

Dimethyl phthalate removal from aqueous system using a photocatalytic membrane reactor with suspended photocatalyst

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Abstract

Dimethyl phthalate is low molecular weight phthalate used on a wide scale within industry for manufacture of plastics, solvents, adhesives, lubricants, coatings and due to its poor biodegradability is not removed by classic wastewater treatment processes. It was proved that it affects the endocrine system, presenting carcinogenic, teratogenic and mutagenic effects on living organisms. Therefore, there is a need for more advanced treatment methods such as advanced oxidation processes for dimethyl phthalate removal from aqueous systems. A hybrid process consisting from photo catalysis and membrane based processes was investigated and the optimum parameters for dimethyl phthalate removal were established. In respect to photocatalytic process the influence of photo catalyst dose, pH, irradiation time were studied and process kinetics were set up using a synthetic dimethyl phthalate solution. In order to recover and reuse the photocatalyst a membrane process was used and optimum working pressure was determined. In the case of real wastewater matrix the addition of hydrogen peroxide was needed, in the photocatalytic stage, in order to improve process efficiency. Four treatment cycles, using real wastewater spiked with dimethyl phthalate, were performed with the reuse of photo catalyst proving that the use of photocatalytic membrane reactor with suspended photo catalyst represents a promising method for phthalates removal from aqueous systems.

Keywords: *dimethyl phthalate, endocrine disruptor, membrane, photo catalysis, photocatalytic membrane reactor*

INTRODUCTION

Phthalates, the alkyl diesters of 1,2-benzenedicarboxylic acid (phthalic acid), are one of the most used chemicals within industry mainly as plasticizers but also can be found in textiles, lubricants, adhesives, insecticides, personal care products, coatings, varnishes or cleaning products [1-4].

Due to their intense use, the annual worldwide phthalate production increases from 2 million tonnes in 1975 up to 8 million tonnes in 2011 [5-7]. Moreover, a study from 2018 estimated a 1.3% growth of phthalate use from 2017 to 2022 [8].

Phthalates with high molecular weight such as di-n-octyl phthalate (DOP) and di-(2-ethylhexyl) phthalate (DEHP) are used for furniture and construction materials. On the other hand, phthalates with low molecular weight phthalates such as dimethyl phthalate (DMP), diethyl

phthalate (DEP) and dibutyl phthalate (DBP) are used for example for manufacturing of plastics, solvents, adhesives, lubricants, coatings and varnishes [6,9].

Due to their resistance on natural degradation processes, these compounds are accumulating within natural receivers reaching concentrations between $\mu\text{g/L}$ (during summer) and tens to hundreds of $\mu\text{g/L}</math> (during winter) [10]. Moreover, numerous studies proved that these compounds are affecting endocrine system and interfere with biological processes, generating potential teratogenic, carcinogenic and mutagenic effects upon living organisms [11-14].$

Taking into consideration both parabens' high resistance to degradation and their toxic characteristics, more destructive treatment methods, such as advanced oxidation processes (AOPs) needed for their advanced removal from aqueous systems.

Some studies on DMP degradation focussed on use of thin film TiO_2 deposited on Ti plate (surface 40 cm^2) using UV-LED with irradiance of $10\text{-}120\text{ mW/cm}^2$ [15].

DMP degradation efficiency on UV-LED/ TiO_2 system decreases from 48% to 28% with the increase of initial pH from 2 to 6, in similar operating conditions ($I_0 = 120\text{ mW/cm}^2$, $[\text{DMP}]_0 = 10\text{ mg/L}$, $[\text{O}_2] = 8\text{ mg/L}$, light period = 5 s, dark period = 5 s, irradiation time = 60 min). This is explain by the presence of excess protons which are in favour of reaction between photo generated electrons and molecular oxygen adsorbed on TiO_2 surface and the concentration level of hydroxyperoxyl radicals involved in pollutant's degradation increases [16-18].

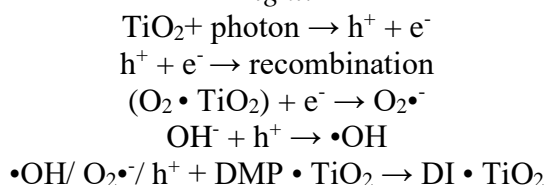
Increase of DMP initial concentration from 5 mg/L to 20 mg/L in identical operating conditions ($I_0 = 120\text{ mW/cm}^2$, $\text{pH}_0 = 6$, $[\text{O}_2] = 8\text{ mg/L}$, light period = 5s, dark period = 5 s, irradiation time = 60 min) led to DMP degradation efficiency decrease from 34% to 20%, due to the fact that high DMP concentration and presence of its degradation products on photo catalyst surface imposes prolonged time for their desorption.

