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Paul Henri Allé, Patricia Garcia-Muñoz, Kopoin Adouby, Nicolas Keller, Didier Robert. Efficient photocatalytic mineralization of polymethylmethacrylate and polystyrene nanoplastics by TiO₂/β-SiC alveolar foams. *Environmental Chemistry Letters*, Springer Verlag, 2020, 10.1007/s10311-020-01099-2 . hal-03093306

HAL Id: hal-03093306

<https://hal.archives-ouvertes.fr/hal-03093306>

Submitted on 5 Jan 2021

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Efficient photocatalytic mineralization of polymethylmethacrylate and polystyrene nanoplastics by TiO₂ /β-SiC alveolar foams

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Abstract

Many household wastewaters contain Microplastics (MPs) and nanoplastics (NPs). Most of this type of pollution is not stopped by current wastewater treatment plants provoking their entrance into the global aquatic systems. This is an emerging issue and potential threat to marine life and human health. However, advanced technologies for efficient MPs and NPs control and elimination remain largely underdeveloped. Heterogeneous photocatalysis represents an attractive and efficient decomposition technique for the nanoplastic particle degradation. The first objectives of this work were i) to study the feasibility of nanoplastic degradation by photocatalysis and ii) to determine the influence of certain reaction parameters i.e. the flowrate, the pH₀ and the light intensity on the photocatalytic degradation of calibrated polymethylmethacrylate (PMMA) and polystyrene (PS) nanoparticles with TiO₂-P25/β-SiC foams under UV-A. The first results are very encouraging, because to our knowledge, we are the first to show that it is possible to mineralize PMMA and PS nanobeads

by UV-A photocatalysis. We were able to convert in 7 hours, 50% of an aqueous suspension loaded with PMMA nanobeads (TOC = 12 mg/l) by working at an irradiance of 112 W/m², with a flowrate of 10 mL/min and at initial pH value of 6.3, using TiO₂-P25/β-SiC foams in a flow-through mode. We also showed that the photocatalytic treatment can be applied to various polymers, such as polystyrene and PMMA.

Keywords: nanoplastic, polymethylmethacrylate, Polystyrene, water treatment, photocatalysis, β-SiC

1. Introduction

Nowadays, we can find micro- and nano-sized plastics (MPs and NPs) worldwide in coastal regions and aquatic ecosystems transported by wind and ocean currents. In a recent report of the European Union (European Commission 2017), microplastics most commonly defined as man-made plastic items smaller than 5 mm, are of particular concern for the marine and inland aquatic environment. The scientific community has not given a precise definition for nanoplastics but we can consider that they represent plastic particles less than ten micrometers. The potential impacts of micro and nanoplastics present in products on the (aquatic) environment and possibly on the human health have generated concerns in Member States of the European Union and worldwide, with several implemented or proposed bans/restrictions taking various different forms.

In the past decade, there has been a major change in the pollution potential for nanoplastic pollution (Moore, 2008) in the oceans, with the shift from natural exfoliators to nanoplastics in skin cleansers. Consequently, certain NPs such as nanobeads derived from toothpaste and facial cleanser are directly introduced into wastewater by human activities. In the 1990s, these nanoplastics were mainly present in hand cleaners, in the form of soaps plastic-sand liquids, but recognized as a minor source of plastic pollution (Gregory, 1996). However, as nanoplastics have now replaced natural exfoliating materials (pumpkin seeds, apricot kernels...) in facial cleansers, many consumers now

have a product containing nanoplastics (nanobeads) at home and uses it daily. Even if some countries have started to ban personal care products containing plastic nanobeads (SAM 2019), due to their persistence, the threat will still be here for long time to the environment (Nemls et al. 2019).

Then the nanobeads travel through the wastewater systems of the cities, but because of their small size a large part pass through the filters of the wastewater plants (typically coarse, >6 mm, and fine filters, 1.5–6 mm Vesilend, 2003) and enter the oceans (Browne et al., 2007). Thus, wastewater treatment plants (WWTPs) can be also considered as one of the most important source points of MPs and NPs release (Cole 2011 and Talvitie 2015) in the aquatic and marine environment. While the larger plastic particles are efficiently removed in WWTPs, this is not the case for the NPs that are entering and accumulating in the aquatic environments (Murphy 2016). MPs and NPs can be considered as emerging pollutants of growing particular concern for human health and environment. NPs are strong adsorbents for hydrophobic toxic pollutants and may affect their fate and toxicity in the environment. For example, photosynthesis disruption was reported in studies investigating effects on phytoplankton. Current literature suggests that the plastic particle toxicity depends on the concentration, the particle size, the exposure time as well as the shape and the type of the polymers.

