

Editorial

Editorial Catalysts: Special Issue on Photocatalytic Membrane Reactors

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Received: 31 July 2020; Accepted: 11 August 2020; Published: 22 August 2020



The themed collection of articles in the Special Issue on *Photocatalytic Membrane Reactors* in the journal *Catalysts* constitutes some significant and highly representative publications referring to this topic. This research area, combining knowledge of photocatalysis and membranes, is relatively young and we can say it was born around year 2010. From Figure 1 it can be seen that in last six years (2015–2020) the research interest on photocatalytic membrane reactors is significantly increased compared to only photocatalysis and only membranes.

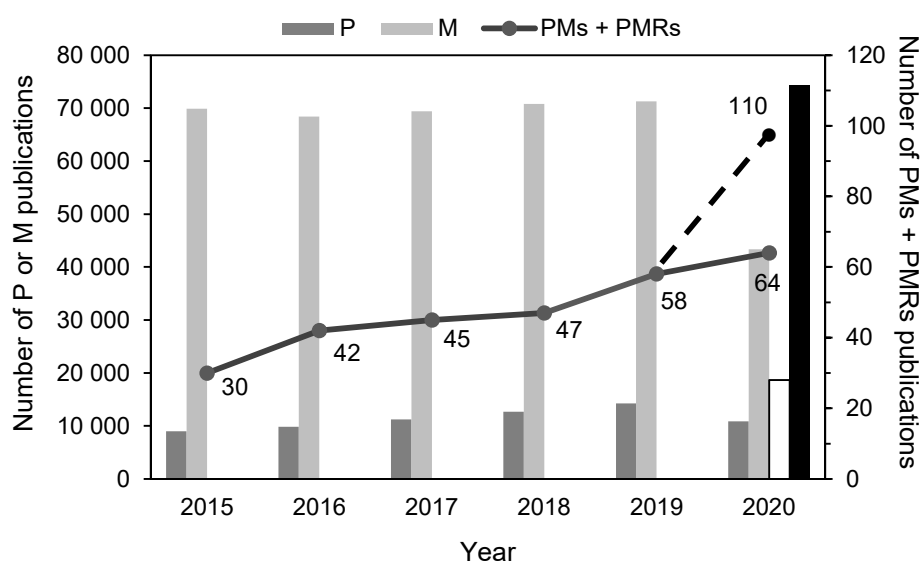


Figure 1. Development of publications on photocatalysis (P), membranes (M), and photocatalytic membranes + photocatalytic membrane reactors (PMs + PMRs) (Scopus, 31 July 2020). The data for 2020 represent the status at 31 July 2020. Additionally, the data for 2020 were extrapolated for the whole year assuming a constant rate of publishing (white and black bars, and black point with dotted line). Keywords: P—photocatal*; M—membrane; PMs + PMRs—“photocatalytic membrane” AND “membrane photoreactor”.

Going back in the time we can say that applications on photocatalysis start with the investigations on photocatalytic splitting of water on TiO₂ semiconductor electrodes, conducted in the 80's of 20th century by Honda and Fujishima, which opened new research directions in the area of environmental technologies. Since then the interest of scientific world in various applications of photocatalysis has

been systematically increased and in the last six years it is quite stabilized (see Figure 1). The possibility of the removal of toxic compounds or synthesis of useful substances have positioned photocatalysis amongst processes following the Green Chemistry principles. Photocatalysis was proposed to be applied in air and water/wastewater purification as an efficient method of degradation of organic contaminants to innocuous products, such as water, carbon dioxide or inorganic salts, as well as of removal of toxic metals. A more recent application of photocatalysis is organic synthesis.

On the other side, membrane applications started in 1748 with the discovery of the osmosis phenomenon by Nollet and the research in the last six years is quite stabilized also (see Figure 1). The coupling of membrane techniques with photocatalysis shows significant advantages compared to the single technologies. The synergy of membrane separation and photocatalysis results in design of systems that can operate continuously with the simultaneous recovery and reuse of the photocatalyst (immobilized or in suspension), the separation of substances from the treated solution and/or the recovery of the reaction products. These systems are known as Photocatalytic Membrane Reactors (PMRs), which can be defined as devices existing in various configurations and synergistically combining the action of a photocatalyst and a membrane leading to chemical transformations. Two main types of PMRs configurations are (i) PMRs with photocatalyst suspended in the reaction mixture (slurry systems) and (ii) PMRs with photocatalyst immobilized in/on a substrate material acting as a membrane (photocatalytic membrane, PM). Improvement of process efficiency compared to conventional photoreactors, modularity and easy scale up resulted in a significant growth of interest in the area of PMRs observed in the recent years (Figure 1).