DMP degradation performance is positively influenced (from 20% to 38%) by the increase of dissolved O_2 concentration (from 0.4 mg/L to 32 mg/L) in similar operating conditions ($I_0 = 120\text{ mW/cm}^2$, $\text{pH}_0 = 6$, $[\text{DMP}]_0 = 10\text{ mg/L}$, light period = 5 s, dark period = 5 s, irradiation time = 60 min). This is due to presence of excess O_2 which is in favour of reaction with photo generated electrons, and regenerated photo catalyst surface (in dark period) is more rapidly available for adsorption of pollutant molecules [19, 20].

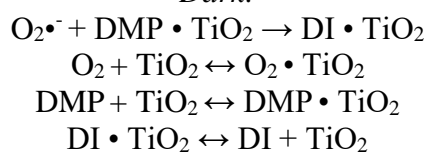
Irradiance increase from 10 mW/cm^2 to 120 mW/cm^2 results in an increase of DMP conversion from 5% to 34% in identical operating conditions ($\text{pH}_0 = 6$, $[\text{DMP}]_0 = 10\text{ mg/L}$, $[\text{O}_2] = 8\text{ mg/L}$, light period = 5 s, dark period = 5 s, irradiation time = 60 min). This can be explain by the fact that with the increase of incident irradiance the number of photons adsorbed on photo catalyst is increasing [21-23].

DMP degradation mechanism proposed for UV-LED/ TiO_2 with intermittent irradiation can be described by the following reactions:

Light:



Dark:



When photo catalyst is irradiated, holes and electrons are generated and reacts with hydroxyl ions and oxygen adsorbed on photo catalyst surface. On the same time DMP molecules adsorbed on

photo catalyst surface are oxidised to degradation intermediates (DI) through radical species $\bullet\text{OH}$, $\text{O}_2\bullet^-$ and holes h^+ . Processes that take place in the dark but can occur also in the light are adsorption/desorption of reagents and degradation intermediates [24].

Admitting that holes and electrons are involved in the following reactions: DMP oxidation, OH^- oxidation, oxygen reduction, holes and electrons recombination, results that prolonged irradiation is in favour of charges recombination because the surface on which hydroxyl ions and DMP are adsorbed is decreasing, therefore negatively influencing degradation performances.

Other studies focussed on DMP degradation using TiO_2 catalyst doped with C (C- TiO_2) obtained via sol-gel method using Ti isopropoxide and carbon aerogel. Prepared composite material with 15% C (weight) and porous structure, average pores diameter = 9.3 nm, presented superior photocatalytic activity (83% DMP degradation efficiency) compared with non-doped TiO_2 (70% DMP degradation efficiency) in the following working conditions: $I_0 = 85 \text{ mW/cm}^2$ (Xe lamp), $\text{pH}_0 = 6$, $[\text{DMP}]_0 = 2 \text{ mg/L}$, photo catalyst dose = 1 g/L, irradiation time = 180 min. It was proved that pores' diameter significantly influenced degradation process performance.

Thus, in the same operating conditions, composite materials with lower pores' diameter (3.1 nm) allows DMP degradation with an efficiency of 50%. If the aerogel pores' diameter is higher, TiO_2 can deposit within pores interior and exterior forming micro-pores on which recombination process is hampered, assuring better degradation. Another explanation of photo catalyst behaviour is linked with its capacity to adsorb water molecules, to its hydrophobicity and its pores diameter. Thus, the catalyst with higher hydrophilicity and larger pores' diameter exhibits better photocatalytic activity therefore will generate a higher concentration of hydroxyl radicals (generated by water reaction with holes and/or superoxide radicals).

EXPERIMENTAL PART

Photocatalytic experiments were performed using a Heraeus type reactor equipped with a TQ-150-Z3 medium pressure mercury lamp which emits within $\lambda = 320\text{-}550 \text{ nm}$. Reactor volume was 400 mL. Stirring was done with the help of a magnetic stirrer Velp Scientifica with adjustable speed.