In a recent review, authors describe nanoplastic removal methods in wastewater that include sorption and filtration, removal based on chemical phenomena, biological ingestion treatments and advanced oxidation technologies (Padervand et al 2020). Among the different advanced oxidation technologies (AOTs) able to remove nanoplastics from wastewater, heterogeneous photocatalysis represents an attractive and efficient technique for the degradation of these particular pollutants. Heterogeneous photocatalysis is the most efficient and economically most feasible method from the mineralization point of view, compared to ozonation or chlorination. Moreover, with chlorination, there is the risk of forming organochlorine intermediates which are carcinogenic. Nanofiltration

could be considered, but it is an expensive technique, which does not eliminate plastic nanoparticles but displace this pollutant. There is also a great risk of fouling the filters.

Very few works has been done on the elimination of plastics particles by heterogeneous photocatalysis and most of them concern polymeric films such as Polyvinylchloride PVC (Horikoshi et al 1998), Low Density PolyEthylene LDPE (Ali et al 2016, Tofa et al 2019) and Polystyrene PS (Shang et al 2003). To our knowledge, in the literature only one example concerns the photocatalytic removal of polymer nanoparticles (Wang et al 2019). The authors used a photocatalytic TiO₂-based micromotor (Au@mag@TiO₂, mag = Ni, Fe) for the elimination of nanoplastics contained and extracted from washing powders, toothpastes and face cleansing creams.

Although TiO₂ in the powder form demonstrated high photocatalytic activity under UV-A light in the degradation of a wide range of molecules in water, the filtration process required after the water treatment makes its application on an industrial scale complex and costly. To solve this problem, we used open-cell β -SiC alveolar foams as photocatalyst support. The integration of these materials in a photoreactor allows operating in a continuous mode (Kouamé et al 2013, M'Bra et al 2019).

In this manuscript, we use a β -SiC foam supported TiO₂-P25 photocatalyst integrated into a flow-through photoreactor for nanoplastics removal in wastewater. We took calibrated polymethylmethacrylate (PMMA) and polystyrene (PS) nanobead particles as model systems for microplastic pollutants. The photocatalytic performances have been evaluated by analyzing the time-evolution of the total organic carbon (TOC) upon UV-A irradiation. The influence of some important operating parameters (ie. pH, flowrate, incident irradiance in the photoreactor, particles size...) on the photocatalytic removal of PMMA and PS nanobeads has been studied in order to optimize the process.

2. Experimental part

2.1. Photocatalytic materials and calibrated polymer nanobeads

Open-cell β -Silicon carbide alveolar foams were employed as structured support for the Aeroxide[®] TiO₂-P25 photocatalyst (Evonik, Germany) due to their high chemical and thermal stability, as well as their large open porosity that maintain ultra-low pressure drop and favors the light transmission into the reactor core. In order to obtain a homogeneous TiO₂ coating inside the 3D structure of the foam, the dip-coating technique followed by thermal annealing has been employed to obtain a high adhesion of the TiO₂-P25 coating on the substrate. For a detailed preparation protocol, please refer to Marien *et al* 2019. Finally, these foams were integrated in a photoreactor especially designed for this study (see figure 1).

In order to measure the efficiency of the process, we used commercial monodisperse suspensions of polymers supplied by Microparticles GmbH. The calibrated polymer nanoparticles have a high monodispersity (CV < 3.8 %), spherical shape, high optical transparency, high mechanical, and chemical stability as well as low density (1,05 g/cm³). Polystyrene and polymethylmethacrylate products in the nanometer size range are as 5 % (w/v) aqueous suspensions. For this study, we used three monodisperse suspensions of nanobeads: one with polymethylmethacrylate nanobeads (NBs-PMMA (C₅O₂H₈)_n) particles size: 105 nm with a standard deviation of 0.005 μ m) and two with polystyrene nanobeads (C₈H₉)_n) (NBs-PS1 particles size: 140 nm, Standard Deviation : 0.005 μ m and NBs-PS2 particles size: 508 nm Standard Deviation : 0.015 μ m).

