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# Solar energy for liquid wastewater treatment with novel TiO<sub>2</sub> supported catalysts

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## Abstract

Photocatalytic oxidation is promising technology for removal of recalcitrant pollutants from water. Solar energy can be an interesting radiation source since the operating costs can be lower. However, the use of powder photocatalyst is a major drawback of the technology since suitable separation technologies are required and catalysts recovery is difficult. This work aims to test the suitability of using polymeric supports to immobilize TiO<sub>2</sub> in the reactor and apply it for parabens removal from water by solar photocatalytic oxidation. Polyurethanes (PU) and polydimethylsiloxane (PDMS) membranes were prepared and modified with TiO<sub>2</sub>. While PU materials are only able to adsorb (35% in 1 h) parabens whichever the modification applied, modified PDMS was able to promote parabens photocatalytic oxidation removing 20% in 1 h under solar energy. Plasma/UV modification was able to active PDMS membranes (16% of methyl paraben (MP) removal) and further entrapment of TiO<sub>2</sub> in the polymeric matrix did not improve the process (18% of MP removal). Thus, only the superficial TiO<sub>2</sub> was active. Results show that PDMS is suitable material to support TiO<sub>2</sub> aiming photocatalytic wastewater treatment process using the Sun as a clean and renewable energy source.

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**Keywords:** Solar energy; Contaminants of emerging concern; Parabens; Polymeric supports; Solar photocatalytic oxidation; Supported TiO<sub>2</sub>

## 1. Introduction

Public health and ecological concerns regarding the presence of contaminants of emerging concern such as pharmaceuticals and personal care products (PPCPs) in water are growing. These compounds are not efficiently

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removed by the conventional wastewater treatment due to their refractory characteristics. Thus, are discharged untreated to natural water courses and are being detected in water sources and their potential impact is not well known [1]. Among those substances' parabens are used as preservative and antimicrobial agents in many PPCPs [2]. Parabens constitute an important group of concern also due to their additive estrogenic character. Thus, the seek for suitable tertiary treatment processes is a scientific challenge and different approaches can be found in the literature for the abatement of these contaminants. Advanced oxidation processes such as photocatalytic oxidation, photocatalytic ozonation using solar energy as radiation source appear as suitable alternatives for their removal [3–5].

Photocatalytic oxidation can be performed at ambient pressure and temperature conditions using a catalyst with semiconductor characteristics. This methodology gains more potential specially if solar energy can be used as a costless and clean radiation source.  $\text{TiO}_2$  is the most usual photocatalyst in this approach since it can produce hydroxyl radicals in the presence of suitable radiation. Typically, this catalyst is used as powder to minimize the mass transfer resistances as well as maximizing the catalytic area exposed to radiation energy [6] However, when applied in suspension in the liquid bulk it brings problems for the catalyst recovery and reuse. Alternatively, to allow the catalyst reuse, powder can be immobilized onto a support, that can have different sources. In this study will be focus polymeric supports, such as PU and silicones. Ata et al. [7] immobilized N- $\text{TiO}_2$  onto the polystyrene (PS) surface for photocatalytic oxidation of methylene blue and compared its performance with N- $\text{TiO}_2$  powder. The high amount of N- $\text{TiO}_2$  onto PS surface has similar results with the powder which means low diffusional resistances. Therefore, the immobilization of  $\text{TiO}_2$  in a suitable support has several advantages over its use in aqueous medium suspension. One of them is the fact that no expensive post-treatment is necessary for the recovery of catalyst particles after oxidation from the purified water enabling a continuous operation of the reactor [8]. However, immobilization of  $\text{TiO}_2$  on a support may also bring some disadvantages that may compromise oxidation efficiency. As an example, interaction between sunlight photons as well as reactants with the catalyst's surface may be reduced. Additionally, photocatalytic reaction is limited by the rate of mass transfer of reactants between the bulk fluid and the catalytic surface [9]. Finally, by increasing the thickness of the catalyst film, the internal mass transfer might play a dominant role while limiting the photocatalysis at the support surface. Therefore, a possible strategy to maximize  $\text{TiO}_2$ /photons/reactants interactions is by promoting an effective immobilization of the catalyst in the surface of the support. This may be achieved by several techniques and a plasma surface treatment is one the most effective, particularly when the original surfaces have no chemically reactive groups [10].