Nonetheless, the full-scale applications of PMRs still need detailed investigations to improve the processes performance. This Special Issue is devoted to all aspects of hybrid photocatalysis–membrane systems, including both photocatalytic membranes and reactors with suspended photocatalyst. A detailed overview of recent reports on PMRs in organic synthesis as well as water and wastewater treatment is presented in the paper by Molinari et al. [1]. After the brief introduction to the slurry PMRs, the discussion on PMs and methods of their preparation is given. Moreover, the process parameters affecting the performance of various type PMRs are characterized. The second part of the review is devoted to the applications of PMRs in organic synthesis, especially in photocatalytic conversion of CO₂, synthesis of KA oil by photocatalytic oxidation, conversion of acetophenone to phenylethanol, synthesis of vanillin and phenol, as well as hydrogen production. In the subsequent sections the applications of PMRs for removal of organic contaminants from model solutions, natural water and municipal or industrial wastewater are summarized and discussed. This paper [1] makes a good basis for the research papers published in the Special Issue. These are related to both photocatalytic membranes [2–4] and slurry-type PMRs [5,6]. The papers on PMs are focused on fabrication of polymeric photocatalytic membranes with TiO₂ as a photocatalyst [2] and application of TiO₂-coated membranes in various reactor configurations [3]. Another approach was presented in [4], in which an inorganic silicon carbide membrane covered with TiO₂ and SiO₂ by sol-gel and dip-coating procedures was applied for treatment of olive mill wastewater in a novel submerged PMR (SPMR). The papers on slurry PMRs present application of PMRs for removal of viruses from drinking water [5] and green production of vanillin in a PMR utilizing dialysis [6].

The PM presented by Fischer et al. [2] was fabricated by a dip-coating approach using TiO₂ obtained from titanium(IV) isopropoxide and a polyethersulfone microfiltration membrane. To enhance the photocatalytic activity the synthesis temperature was optimized. Moreover, the ultrasound modification of nanoparticles and membrane pre-modification with carboxyl groups was conducted to improve the distribution of nanoparticles. The proposed method was found by the authors to be an efficient approach for fabrication of a PM membrane with good stability and performance during nine cycles of carbamazepine decomposition [2]. Such a conclusion shows the importance of evaluation of PMs membranes stability, which can be lost in time not only due to the detachment of photocatalyst particles, formation of deposits (scale, non-degraded compounds, etc.) or photocorrosion of a photocatalyst

(e.g., in case of CdS), but also due to degradation of polymeric membrane matrix upon the action of irradiation, especially in case of application of UV light sources.

An interesting comparison of various configurations of PMRs equipped with a TiO₂-coated PM membrane was presented by Regmi et al. [3]. The authors have compared the performance of reactors with different flow design: batch, flow-along and flow-through, using parameters such as space-time yield (STY) and photocatalytic space-time yield (PSTY), specific energy consumption (SEC) and degradation rate constants. On a basis of decomposition of a model dye, methylene blue, under UV-LED irradiation it was concluded that the most efficient design was the flow-through one. For that configuration the PSTY1/PSTY2 values were approximately 10 times higher than calculated for the batch and flow-along processes. The observed improvement was attributed to the intensification of mass transfer and the increased area available for pollutant degradation [3]. The paper reveals the importance of the reactor configuration in the process intensification. Nonetheless, further investigation on PMRs system design are of high importance, especially in terms of its effect on mineralization of organic contaminants, not only their decomposition.

The problem of stability of PMs membranes, mentioned earlier, can be solved by application of inorganic membranes instead of polymeric ones. Such an approach was presented by Fraga et al. [4]. A TiO₂ and SiO₂-coated silicon carbide membrane was applied to treat real olive mill wastewater in an SPMR. A very high removal of total organic carbon (87%), chemical oxygen demand (89%) and phenolic compounds (95%) was obtained within 20 min of the reactor operation. However, a gradual decrease of the treatment efficiency was observed until 2 h of process. The observed deterioration of the SPMR performance was attributed to formation of a fouling layer on the membrane surface due to a high concentration of suspended solids in the wastewater, which prevented the irradiation from reaching the photocatalytically active membrane surface. As a solution for this problem the application of the wastewater pretreatment and/or membrane backwash/backpulse was proposed [4]. The advantage of the proposed PMR configuration was application of the depressurized mode, less prone to fouling than the pressurized one, as well as utilization of a ceramic membrane, which is resistant to the action of UV radiation and photogenerated oxidative species (e.g., hydroxyl radicals). In case of the setups based on PMs such a solution seems especially promising.