Prior to irradiation all samples were bubbled with air ($Q = 50 \text{ L/h}$) in the dark for 30 minutes in order to avoid holes – electrons recombination. Catalyst separations were performed using a KMS laboratory cell CF-2 membrane separation module. Hydrosart type membrane were used for photo catalyst separation. The following reagents were used: DMP (Merck), TiO_2 (Merck), ultrapure water (for preparation of synthetic solutions) obtained in the laboratory with a Milli Q Millipore equipment.

The DMP concentration was determined via gas chromatography using an Agilent 6890N GC-FID equipment.

RESULTS AND DISCUSSION

Influence of photo catalyst dose

In order to assess the photo catalyst dose influence, DMP degradation experiments were performed using a synthetic solution of DMP with the initial concentration of 9.13 mg/L for an irradiation time of 30 minutes and photo catalyst doses between 100-400 mg/L. Obtained results are presented within table 1.

Table 1. DMP degradation experiments on UV-VIS/ TiO_2 system,

$[\text{DMP}]_0 = 9.13 \text{ mg/L} = 4.7 \times 10^{-5} \text{ M}$, irradiation time = 30 min, $\text{pH} = 6.4$, $[\text{TiO}_2] = 100\text{-}400 \text{ mg/L}$

$[\text{TiO}_2]$, mg/L	Efficiency, %	k , min^{-1}
100	89.70	0.0718
200	90.14	0.0725
300	92.11	0.0847
400	89.05	0.0708

The increase of photo catalyst dose in the domain 100-300 mg/L led to an increase of DMP degradation efficiency up to 92.11% (corresponding to a pseudo first order rate constant $k = 0.0847$

min⁻¹ and to a residual DMP concentration of 0.72 mg/L) due to increase of catalyst specific surface available for degradation. Further increase of photo catalyst dose led to a decrease of process efficiency due to light scattering process. Therefore, photo catalyst dose was set to 300 mg/L.

Influence of initial pH

Since one of the main factors affecting heterogeneous photocatalysis is represented by the pH of initial DMP solution, process efficiency was investigated in neutral, acidic and alkaline conditions. Degradation experiments were performed using the same DMP synthetic solution with a concentration of 9.13 mg/L and optimum photo catalyst dose of 300 mg/L. Obtained experimental results are presented within figure 1.

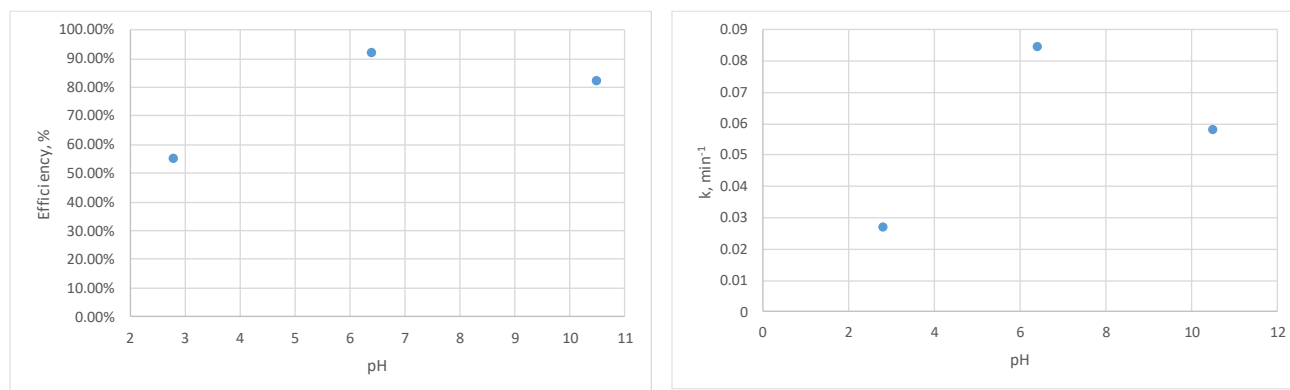


Fig. 1. pH vs. DMP degradation efficiency and pseudo-first order rate constant, [DMP]₀ = 9.13 mg/L = 4.7 x 10⁻⁵ M, irradiation time = 30 min, [TiO₂] = 300 mg/L

Experimental results proved that optimum pH is the neutral one. TiO₂ is an amphoteric with a neutral point of zero charge. Below and above neutral pH, photo catalyst surface will be positively or negatively charged. DMP is neutral for the studied pH domain so there are not significantly attractions between DMP and photo catalyst. Obtained results are in accordance with other studies on DMP photocatalytic degradation [25].