In this work, three different materials (one PDMS and two PU) were used to prepare films. These materials present several characteristics which present themselves as highly advantageous for the purpose of this work, namely their transparency and flexibility as well as the ability to adhere to glass. The novelty of this work was focused on the assessment of the oxidation efficiency of parabens when using these polymeric materials as support matrices for the photocatalyst  $\text{TiO}_2$ . For this purpose,  $\text{TiO}_2$  was immobilized in the polymeric films either by entrapment (achieved during films preparation) or superficially (achieved by plasma followed by UV irradiation). The oxidation efficiency of  $\text{TiO}_2$  was then evaluated for both immobilization techniques by using a parabens mixture (methyl-MP, ethyl-EP and propyl-PP paraben). The use of low-cost, clean and renewable energy from the Sun to promote oxidation is an important advantage of such process when compared with other energy sources such as UV lamps that will increase the wastewater treatment energetic cost.

## 2. Materials and methods

### 2.1. Chemicals

MP, EP and PP were purchased from Sigma-Aldrich.  $\text{TiO}_2$  (Aeroxide Degussa P25) was purchased to Evonik Industries. Desmopan<sup>®</sup> 481 (481) and Desmopan<sup>®</sup> 3330 (3330) were obtained from Bayer Material Science AG and Sylgard<sup>®</sup> 184 (PDMS), a kit containing two parts, a liquid silicon rubber base and a curing agent, was purchased from DOW-Corning. Dimethylformamide >95% (DMF) was acquired from Fisher Chemical.

### 2.2. Films preparation and immobilization of $\text{TiO}_2$

Desmopan<sup>®</sup> based PU films were prepared by casting (solvent evaporation). Desmopan<sup>®</sup> was dissolved in DMF to a 10% (w/v) PU solution. This solution was poured into glass Petri plates. Then, the Petri dishes were stored in

an oven, at 60 °C for 24 h and afterwards 1 mm films were obtained and removed from the dishes. Sylgard® 184 PDMS pre-polymer and cross-linking agent were mixed at the ratio of 10:1 (wt/wt) and degassed under vacuum. Films with 2 mm thickness were obtained by curing at 65 °C during 4 h.

Several approaches were followed to immobilize TiO<sub>2</sub> into the polymeric membranes. The first method was the entrapment of the photocatalyst in the polymeric matrix (E). During this methodology, 1.27 mg of TiO<sub>2</sub>/g of polymer were homogeneously mixed in the liquid polymer and once curing occurred, a uniform distribution of the agent was obtained. The other approach involved the linkage of TiO<sub>2</sub> to the surface of the films, which was achieved by creating radicals on the polymer's surface by argon plasma irradiation (P). For that purpose, a laboratory and small-scale production plasma system FEMTO (low pressure plasma), manufactured by Diener Electronics, with a stainless-steel plasma chamber of 100 mm diameter and 270 mm length, was used for the plasma surface modification experiments. The PU membranes were placed 80 mm from the electrode. The membranes were plasma treated with Argon, a chamber pressure of 0.6 mbar, for 2 min and energy power of plasma of 100 W [11]. Then, two methodologies were evaluated: a) a thin layer of TiO<sub>2</sub> solution (70 mg/L) was poured onto the plasma-treated surface and further plasma irradiated (Plasma); b) the plasma-treated membranes were dipped into a (70 mg/L) TiO<sub>2</sub> aqueous solution and UV energy irradiated in an UV chamber (Dr. Grobel UV-Elektronik GmbH, Model BS-02) for 30 min (plasma/UV). Afterwards, all the films were washed abundantly with water and dried until constant weight. Finally, a combination of both techniques was applied. Therefore, films with entrapped TiO<sub>2</sub> were prepared and further treated with plasma/UV following the previously described methodology (E+P).

