

Elimination of nanoplastics from water by Photocatalytic process: a preliminary study

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INTRODUCTION and PROBLEMATIC

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. The potential impacts of micro and nanoplastics present in products on the (aquatic) environment and possibly on the human health have generated concerns in worldwide.

In the past decade, there has been a major change in the pollution potential for nanoplastic pollution 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 (fig 1).

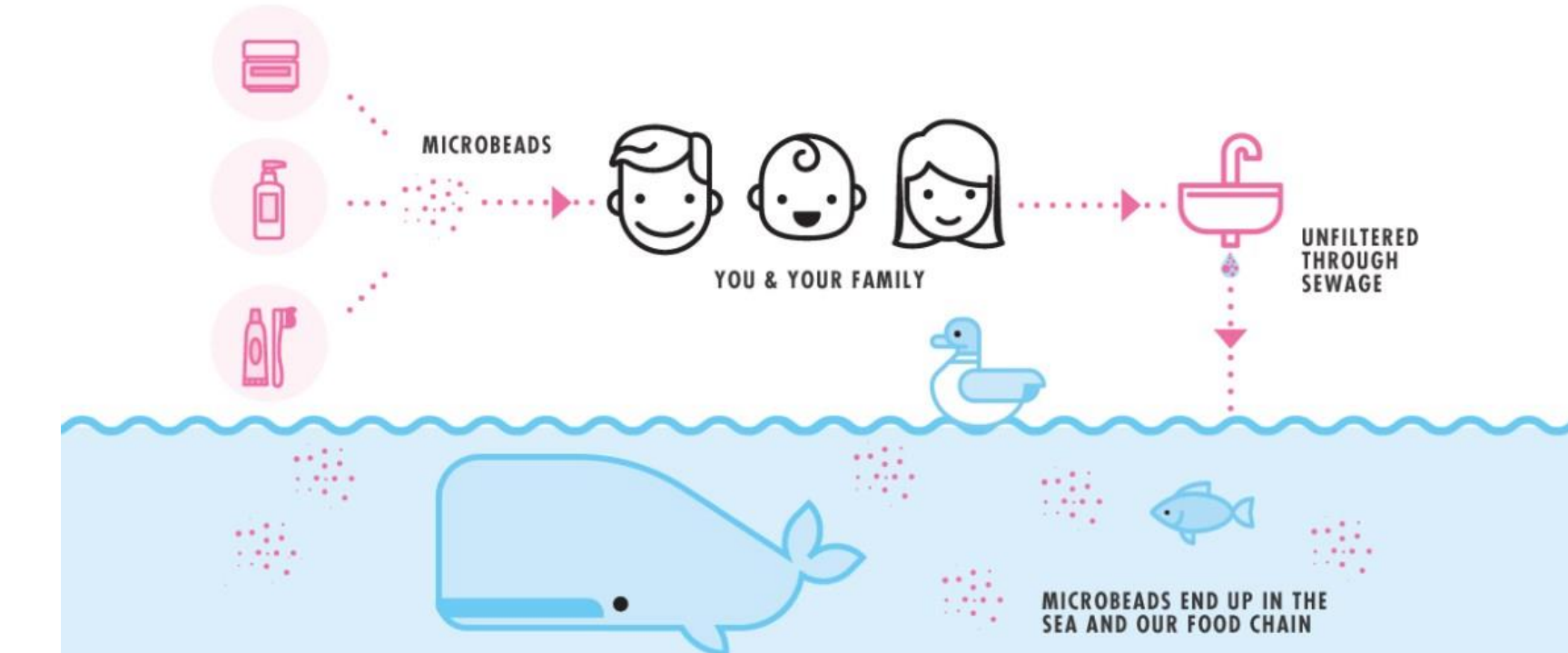


Figure 1 (by Plastic Soup Foundation)

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 and finally in the aquatic and marine environment. 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.

PROPOSED SOLUTION

Different methods of nanoplastic removal in wastewater include sorption and filtration, removal based on chemical phenomena, biological ingestion treatments and advanced oxidation technologies (AOTs) has been proposed. Among (AOTs) able to remove nanoplastics from wastewater, **heterogeneous photocatalysis** represents an attractive and efficient technique for the degradation of these particular pollutants.

