentration=50 μM) in lake waters. The results in figure 4 showed that the DFS degradations in lake water are weaker than it's in distilled water. Moreover, in case of lake water, the DFS elimination is also depended on the physico-chemical character of every lake. The values of TOC, COD and alkalinity in lake waters which influence directly on degradation effect are differents.

Table 1 : Some determined physico-chemical parameters in lake waters in Hanoi

Parameters	*Units*	*West lake*	*Dong Da lake*	*Hoan Kiem lake*	*Bay Mau lake*
pH		7,77	8,21	8,70	7,92
$COD_{(KMnO4)}$	$mg.L^{-1}$	23,4	17,3	39,4	12,8
Alkalinity $_{(CaCO3)}$	$mg.L^{-1}$	125	133	43	129,5
TOC	$mg.L^{-1}$	8,2	9,6	74,1	7,9

The comparison between of these degradation effects was represented by k_{app} constant which is calculed from experimental result (table 2).

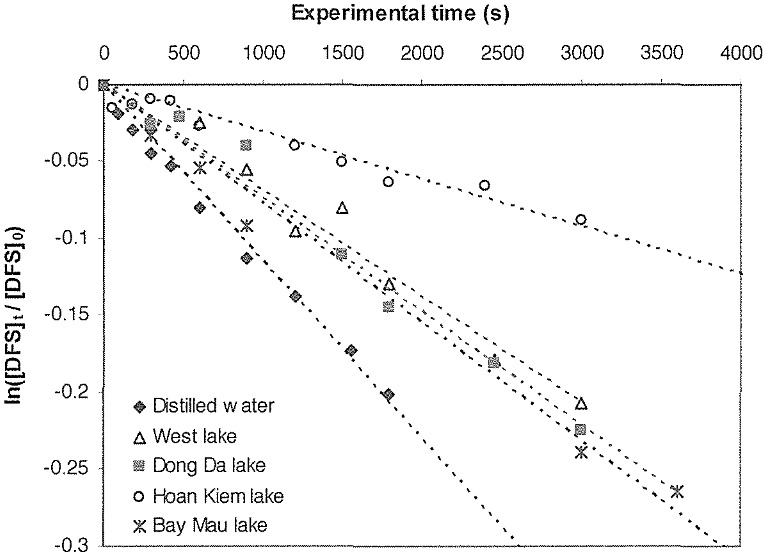

Figure 4: Degradation effects of DFS in natural lake water under solar light

$([DFS]_0 = 50\ \mu M\ ;\ m^*_{TiO_2} = 285\ mg.L^{-1})$

Table 2: The determined k_{app} constants from DFS degradation experiments in aqueous

Kind of used water	k_{app} (s^{-1})	R^2
Water distilled	$10{,}62\ 10^{-4}$	0,99
West lake	$6{,}11\ 10^{-4}$	0,97
Dong Da lake	$6{,}55\ 10^{-4}$	0,98
Bay Mau labo	$6{,}81\ 10^{-4}$	0,99
Hoan Kiem lake	$2{,}74\ 10^{-4}$	0,94

In all of surface waters, the organic compounds and bicarbonate ions parameters could be the factors that they can reduce the active photocatalytic reaction. This is presented by the following reactions which are their combination with hydroxyle radicals :

$$\text{Organic compounds} + OH^\circ \longrightarrow \text{Oxidation by-product}$$

$$HCO_3^- + OH^\circ \longrightarrow CO_3^{2-} + H_2O \qquad k = 1.5\ 10^7\ M^{-1}.s^{-1}$$

In order to test the presence of these parameters in lake, the chemical analyses have been carried out. The exposed results in table 3 showed that amount of organic compounds in Hoan Kiem lake is very high which is presented by TOC value. The alkalinity in this lake is although low but it is interesting to see that the DFS degradation effect is very bad (k_{app} = 2.74 10^{-4}). Meanwhile, TOC and alkalinity values in West lake, Dong Da lake and Bay Mau lake are similar so that the DFS degradation curves are also approximative. From these results, we have remarked that the TOC amount is always one of the important factor which influences directly on the photocatalytic degradation effect.