Kinetics

Langmuir-Hinshelwood model is applied for degradation of organic compounds via TiO₂ assisted photo catalysis. DMP degradation rate can be described by the following equation:

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

where r_0 – initial degradation rate of DMP; $[DMP]_0$ – initial DMP concentration; $[DMP]$ – DMP concentration at a given t time; K_{ads} – equilibrium constant of DMP adsorption-desorption on TiO₂ particles; k_r – DMP degradation rate constant; t – irradiation time

By integration, equation 1 transforms into a linear form:

$$\frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r K_{ads} [DMP]_0} \quad (2)$$

Degradation rate constant k_r and equilibrium constant of DMP adsorption-desorption on TiO₂ particles K_{ads} were calculated from graphic plot of equation 2 (presented within figure 2) where: $1/k_r$ is representing the intercept and $1/k_r K_{ads}$ the slope of graphical plot.

Initial pollutant degradation rate r_0 (M min⁻¹) was calculated from experimental data obtained after 30 minutes of irradiation. In order to plot the equation 2, the initial concentration of DMP was varied between 9.13-38.16 mg/L. From the graph's slope and intercept, the following values were calculated: $k_r = 6.76 \times 10^{-6}$ M min⁻¹, $K_{ads} = 5866$ M⁻¹.

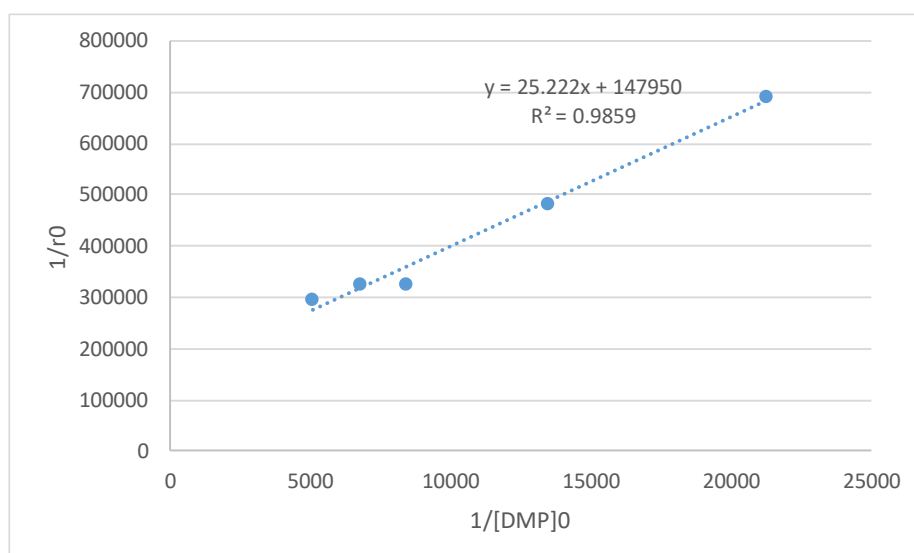


Fig. 2. Langmuir-Hinshelwood model applied to DMP photocatalytic degradation

DMP degradation fits well into Langmuir-Hinshelwood model suggesting that DMP degradation occurs on surface of TiO_2 particles where generated radical species were also adsorbed.

Influence of real wastewater matrix

In order to develop a more cost effective process for DMP removal, the photocatalytic process was coupled with membrane separation in order to separate and reuse the catalyst [27]. Moreover a real wastewater sample with the initial COD = 220 mg O_2/L was used. The sample was spiked with DMP up to an initial concentration $[\text{DMP}]_0 = 20.71$ mg/L. Established optimum dose of $\text{TiO}_2 = 300$ mg/L was added to the sample and following the same procedure as for synthetic solutions degradation tests were performed.

As it was expected the DMP efficiency degradation decreases compared with synthetic solution, after 30 minutes of irradiation to 74.22%. In these conditions a test was performed with the addition of H_2O_2 in a molar ratio of $[\text{H}_2\text{O}_2]/[\text{DMP}]_0 = 1:1$.

Obtained results are presented within table 2.