Another configuration of SPMR was presented by Cheng et al. [5]. The authors applied a flat-sheet polyvinylidene fluoride membrane and TiO₂ photocatalyst suspended in a feed for removal of bacteriophage f2 (a model virus) from simulated surface water in the presence of humic acid (a representative of natural organic matter). The UV light source was positioned in the same tank as the membrane but the two connected parts were partially separated by a non-transparent baffle to protect the membrane from damage by the radiation. A competitive adsorption between the virus and humic acid on the photocatalyst resulted in a significant decrease of the disinfection efficiency. To solve this problem and mitigate the negative effect of humic acid the authors proposed an intermittent operation mode or application of a higher membrane flux [5]. The presented data show that PMRs can not only serve as a tool for removal of organic contaminants from water but also can help in inactivation of pathogenic organisms.

A very different approach regarding PMRs is presented by Camera-Roda et al. [6]. The authors reported the results on application of the hybrid system coupling dialysis and photocatalysis for production of vanillin by partial photocatalytic oxidation of ferulic acid in an aqueous solution at ambient temperature. The applied dense polyether-block amide membrane allowed continuous extraction of vanillin preventing from its successive oxidation and thus intensification of the synthesis process was achieved. The total amount of vanillin produced after 5 h in the PMR was more than one-third higher than in the photocatalytic process alone. To analyze the process in details a mathematical model was applied. The results of modeling revealed that a limiting factor can be concentration polarization. The negative effect of this phenomenon cannot be neglected and therefore, a careful design of the module and operational parameters is of high importance [6].

As guest editors of this Special Issue we thank all the authors for their valuable contributions. The above brief overview of the current state of the art in the area of PMRs shows a great potential of this technology in numerous applications. PMRs can be considered as useful green systems for water/wastewater treatment as well as organic synthesis. However, further extensive investigations on this subject are necessary to improve the process performance, develop new reactor configurations or investigate the process mechanisms. It must be also noted that a sustainable PMR operation requires exploitation of the solar energy as a cheap and clean source of light. Thus, the development of new photocatalysts with high activity under visible light is a mandatory task. Another key issue is development of membranes resistant to the harsh conditions prevailing in these systems. All these studies are urgently needed to take advantage of the potentiality of PMRs at industrial level.

Funding: This paper received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Molinari, R.; Lavorato, C.; Argurio, P.; Szymański, K.; Darowna, D.; Mozia, S. Overview of Photocatalytic Membrane Reactors in Organic Synthesis, Energy Storage and Environmental Applications. *Catalysts* **2019**, *9*, 239. [\[CrossRef\]](#)
2. Fischer, K.; Schulz, P.; Atanasov, I.; Abdul Latif, A.; Thomas, I.; Kühnert, M.; Prager, A.; Griebel, J.; Schulze, A. Synthesis of High Crystalline TiO₂ Nanoparticles on a Polymer Membrane to Degrade Pollutants from Water. *Catalysts* **2018**, *8*, 376. [\[CrossRef\]](#)
3. Regmi, C.; Lotfi, S.; Espíndola, J.C.; Fischer, K.; Schulze, A.; Schäfer, A.I. Comparison of Photocatalytic Membrane Reactor Types for the Degradation of an Organic Molecule by TiO₂-Coated PES Membrane. *Catalysts* **2020**, *10*, 725. [\[CrossRef\]](#)
4. Fraga, M.C.; Huertas, R.M.; Crespo, J.G.; Pereira, V.J. Novel Submerged Photocatalytic Membrane Reactor for Treatment of Olive Mill Wastewaters. *Catalysts* **2019**, *9*, 769. [\[CrossRef\]](#)
5. Cheng, R.; Shen, L.; Wang, Q.; Xiang, S.; Shi, L.; Zheng, X.; Lv, W. Photocatalytic Membrane Reactor (PMR) for Virus Removal in Drinking Water: Effect of Humic Acid. *Catalysts* **2018**, *8*, 284. [\[CrossRef\]](#)
6. Camera-Roda, G.; Parrino, F.; Loddo, V.; Palmisano, L. A Dialysis Photocatalytic Reactor for the Green Production of Vanillin. *Catalysts* **2020**, *10*, 326. [\[CrossRef\]](#)



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