3.4. SCE degradation in lake water

The similar experiments were carried out SCE added on distilled water and 4 kinds of lake waters (West lake, Bay Mau lake, Dong Da lake, Hoan Kiem lake) with 50 μM initial concentration. The researched results in figure 5 showed that the SCE degradation in lake waters are much less effect than in distilled water. However, the photocatalytic degradations of SCE in the lake substrates were limited by the competitive factors which caused the degradation of SCE is weaker than DFS.

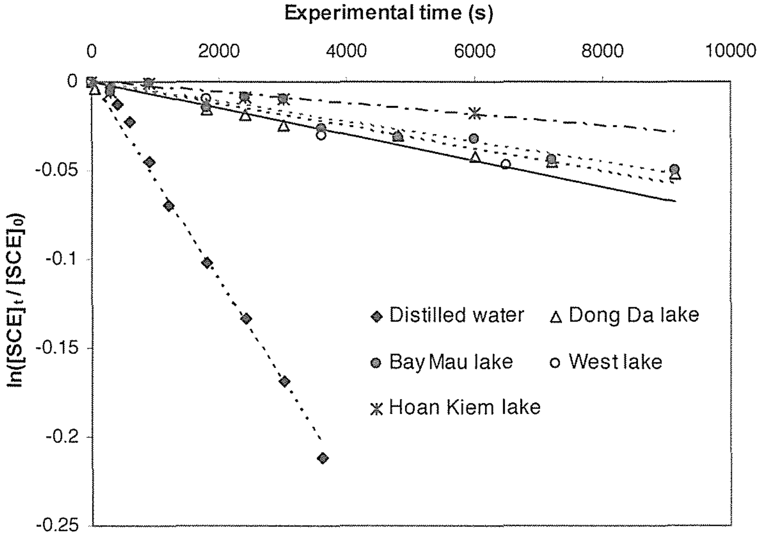

Figure 5 : Evaluation of SCE degradation by photocatalyst under solar in water

($[SCE]_0 = 20\ \mu M;\ m^*_{TiO_2} = 285\ mg.L^{-1}$)

Elimination effects of SCE have been determined by k_{app} constant values with distilled water and 4 kinds of used water which are represented in table 4. The results showed that the degradation effect of SCE is lower than DFS, this can be explained by 2 means: 1- SCE has a chemical durable structure, 2- The organic compounds in lake water could be easier degraded than SCE.

Table 4: The determined k_{app} constants from the experiments SCE degradation in water

Kind of used water	k_{app} (s^{-1})	R^2
Distilled water	5,01 10^{-4}	0,99
West lake	6,53 10^{-5}	0,98
Dong Da lake	5,59 10^{-5}	0,95
Bay Mau lake	5,26 10^{-5}	0,93
Hoan Kiem lake	2,72 10^{-5}	0,84

3.5. Comparison of photocatalytic degradation between SCE and DFS

In order to compare photocatalytic degradation between SCE and DFS, a series of experiments were carried out with SCE and DFS changed concentrations from 0 to 200 mM. The used masses of TiO_2 on paper are always 100 mg/L. Irradiation was used 3 UV lamps 365 nm. The results in figure 6 and

7 showed that DFS degradation is 2.8 faster than SCE. It may be that the difference of molecule structure is the main reason which caused the difference of breaking. This was demonstrated by some previous researcher on degradation some organic compounds [**5**; **6**].