Table 2. DMP degradation experiments on UV-VIS/ TiO_2 system, irradiation time = 30 -150 min, neutral pH, $[\text{TiO}_2] = 300$ mg/L, real wastewater

Time, min	$[\text{DMP}]$, mg/L	Efficiency, %
30	18.64	12.53
60	14.87	30.22
90	6.981	67.24
120	3.143	85.25
150	2.079	90.24

Since a DMP degradation efficiency of more than 85% was obtained, it was established an optimum irradiation time of 120 minutes for real wastewater samples. Moreover, since in the following cycles the catalyst together with a part of treated solution will be separated using the membrane module (as concentrate) and recirculated in the photocatalytic process it was expected that the initial concentrations for further photo catalytic cycles to be significantly lower and DMP removal efficiency to improve. As for COD, after UV irradiation, the COD value decreases from to 220 mg O_2/L to 81.6 mg O_2/L that corresponds to a mineralization efficiency of 76% (after 150 min).

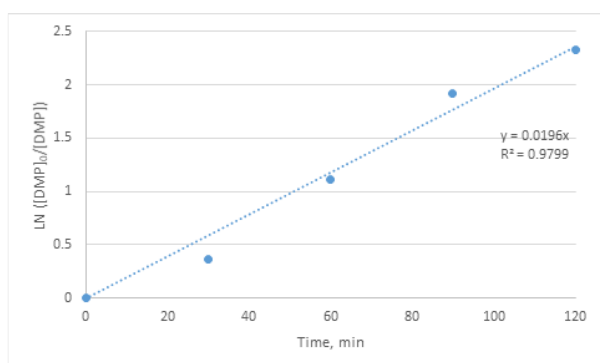
Photo catalyst separation and reuse

Experiments for photo catalyst separation via membrane processes were performed using a 30 kDa cellulose based membrane, that assures an adequate photo catalyst separation at an optimum working pressure at 5 bar (selected using determination of average distilled water flows).

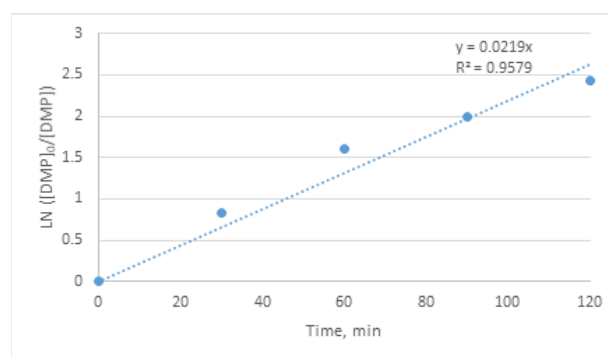
An concentration degree of 1:2 was maintained during all separation experiments. Obtained concentrate was entered in a new DMP degradation cycle and permeate was analysed. The photo catalyst concentration within UV reactor was maintained constant at 300 mg/L and irradiation time was kept at 120 minutes (for cycles 2-4). Obtained results are presented within table 3 and figure 3.

Table 3. DMP degradation efficiency vs. treatment cycle

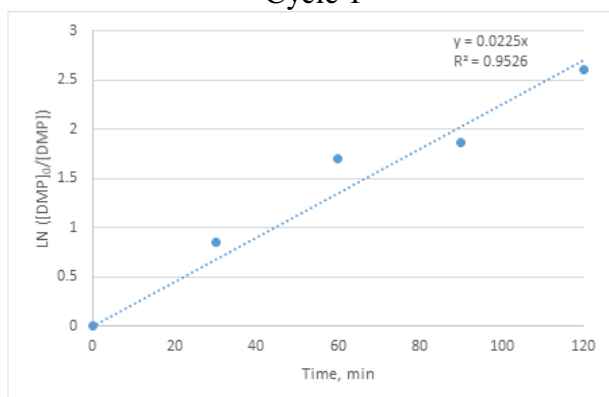
Cycle	[DMP] ₀ , mg/L	[DMP] after UV, mg/L	Efficiency after UV, %	[DMP] after membrane, mg/L	Efficiency after membrane, %
1	21.31	2.079	90.24	0.817	96.17
2	13.33	1.173	91.20	0.280	97.90
3	10.25	0.754	92.64	0.120	98.83
4	11.79	0.964	91.83	0.160	98.64