TiO₂ is one of the most studied semiconductors due to its non-toxicity, high chemical stability (particularly to photocorrosion) and photocatalytic efficiency. Photocatalytic removal of organic pollutants consists in illuminating TiO₂ with UV-light, to produce hydroxyl and superoxide radicals.

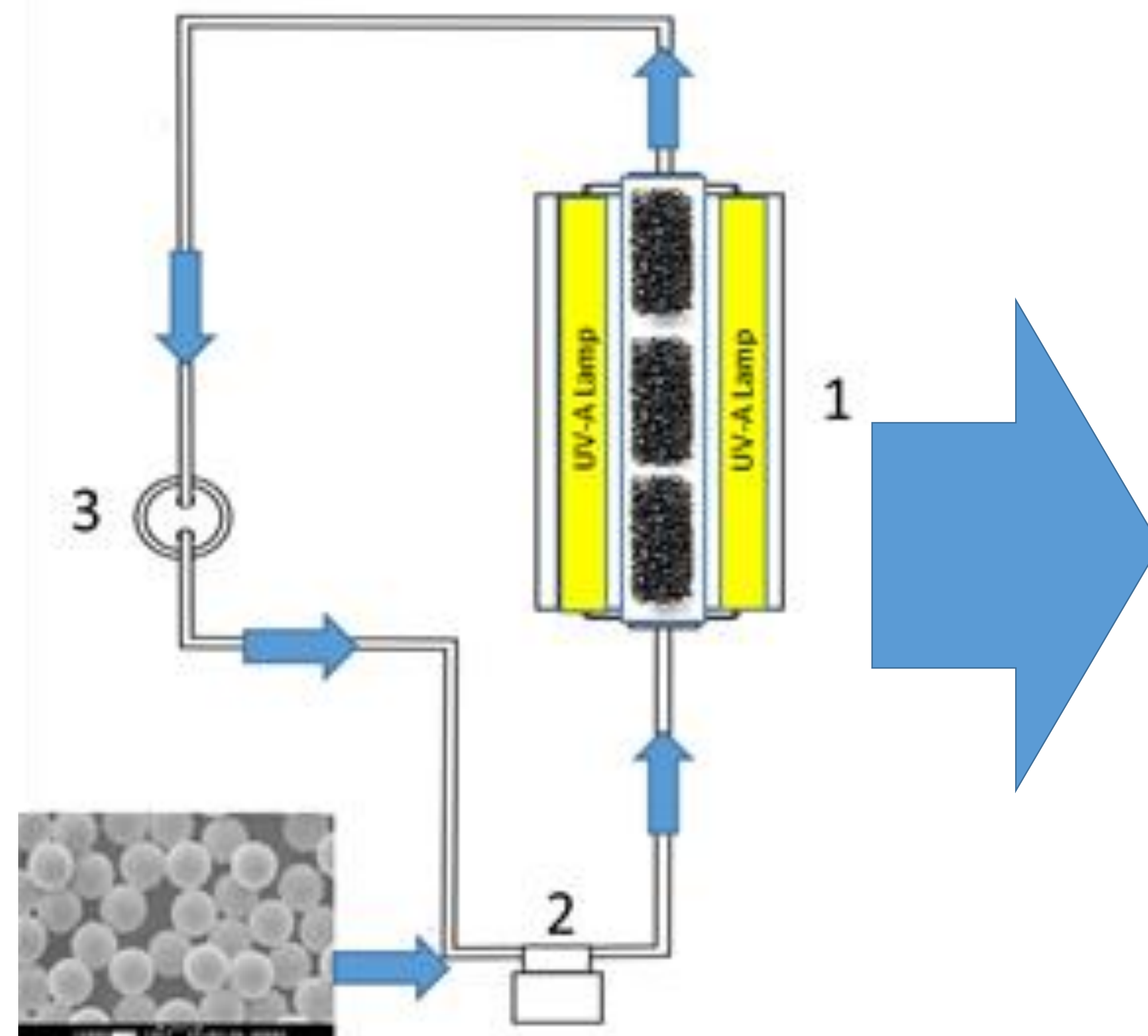
In this work, we use a β-SiC foam supported TiO₂-P25 photocatalyst integrated into a flow-through photoreactor for nanoplastics removal in wastewater. We took calibrated polymethylmethacrylate (PMMA) and polystyrene (PS) nanobead particles as model systems for microplastic pollutants. The photocatalytic 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.