### 2.3. Solar photocatalytic oxidation experiments

The photocatalytic activity of the prepared materials was evaluated under sunlight conditions and at dark conditions. Experiments were carried out at the Department of Chemical Engineering of the University of Coimbra (40.186622°, -8.4182372°). A mixture of 3 parabens: MP, EP and PP was prepared (1 mg/L of each in ultrapure water). A circular membrane covering the glass reactor (50 mL) bottom were placed and the liquid stirring was promoted by bubbling air. The reactor is exposure to the sunlight radiation directly without any concentrator. The average solar radiation power was around 700 ± 150 W/m<sup>2</sup> during the experiments.

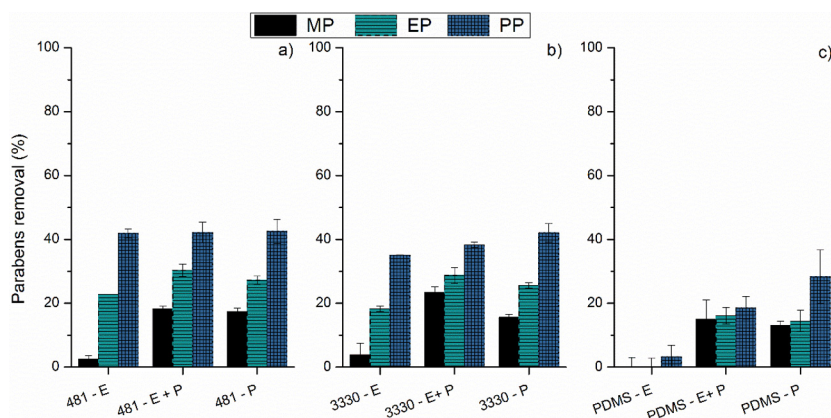
The concentration of parabens during the experiments was measured by the high-performance liquid chromatography (HPLC) equipped with a diode array detector (DAD) (UFLC, Shimadzu). The mobile phase is composed by a ratio of 50:50 of methanol and ultrapure water acidified with 0.1% of phosphoric acid. The flow rate of this phase through the column C18 (SiliaChrom) at 40 °C was 0.5 mL/min. The detection of parabens was performed at a wavelength of 255 nm.

## 3. Results and discussion

### 3.1. TiO<sub>2</sub> immobilization methodology effect

The TiO<sub>2</sub> immobilization methodology is a parameter that may influence the photocatalytic effect of TiO<sub>2</sub> over the paraben's mixture degradation. In a primary assessment of the immobilization methodology effect the 3 main strategies were evaluated: entrapment (E), plasma/UV treatment (P) and entrapment + plasma/UV treatment (E+P). Fig. 1 shows parabens removal by photocatalytic oxidation after 1 h of sunlight energy (700 ± 150 W/m<sup>2</sup>) exposure using as catalyst the materials referred.