2.2. Photocatalytic reactor and analysis

Photocatalytic experiments were performed in a recirculation mode photoreactor. The photocatalytic system is presented in detail in figure 1. Three TiO₂-P25/ β -SiC foams (diameter 38 mm; length 30 mm) were inserted in the tubular quartz reactor (diameter 40 mm; length 200 mm, volume 250ml) surrounded by 2 to 4 UV-A lamps (1 cm between the quartz tube and the lamps). Each foam sample (10 g) contains 10 \pm 1 wt% of TiO₂. Effluent inlet and outlet diameters are 5 mm. Each lamp (Philips T5 15W 10 Actinic BL) have a maximum emission wavelength at 354 nm. A volume

of 600 ml of aqueous nanoplastic suspension to be treated is introduced into the system. These suspensions are prepared by mixing 300 mg of commercial monodisperse solution in 1000 mL of distilled water. This corresponds to an initial Total Organic Carbon, (TOC_0) around 12 mg/L. The reactor was connected to a peristaltic pump (Masterflex L/S, Cole Parmer) to control the flow rate of the nanobeads suspension in the photoreactor. The lamps are switched on after 30 min under recirculation in the dark for allowing the establishment of the equilibrium of the system. Except for the experiments with pH control, all the tests were carried out at free pH_0 .

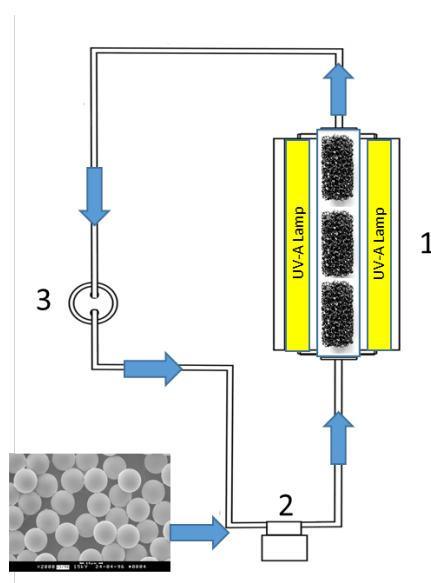


Fig. 1. Photocatalytic tubular reactor made with (1) a 4 UV-A lighting system + a quartz tube + 3 $\text{TiO}_2/\beta\text{-SiC}$ foams, (2) polymer nanobeads solution and (3) a peristaltic pump.

During the process under irradiation, 10 mL of solution were taken at regular time-intervals to evaluate the Total Organic Carbon without filtration. The TOC measurement is not directly related to the concentration of polymer nanobeads during irradiation. However, it can demonstrate the transformation of polymer nanoparticles under the action of photocatalysis. TOC measurements were determined by a Shimadzu TOC-L apparatus.

3. Results and discussion

The main objective of this work is to demonstrate the feasibility to degrade polymer nanobeads in aqueous solution by heterogeneous photocatalysis with $\text{TiO}_2\text{-P25}/\beta\text{-SiC}$ foams under UV-A irradiation. The tests were carried out on diluted suspensions of NBs-PMMA and NBs-PS corresponding to approximately 12 mg/L of total organic carbon (TOC_0). We followed the TOC concentration of unfiltered solutions during the UV-A irradiation time. The residual concentration of organic carbon in the solution during irradiation process is a good indicator of the polymer degradation, although the TOC is not directly related to the concentration of nanoplastic during irradiation. Indeed, the value of the TOC during the irradiation represents the intermediates of degradation of the polymer nanoparticles which have been photo-oxidized by TiO_2 under irradiation, but also the polymer nanoparticles which remains in suspension.

The first preliminary results showed that it is possible to oxidize PMMA and PS nanobeads in the presence of $\text{TiO}_2\text{-P25}/\beta\text{-SiC}$ foams. As it can be observed in figure 2a, TOC evolution without irradiation and photolysis (without TiO_2) of NBs-PMMA are very low, while after 7 h of irradiation with $\text{TiO}_2\text{-P25}/\beta\text{-SiC}$, the half of the organic carbon contained in the PMMA nanobeads is transformed into carbon dioxide, and consequently mineralized. The reaction follows a zero-order reaction kinetics (limitation by mass transfer) with a kinetic rate constant of 0.0141 mg/L.min which is conventional in supported catalysis (Ollis 2018).