EXPERIMENTAL

Photocatalytic experiments were performed in a recirculation mode photoreactor. 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 ± 1 wt% of TiO₂. A volume of 600 ml of aqueous nanoplastic suspension to be treated is introduced into the system.

In order to measure the efficiency of the process, we used commercial monodisperse suspensions of PS and PMMA supplied by Microparticles GmbH.

Fig. 2. Photocatalytic tubular reactor made with (1) a 4 UV-A lightning system + a quartz tube + 3 TiO₂/β-SiC foams, (2) polymer nanobeads solution and (3) a peristaltic pump.



ANALYSIS

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.



RESULTS AND DISCUSSION

The first preliminary results showed that it is possible to oxidize PMMA and PS nanobeads in the presence of TiO₂-P25/β-SiC foams.

- The reaction follows a zero-order reaction kinetics (limitation by mass transfer)
- 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 (fig 3b).
- At free pH 6.3, we are working under optimum conditions for the photo-oxidation. On the contrary, at basic pH, 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 (fig 4b).
- Light intensity effect has been studied by varying the number of UV-A lamps irradiating the TiO₂-P25/β-SiC foams (Figure 4b), 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.

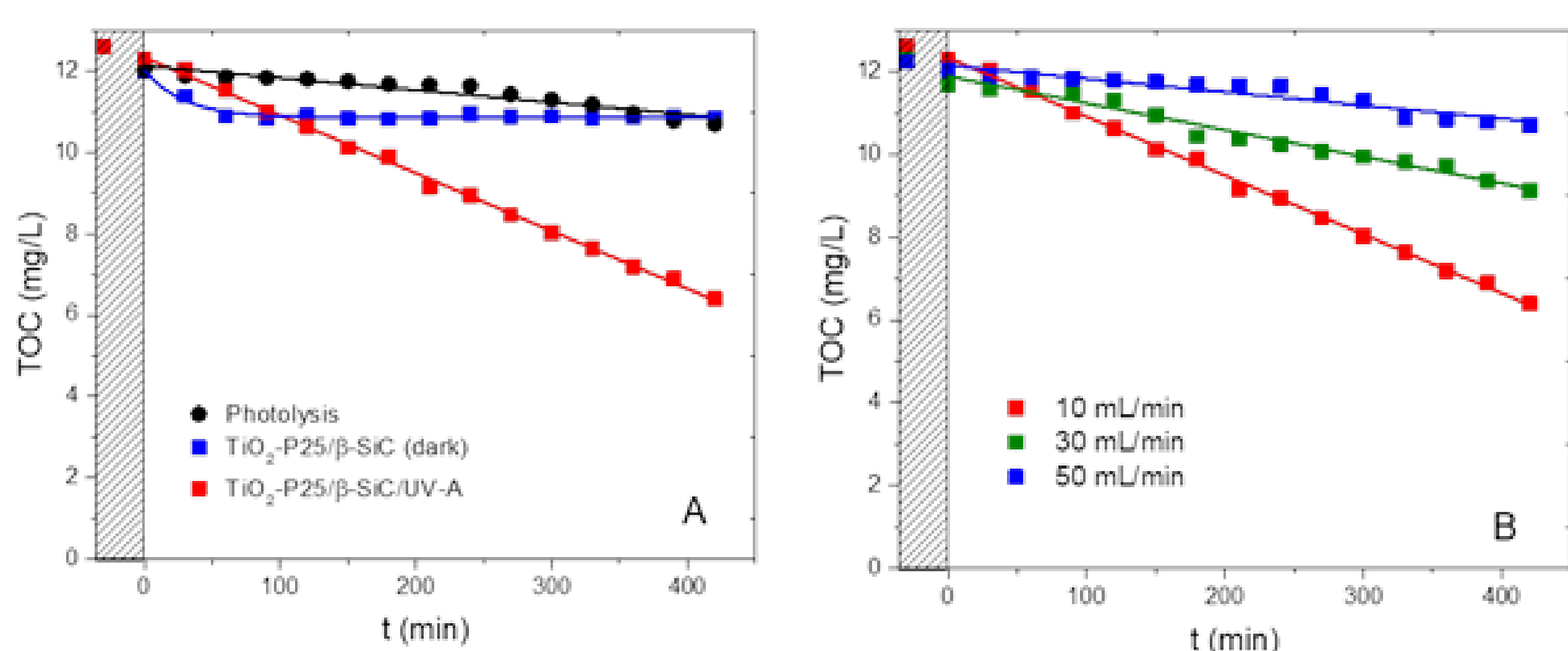


Fig. 3. a) Mineralization kinetic of NBS-PMMA on TiO₂-P25/β-SiC without and under UV-A irradiation and photolysis (Flow rate = 10 mL/min, pH = 6.3); b) Flow rate effect on the photocatalytic degradation of NBS-PMMA solution on TiO₂-P25/β-SiC (pH = 6.3). A pseudo-zero order model is applied to the TOC evolution data set.