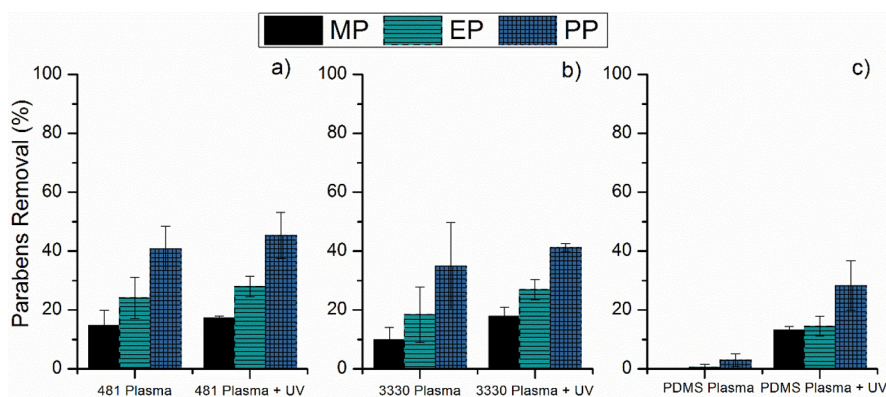
The parabens removal is not a function of TiO<sub>2</sub> immobilization method when the support is PU (either 481 or 3330). Still, the use of plasma/UV seems to slightly increase MP removal when compared to the case where the membranes were not subjected to plasma treatment, probably due to the increase in their hydrophilicity [10]. Different results are found for PDMS membranes. While degradation was very low (below than 5%) when membranes with entrapped TiO<sub>2</sub> (E) were used, removals of about 30% for PP were obtained when PDMS was modified using plasma/UV and TiO<sub>2</sub> was added to the surface. Moreover, no further improvement was achieved when TiO<sub>2</sub> was added by both methods (E+P). Thus, one may conclude that only superficial TiO<sub>2</sub> is available for the degradation reactions since it is exposed to both pollutants and light energy. Light has further difficulty on reaching TiO<sub>2</sub> in the polymeric matrix. Besides, diffusional resistances difficult pollutants to get those active sites.



**Fig. 1.** TiO<sub>2</sub> immobilization methodology over parabens removal for (a) Desmopan 481; (b) Desmopan 3330; (c) PDMS supports.

### 3.2. Selection of surface modification methodology

When working with hydrophobic materials, entrapment of the catalyst in the polymeric matrix may not be a suitable approach since no contact of the water with the photocatalytic agent will occur. In such cases, and as already confirmed in Section 3.1, polymers' surface modification with immobilization of the catalyst showed to be a more convenient method, by promoting contact between contaminants and TiO<sub>2</sub> and leading to the production of hydroxyl radicals. The degradation of parabens mixture was used as evaluation criteria for the selection of the better surface immobilization solution for TiO<sub>2</sub> (Plasma or Plasma/UV). This was performed using sunlight radiation ( $700 \pm 150 \text{ W/m}^2$ ) along 1 h of exposure (Fig. 2). The incorporation method of TiO<sub>2</sub> will represent an important role for the paraben's degradation performance.

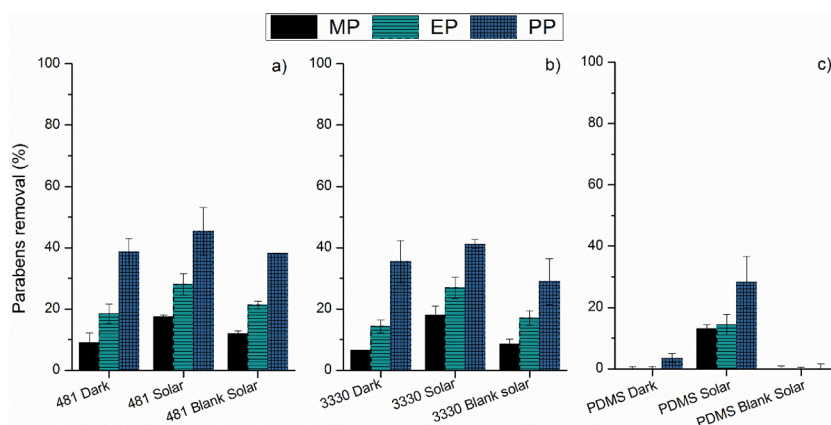


**Fig. 2.** Surface modification method for immobilization of TiO<sub>2</sub>, (a) Desmopan 481; (b) Desmopan 3330; (c) PDMS supports.

The PUs (Desmopan 481 and Desmopan 3330) do not present significant differences in terms of degradation for both incorporation methods (Plasma and Plasma/UV). The results are quite similar but slightly higher when UV radiation was used. However, for PDMS this difference was more evident which proved the beneficial effect of UV radiation on TiO<sub>2</sub> incorporation. The application of UV radiation leads to a more hydrophilic PDMS [12] which has great relevance for TiO<sub>2</sub> activity since water with catalyst will promote the production of hydroxyl radicals. In fact, water presents an important role for the efficiency of microcontaminants removal and hydrophilic membrane improves the parabens degradation (Fig. 2). Another feature relevant for this modification methodology could be related with diffusional resistances. This modification could make the membrane more permeable allowing water and contaminants diffusion to reach active sites of catalyst [12].