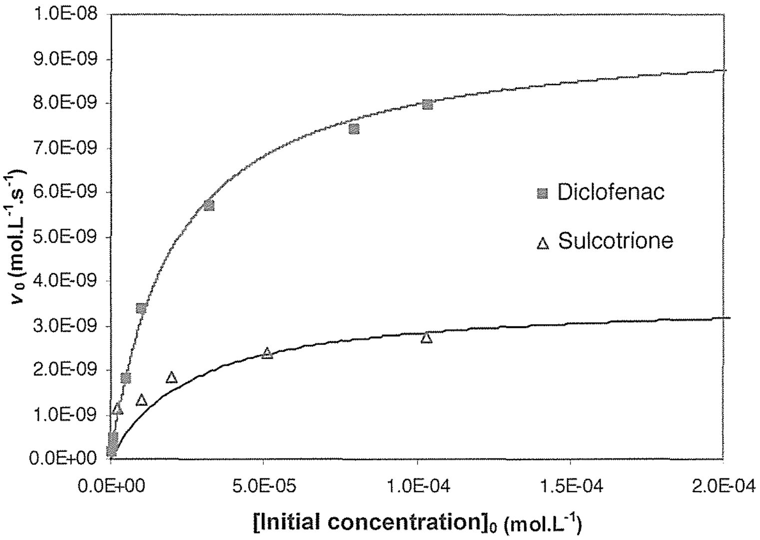

Figure 6: Comparison of photocatalytic degradation effect between SCE and DFS with initial concentration differents

$(m^*_{TiO_p-PC500} = 100\ mg.L^{-1})$

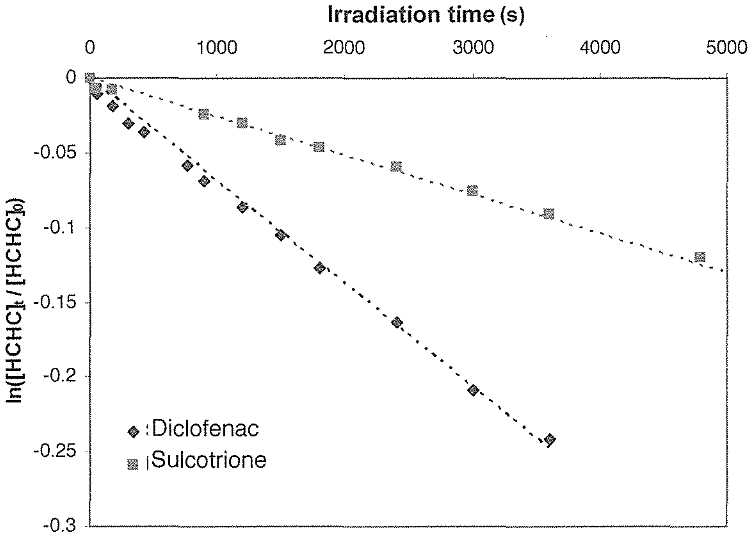

Figure 7: Comparison of photocatalytic degradation effect between SCE and DFS mixed

$([DFS]_0 = [SCE]_0 = 20\ mM,\ m^*_{TiO_p-PC500} = 100\ mg.L^{-1})$

The results after 3 irradiated hours by UV lamps were showed that the DFS amout is degraded about 59% and SCE is only 33%.

4. Conclusion

In this research paper, the photocatalytic degradation process (TiO_2/UV) was carried out with 2 kinds of organic compound which are SCE and DFS in lake substrates. The factors as amount of organic compound (TOC) and HCO_3^- play important role in the photocatalytic reation. Therefore, when this process is applied the evaluation of these parameters is necessarily attended. With some photocatalytic experiments in lake waters such as West lake, Dong Da lake, Bay Mau lake, Hoan Kiem lake, the results showed that the degradation effect is the worst in Hoan Kiem lake because of high concentration of organic compound. The photocatalytic degradation effect in order to remove DFS and SCE in lake waters is of course much less than in distilled water.

The experiment results showed also that the difference of molecule structure between DFS and SCE caused the degradation effect differents in 2 separated or mixed solutions. It was showed that DFS is the easier degraded.

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