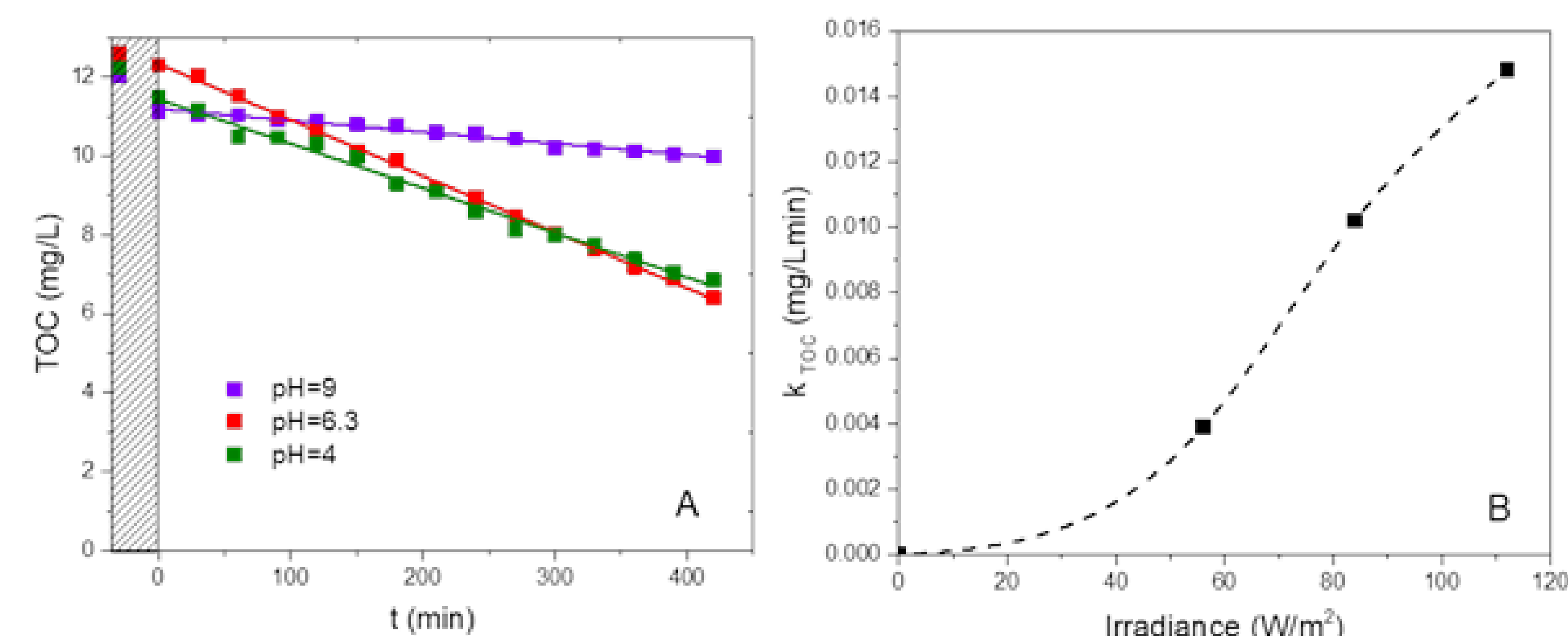


Fig. 4. a) pH influence and b) UV-A light intensity influence on the photocatalytic mineralization of NBS-PMMA using TiO₂-P25/β-SiC foams (flow rate = 10 mL/min). Lines show the pseudo-zero order model fitted to each data set.

