Scale-up and numbering-up of meso- and microphotocatalytic TiO_2 system for organic dyes degradation and phenol oxidation under UV irradiation

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Abstract: *An experimental set-up of a scale-up and serial internal numbering-up of meso- and micro photocatalytic systems was developed to compare the photodegradation efficiency of TiO_2-P25 against Rhodamine B (RB) and Metilen Blue (MB) under UV irradiation. A circular photocatalytic plate constituted of TiO_2 embebbed on PDMS was the elemental unit of the meso and microchemical plants. Different volumetric capacity, from 10 µL to 1000mL, and the different flow rate (0,05 -1mL min^{-1}) were evaluated to understand the best approach to scale-up the photoreaction process. The best multi-photocatalytic microreactor system, built-up plugging six modular microreactor plates, was tested to photoxidize phenol under UV irradiation. P25 catalyst performed different photodegradation efficiency depending on the photocatalytic microreactor design. This observation should call attention for the microfluidic community to create a standard photocatalytic test to enable the comparison between different catalysts or new photocatalytic reactions.*

Key-Words*: scale-up, numering-up, TiO_2, photocatalys, purification water.*

Introduction: The photocatalytic water purification and photoxidation organic synthesis have intensively been studied both for academic and industrial applications. Flow chemistry in microreactor has many advantages compare to batch reactor system, such as, large area surface-to-volume, rapid optimization of operating conditions, uniform irradiation and rapid photon transfer boosting higher reaction selectivity, fast and very efficient mixing, rapid heat and mass transfer, small confinement of organic molecules on the catalytic surface for a rapid diffusion to the reaction site, lower catalyst loading, lower cost reducing solvents-reagents and waste, improvement of safety and sustainability[1]. Nevertheless all the above positive aspects have attracted attentions the intensification process of a photocatalytic reaction on microfluidic device has still considered a bottleneck of the microreactor technology. The intensification process should be observed considering productivity, selectivity and safety of the reaction. On the other hand small throughput and short test can be useful to screen new/expensive catalysts or to optimize new photochemical reactions. The lacks of a standard of photocatalytic device in continuous flow system make difficult to compare different photocatalytic efficiencies or compare new catalyst performances [2]. In this work we compare two different approaches for the intensification of the photocatalytic reaction, by scale-up the volume of a mesoscale reactor and numbering-up microscale reactors. Using only the commercial TiO_2-P25 with different parameters, flow rate and surface-to-volume rate, we point out the necessity to create a standard continuous flow platform for a rapid characterization of new catalysts to enable a comparison of photocatalytic efficiency.

Experimental: The meso- and microreator systems have a common elemental circular photocatalytic plate constituted from a TiO_2 film coating on PDMS support as previously published [3]. Depending on the prototype set-up we had created a planar chamber with 12 mm of diameter and variable height reactor chamber from 100 µm to 8 mm. A photomicroreator device was constructed sealing, with O_2 plasma, two PDMS layers without the TiO_2 photocatalyst for the photolysis tests. For the individual photocatalytic microreactor (M1) one of the PDMS layer where coating with commercial TiO_2/P25. The design of a multi-photocatalytic microreactor (mPCM) system, with a serial numbering-up approach, was built-up plugging modular microreactor plates. We have scaled the mPCM from 1 microreactor unit (M1), with internal volume of 10µL, to 6 planar microreactor chambers (M6-60µL). An internal numbering-up of two M1 units, allowed to prototype a modular reactor plate M2-20µL. Two internal numbered-up plates M2 were plugged each other, with PFA tubing, to obtain a serial modular reactors assembly with 4 microreactor units (M4-40µL). Finally, plugging three M2 units we obtained a serial microreactor plant with 6 microreactor units (M6).
The mesoscale continuous-flow photocatalytic reactor, was assembled on a homemade steel holed support aligning and screwing in sequence: a clean glass microscope slide; a 13 mm holed flow cell with two rubber

rings to avoid leak of solution; and the TiO_2/PDMS coated composite. To scale-up the mesophotocatalytic reactor, we used flow cells with different depth (4, 6 and 8 mm), respectively, with 0.5, 0.8 and 1.0 mL volume capacity. The 365nm UV light pass through the hole directly to the photocatalytic layer located at the bottom of the flow cell reactor system. In the same system, it is possible to replace a TiO_2/PDMS composite with another clean glass microscope slide and use it as a control system to evaluate the photolysis phenomena.
The photocatalytic efficiency of the scaled-up and serial numbered-up photocatalytic systems was monitored by UV-VIS spectroscopy from 30 minutes to 16 hours. The photodegradation of 10 mL ($1{,}2x10^{-5}$ mol L^{-1}) organic-dyes, RB MB with and without the photocatalyst, was evaluated changing the peristaltic pump's flow rate from 0,05 to 1,0mL min^{-1}. Finally, the best mPCM system M6 was used to test the photoxidation of phenol and the reaction mixture was analyzed by HPLC.