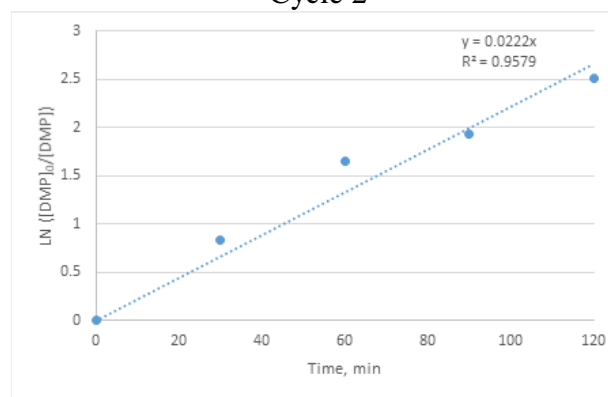
Cycle 1



Cycle 2



Cycle 3



Cycle 4

Fig. 3. Pseudo-first order kinetic for four treatment cycles

DMP removal efficiencies presented values of 91.4775 ± 1.1625 % and DMP degradation rate constants considering a pseudo-first order kinetic were situated within the domain $0.0196 - 0.0225 \text{ min}^{-1} = 3.26 \times 10^{-4} - 3.75 \times 10^{-4} \text{ s}^{-1}$. On the other hand treated solution COD was determined to be $70.125 \pm 12.375 \text{ mg O}_2/\text{L}$.

The fact that DMP removal efficiencies are always higher after passing the membrane module compared with the photocatalyse exit shows that the membrane is playing a double role, both for TiO_2 separation as well as for DMP removal.

Values determined for average distilled water flows after each photo catalyst separation (figure 4) proves that membrane can be further used for catalyst separation. This is sustained also by the values of separation flows for each treatment cycle (figure 5).

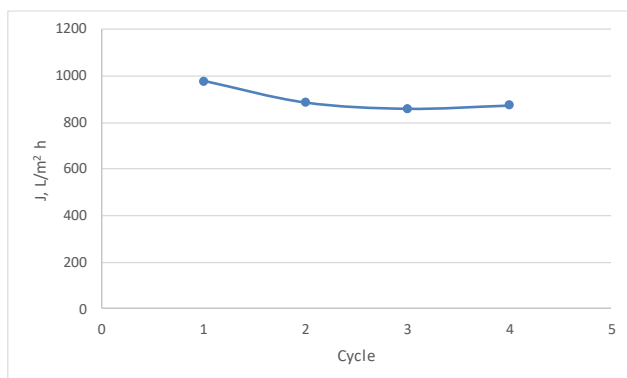


Fig. 4. Average distilled water flows after catalyst separation

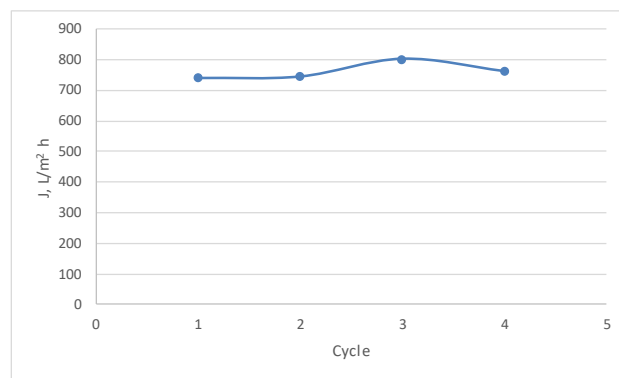


Fig. 5. Separation flows after each treatment cycle

CONCLUSIONS

The process for DMP removal using a coupled system photocatalysis – membrane separation is characterised by the following parameters:

- Photo catalyst dose $[TiO_2] = 300 \text{ mg/L}$;
- Molar ratio $[H_2O_2] : [DMP] = 1:1$;
- Irradiation time = 120 minutes;
- DMP degradation follows a pseudo-first order kinetic with DMP removal efficiencies of $91.4775 \pm 1.1625 \%$ corresponding to a degradation constant rate of $0.0196 - 0.0225 \text{ min}^{-1}$;
- Photo catalyst can be reused for more than 4 treatment cycles;
- Membrane plays a double role, both for photo catalyst separation and reuse and as barrier for advanced removal of DMP. The final DMP removal efficiencies were situated in the domain $96.17 \% - 98.83 \%$.

Hybrid system like photocatalytic membrane reactor with catalyst in suspension seems to be a promising method for the advanced removal of poorly biodegradable compounds like DMP.

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