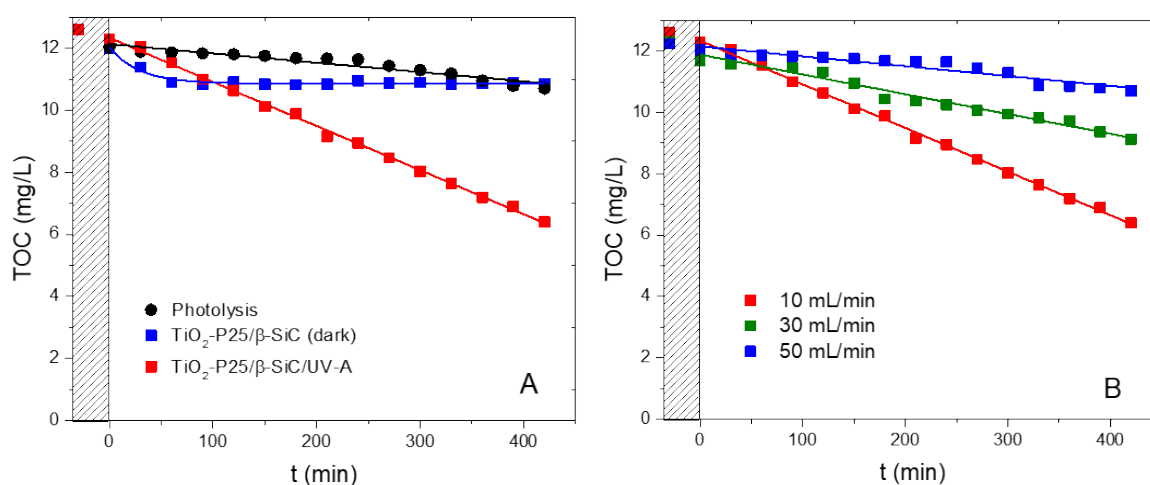


Fig. 2. a) Mineralization kinetic of NBs-PMMA on TiO₂-P25/β-SiC without and under UV-A irradiation and photolysis (Flow rate = 10 mL/min, pH₀ = 6.3); b) Flow rate effect on the photocatalytic degradation of NBs-PMMA solution on TiO₂-P25/β-SiC (pH₀ = 6.3). A pseudo-zero order model is applied to the TOC evolution data set.

The oxidation rates and the efficiency of the photocatalytic system are highly dependent on a number of operation parameters that govern the kinetics of the photomineralization. Therefore, we have determined the influence of some parameters like flow rate, pH₀ and light intensity on the photocatalytic degradation of the nanoplastics.

3.1. Flow rate influence

As shown in Figure 2b, a significant effect of the flow rate on the nanoplastic photocatalytic degradation is observed, which means that an external transfer limitation intervenes, at least at low flowrate values. The higher the flowrate, the lower the kinetic rate constant and consequently the lower the TOC conversion achieved. After 7 h of irradiation at a flowrate of 50 mL/min, only 14% of PMMA has been mineralized with a kinetic rate constant of 0.0032 mg/L.min, while this percentage increases to 26% and 50% by working at 30 mL/min and 10 mL/min, respectively, with kinetic rate constants of 0.0066 mg/L.min and 0.01410 mg/L.min, respectively. The residence time of a polymer nanobeads in the photoreactor for a single pass corresponds to 25 min for a flow rate of 10 mL/min, 8.4 min for 30 mL/min and 5 min for 50 mL/min. Indeed, this can be explained by the size of the nanobeads which are much larger than a simple molecule of pesticide or dye (M'Bra et al. 2019). Most importantly, the aggregates of TiO₂ on the foams have sizes of comparable range to those of the nanobeads (a few hundred nanometers). Consequently, there is little point of contact between the solid (NBs-PMMA) and the TiO₂ surface, for this reason the kinetics seem to be long compared to organic molecules.