### 3.3. Supports adsorption effect

Regarding to the previous results the best performance (Fig. 1) seems to be for PU membranes. Meanwhile, it is important to confirm if parabens removal is due to degradation through the catalyst interaction with solar energy or if were just adsorbed to the membrane's surface. This analysis was made comparing the pollutants removal at dark conditions results with those obtained by solar photocatalytic oxidation for membranes prepared by plasma/UV. Also, the adsorption capacity at dark conditions of the membranes without modification was assessed. In fact, the microcontaminants can be easily adsorbed onto the polymeric surface, due to their polarity. It is also expected that the increase of chain length decreases the polarity which makes PP more nonpolar than EP and even more than MP. Fig. 3 compares the results using the modified membranes at dark and solar conditions. For comparative purposes, solar experiments were also performed using non-modified membranes.



**Fig. 3.** Comparison of adsorption and solar radiation with and without TiO<sub>2</sub> for (a) Desmopan 481; (b) Desmopan 3330; (c) PDMS supports.

For PUs (481 and 3330), the degradation of parabens was almost negligible, which indicates their adsorption on the membrane surface as the main mechanism behind their removal from water using these materials (Fig. 3a,b). Besides, even using the non-modified PU (Blank Solar experiments) it was possible to achieve a parabens removal percentage similar to the one obtained when the membranes were modified with TiO<sub>2</sub> (481 Solar and 3330 Solar). This highlights that only pollutants adsorption on the polymeric membrane is occurring when PU materials are used. Thus, the presence of TiO<sub>2</sub> is not important for the process nor the interaction with the solar energy. Moreover, it is possible to see the effect of parabens polarity. The rate of adsorption of each paraben increased with the decrease of polarity since PP presented the highest removal comparing to the other parabens. On the other hand, it is possible to see performance differences for the PDMS membranes subjected to different conditions. For the dark conditions and the membrane without TiO<sub>2</sub> the parabens degradation was almost null. Under the sunlight energy ( $700 \pm 150 \text{ W/m}^2$ ) with the TiO<sub>2</sub> incorporated onto the PDMS membrane was possible to achieve about 15% of removal for MP and EP while achieving about 30% for PP removal. Therefore, it is possible to conclude that with the modified PDMS membranes subjected to light energy, hydroxyl radicals were produced leading to parabens degradation and the contaminants removal was not only due to adsorption. The rates of hydroxyl radical regarding to parabens increases with the chain length [4]. Besides, the presence of TiO<sub>2</sub> is crucial for the photocatalytic activity since negligible parabens removal occurred when PDMS membrane without TiO<sub>2</sub> was used under sunlight conditions.

## 4. Conclusions

PU materials were only able to remove parabens from water by adsorption and no catalytic oxidation was promoted. Contrarily, when PDMS membranes were tested, parabens adsorption was negligible. Thus, parabens removal by TiO<sub>2</sub> modified PDMS membranes under solar energy was achieved by hydroxyl radical's production followed by organic contaminants oxidation. When comparing the performance of membranes modified by different

processes it was concluded that TiO<sub>2</sub> entrapped in the polymeric matrix was not active. Differently, TiO<sub>2</sub> added to PDMS surface by Plasma/UV was the main responsible for the photocatalytic activity. This study proved for PDMS support 30% of PP removal in 1 h of reaction. These results show that PDMS is an interesting material to support TiO<sub>2</sub> in photocatalytic wastewater treatments overcoming the drawback associated to the use of powder catalysts. Thus, this may promote the application of photocatalytic oxidation using clean and cheap solar energy for water treatment and reuse, giving a contribution to ensure access to affordable, reliable, sustainable and modern energy for all (SDG7).