Results and discussion: The percentage of the photodegradation of RB and MB for mesophotocatalytic reactor, (Meso-500, 800 e 1000 µL) and photocatalytic microreactor (M1-10, M2-20, M4-40 e M6-60 µL), with and without the elemental circular photocatalytic plate (TiO_2 embebbed on PDMS) are represented in figura 1A-B. For the mesoreactor system the first order kinetic reaction was monitoring from to 2 until 16 hours, obtaining the total degradation in 16 hours only for the meso-500. While for the numbered-up microreactors the total degradation was observed between 1-8 hours. With the mPCM-M6, increasing the superficial area, the total degradation of the dye solution occurred in only 1 hour. The best performance of the M6 platform was explored for the photocatalytic oxidation of phenol. The HPLC with UV detector was used to monitor the formation of the three reaction products: catechol, hydroquinone and resorcinol. The lowest flow rate, 0,05 ml min^{-1} allows the formation all the three products with the total consuming of the start reagent with only 2 hours.

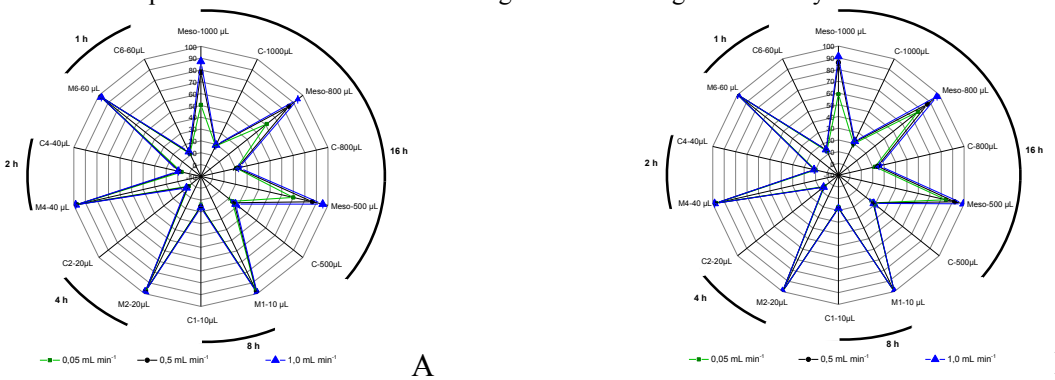

Figure 1. Photodegradation under UV light of 10 mL ($1{,}2x10^{-5}$ mol L^{-1}) organic-dyes, RB (A) and MB (B), on meso- and microphotocatalytic devices, with diferent flow rate (0,05 – 1,0 mL min^{-1}).

Conclusion:
The reduced time consuming of the internal numbered-up microscale reactors (mPCM-M6) compared to the scale-up approach of mesoscale flowreactor allows to confirm that the intensification process of a photocatalytic reaction on microfluidic device may be possible for potential water purification and photocatalytic organic process. In addition, if we may consider the possibility to parallel the M6 microchemical plant, into external numbering-up fashion,[4] we can increase the throughput and reduce the cost of the pilot scale plant. Combining the two ways, internal numbering-up and external numbering-up, industrial scale production may be achieved. It will be successfully convenient compared to the conventional volume scale-up approach, both for batch and mesoflow reactor. In our experiment set-up, only changing two parameter conditions, flow rate and surface-to-volume ratio of the planar flowcell, it was observed different performance of a commercial catalyst P25. Urge to establish standard parameters for continuous flowreactor to evaluate news catalysts and compare them not only against the most viable commercial product P25. Our simple and low cost production of the individual photocatalytic microreactor (M1) and rapid plug-in of M6 microchemical plant can be interested for rapid photocatalytic tests of small and expensive catalysts for academic research.

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