3.2. Initial pH effect

pH is one of the most important operating parameters that affect particularly the surface charge of the TiO₂ photocatalyst crystallites. For Degussa TiO₂-P25, the point of zero charge (pzc) occurs at pH ~6.3 (Carabin et al 2015). At free pH 6.3, we are working under optimum conditions for the photo-oxidation which shows mineralization rate values of 0.0141 mg/L.min (figure 3a). On the contrary, at pH 9, the TiO₂ surface is negatively charged and a part of the ester functions of the nanobeads surface can be hydrolyzed into negative carboxylate groups, causing electrostatic repulsion forces and thus showing a drastic reduction of the TOC conversion (17% in 7 h). Under these conditions, these repulsion forces between TiO₂ and NBs-PMMA lead to hinder the photocatalytic reactions as can be inferred from the decrease of the kinetic constant rate down to k = 0.0116 mg/L.min. At acidic pH, there will be competition between the chloride ions (coming from the HCl solution) and NBs-PMMA towards the active sites of the TiO₂ surface.

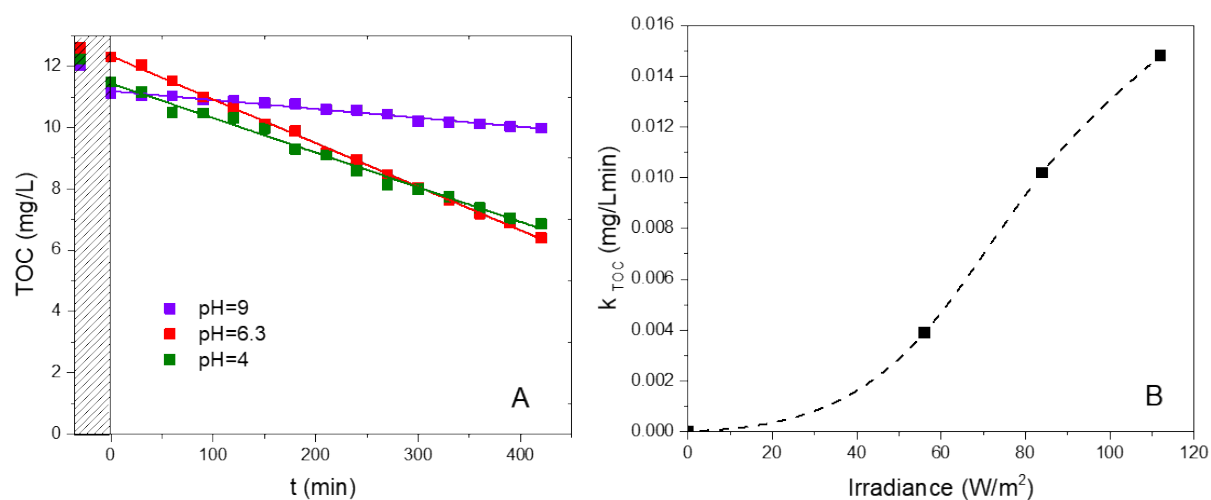


Fig.3. a) pH influence and b) UV-A light intensity influence on the photocatalytic mineralization of NBs-PMMA using TiO₂-P25/β-SiC foams (flow rate = 10 mL/min). Lines show the pseudo-zero order model fitted to each data set.

3.3. Light intensity influence

At high light intensity, the reaction rate is found to be proportional to the square root of light intensity. However, at the low-intensity level, the photodegradation rate is directly proportional to the light intensity (Chen et al 1998). Light intensity effect has been studied by varying the number of UV-A lamps irradiating the TiO₂-P25/β-SiC foams (Figure 3b), in this case also the results are consistent because the process is more efficient with an irradiance value of 112 W/m²) rather than 56 W/m². In our type of reactors with integrated photocatalytic 3D materials (TiO₂/β-SiC foams in our case), it is necessary to achieve efficient exposure of the catalyst to light irradiation. Without photons of appropriate energy, the catalyst shows no activity. In fact, in a photocatalytic reactor, besides conventional reactor complications such as mixing, mass transfer, reaction kinetics, catalyst installation, etc., an additional engineering factor related to the illumination of catalyst becomes relevant. The illumination factor is of utmost importance since the amount of catalyst that can be activated determines the water treatment capacity of the reactor. Figure 3b shows the influence of the irradiance on the removal degree of NBs during the photocatalytic process. The reaction rates and so the TOC conversions increase when increasing the light irradiance from 56 W/m² to 112 W/m², with kinetic rate constants of 0.0039 mg/L.min and 0.0148 mg/L.min.