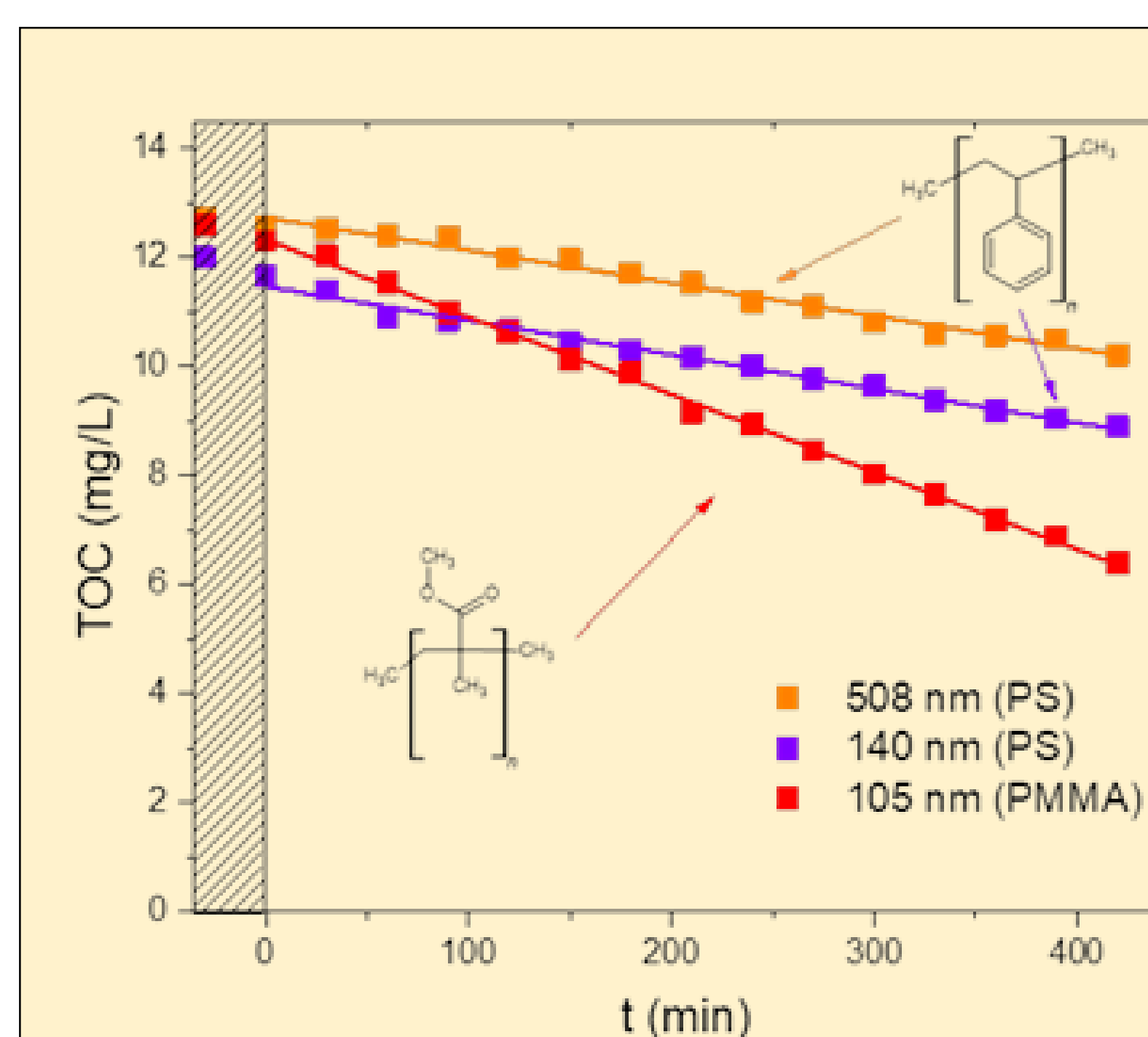


Fig 5: Comparison of photocatalytic mineralization of NBS-PMMA and NBS-PS/PS (Flow rate: 10 mL/min, pH = 6.2)

Chemical structure and particles size effects

- For a similar particle size, PMMA mineralization appears to be faster than PS (k_{NBS-PPMA} = 0.0148 mg/L.min while k_{NBS-PS1} = 0.0065 mg/L.min).
- Size effect: 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.

CONCLUSION

These first results are very encouraging, we have shown that it was possible to mineralize nanobeads of PMMA and PS under irradiation of TiO₂ in aqueous solution. 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.

Acknowledgements

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