### CRedit authorship contribution statement

**Rui C. Martins:** Conceptualization, Formal analysis, Writing – original draft, Writing – review & editing, Funding acquisition. **Ângelo Sacras:** Data curation, Investigation, Formal analysis. **Sanja Jovanovic:** Data curation, Investigation, Formal analysis. **Patrícia Alves:** Writing – review & editing. **Paula Ferreira:** Conceptualization, Writing – review & editing. **João Gomes:** Conceptualization, Supervision, Writing – original draft, Writing – review & editing, Funding acquisition.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### References

- [1] N.H. Tran, M. Reinhard, K.Y.H. Gin, Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions-a review, *Water Res* 133 (2018) 182–217.
- [2] M. Bosio, B. Souza-Chaves, J. Gomes, M. Gmurek, R. Martins, E. Saggiaro, M. Dezotti, J.P. Bassin, M.E. Quinta-Ferreira, R.M. Quinta-Ferreira, Electrochemical oxidation of paraben compounds and the effects of byproducts on neuronal activity, *Energy Rep* 6 (2020) 903–908.
- [3] T. Velegraki, E. Hapeshi, D. Fatta-Kassinos, I. Poullos, Solar-induced heterogeneous photocatalytic degradation of methyl-paraben, *Appl Catal B* 178 (2015) 2–11.
- [4] J. Gomes, I. Leal, K. Bednarczyk, M. Gmurek, M. Stelmachowski, A. Zaleska-Medynska, M.E. Quinta-Ferreira, R. Costa, R.M. Quinta-Ferreira, R.C. Martins, Detoxification of parabens using UV-A enhanced by noble metals – TiO<sub>2</sub> supported catalysts, *J Environ Chem Eng* 5 (2017) 3065–3074.
- [5] E. Domingues, F. Rodrigues, J. Gomes, M.J. Quina, S. Castro-Silva, R.C. Martins, Screening of low-cost materials as heterogeneous catalysts for olive mill wastewater Fenton's peroxidation, *Energy Rep* 6 (2020) 161–167.
- [6] S.C.A. Sousa, J.C. Cardoso, O.C. Monteiro, Improved performance of titanate nanostructures for manganese adsorption and posterior pollutants photocatalytic degradation, *J Photochem Photobiol A: Chem* 378 (2019) 9–16.
- [7] R. Ata, O. Sacco, V. Vaiano, L. Rizzo, G.Y. Tore, D. Sannino, Visible light active N-doped TiO<sub>2</sub> immobilized on polystyrene as efficient system for wastewater treatment, *J Photochem Photobiol A Chem* 348 (2017) 255–262.
- [8] D. Mukherjee, S. Barghi, A.K. Ray, Preparation and characterization of the TiO<sub>2</sub> immobilized polymeric photocatalyst for degradation of aspirin under UV and solar light, *Processes* 2 (2014) 12–23.
- [9] R. Klawekla, M. Arend, W.F. Hoelderich, A Review of mass transfer controlling the reaction rate in heterogeneous catalytic systems, mass transfer - advanced aspects, InTech, ISBN: 978-953-307-636-2, 2011, pp. 667–684.
- [10] H.R. Khaledian, P. Zolfaghari, V. Elhami, M. Aghbolaghy, S. Khorram, A. Karimi, A. Khataee, Modification of immobilized titanium dioxide nanostructures by argon plasma for photocatalytic removal of organic dyes, *Molecules* 24 (383) (2019).
- [11] P. Alves, R. Cardoso, T.R. Correia, B.P. Antunes, I.J. Correia, P. Ferreira, Surface modification of polyurethane films by plasma and ultraviolet light to improve haemocompatibility for artificial heart valves, *Colloids Surf B* 113 (2014) 25–32.
- [12] K. Efimenko, W.E. Wallace, J. Genzer, Surface modification of Sylgard-184 Poly(dimethyl siloxane) networks by ultraviolet and ultraviolet/ozone treatment, *J Colloid Interface Sci* 254 (2002) 306–315.