3.4. Chemical structure and particles size effects

In order to show that the photocatalytic process can be effective for polymers with different molecular structures, we have applied it for the removal of polystyrene nanobeads of two different average sizes: NBs-PS1 (particles size: 140 nm) and NBs-PS2 (particles size: 508 nm). As it can be observed in figure 4, for a similar particle size, PMMA mineralization appears to be faster ($k_{\text{NBs-PPMA}} = 0.0148 \text{ mg/L.min}$ while $k_{\text{NBs-PS1}} = 0.0065 \text{ mg/L.min}$). This is probably due to the C=O and C-O bonds which are more "breakables" than the C-C, C=C and C-H bonds of polystyrene. Indeed recently, Dinood et al (2019), have highlighted the photocatalytic degradation mechanism of polystyrene films by FTIR. According to these authors, PS photodegradation starts with the phenolic rings of PS absorbing UV radiation and getting excited into singlet states and then various photochemical

reactions could be originated from excited triplet from of benzene rings with CC and/or C–H bond scissions at various sites could be initiated. FTIR spectra have shown the formation of CO, –OOH, –OH... groups. But this implies, that the transformation of organic carbon into CO₂ (mineralization) is a step which takes place at the end of the mechanism. On the contrary in the case of PMMA, one of the primary steps is the abstraction of the ester side group -OCH₃ (Vinu et 2008). The polymer radical fragment thus produced can form the formaldehyde, which finally forms carbon dioxide, which explains the faster mineralization of PPMA.

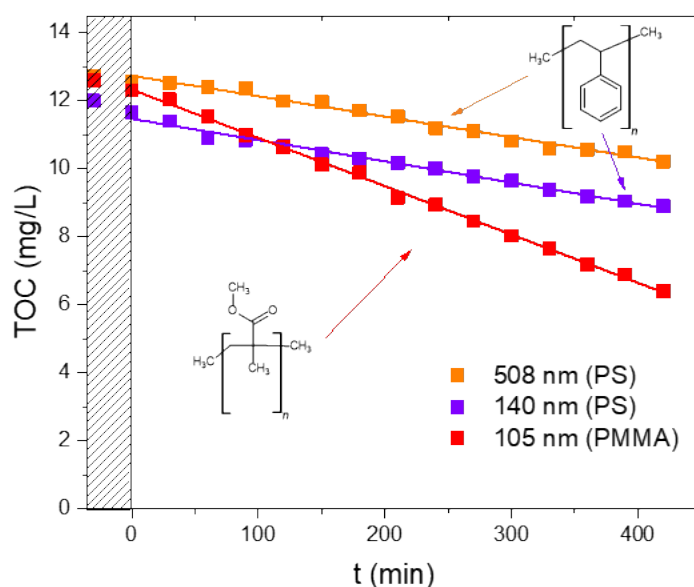


Fig 4: Comparison of photocatalytic mineralization of NBs-PMMA and NBs-PS1/PS2 (Flow rate: 10 mL/min, pH₀: 6,2)

Regarding the influence of particles size (PS) on the photomineralization, the effect is less visible, because there is probably a degradation of the PS nanobeads surface. Nevertheless, the results of figure 4 show that the kinetics are faster with the 105 nm PS nanobeads than those of 540 nm. This result seems logical because smaller particles lead to larger contact area with TiO₂ photocatalyst.

4. Conclusion

We have shown that it is possible to mineralize nanobeads of PMMA and PS under irradiation of TiO₂ in aqueous solution. Working at an irradiance of 112 W/m², with a flowrate of 10 mL/min and at initial pH value of 6.3, using TiO₂-P25/β-SiC foams in a flow-through mode allowed to reach 50% of TOC conversion after 7 h of treatment in the removal of PMMA nanoplastics. We also showed that the photocatalytic process can be effective for polymers with various molecular structures, such as polystyrene and PMMA and also with different average sizes of nanobeads. It is now necessary to optimize the process, but also to better understand the degradation mechanisms. However, one of the most important challenges to take up in this work will be to find an analytical procedure that is easy to implement. In the rest of this work, we have planned to couple several photoreactors in a row for processing in a single pass, which will be better for an application in the case of real effluents.

Acknowledgements

The authors of this article thank Campus France for the grant awarded to Paul Henri ALLE.

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