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Advances in engineered design and performance of photocatalytic membrane reactor for polluted water treatment

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The availability of clean water is a global concern. Photocatalysis is seen to be one of the advanced water treatment technique and coupling it with the membrane will give an upper edge over other methods. This paper presents an in-depth detailing of the photocatalytic membrane reactor (PMR). Different methods of preparation of photocatalytic membranes such as chemical vapor deposition (CVD), layer-by-layer (LbL), spraying, and phase inversion are described with a variety of a photocatalyst. Various factors influencing the performance PMRs and reviews the advances in the design and operational parameters of PMRs are comprehensively described and discussed. The PMRs with both immobilized and suspended photocatalyst are discussed and presented in this review article.

Keywords: Photocatalysis, photocatalytic membrane reactor (PMR), immobilized photocatalyst, suspended photocatalyst.

Introduction

Increased population and rapid industrialization leading to an increase in water demand, with that the contamination of water is also a huge concern. United Nations World Water Development Report suggests that by 2050 over 50 billion people will suffer from access to safe drinking water[1]. So, it is necessary to develop a cost-effective, efficient, and reliable technology to treat water.

The membrane has been extensively used for liquid and gas separation. Some of the commonly used membrane techniques are micro-filtration, ultra-filtration, reverse osmosis, forward osmosis, desalination. The ample use membrane is because of its advantages viz. low capital cost, low operating cost, higher efficiency, and reliability. Fabrication of the membrane has a considerable influence on membrane property such as membrane thickness and uniformity. The mechanisms followed by the membrane to separate particles are particle sieving, surface diffusion, solution diffusion, facilitated transport, ion transport.

The basic mechanism of photocatalysis as shown in Fig. 1, when the surface of the photocatalyst is illuminated with light. Initially, the light will be absorbed by the photocatalyst by which a pair of electron and hole will be generated and charges get separated. The generated electrons (e^-) and holes (h^+) will be transferred to photocatalysts surface where charges will be utilized for a surface redox reaction, by which the pollutant will be treated[3].

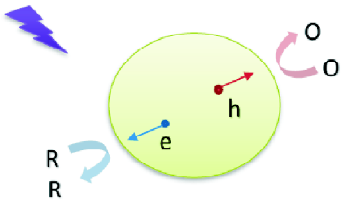

Fig. 1. Schematic illustration of charge transfer and redox reaction on photocatalyst[2].

In photocatalytic membrane reactor (PMR), the membrane is coupled with photocatalyst for the treatment of pollutants. In this paper, an overview of typical configurations of PMRs is discussed to give a brief outline of PMR configurations and their technology. In addition to that, the method of membrane preparation, the immobilized and suspended photocatalytic reactor are briefly discussed.

Materials and methods

Selection of photocatalysts:

A good photocatalyst will have properties like high activity in presence of light energy, physical and chemical stability under different conditions, and mechanical stability and resistance to attrition. Semiconductors show promising photocatalytic activity, such as oxides and sulfides (TiO_2, ZnO, ZrO_2, WO_3, Fe_2O_3, CdS, ZnS, etc.). Semiconductors are photoactive because of the bandgap difference, which helps them to generate electrons and holes when it is exposed to light energy. Wide bandgap semiconductors will require more energy to generate a pair of electrons and holes, this makes some of the photocatalysts work only in the UV region. Many researchers achieve photocatalysis in visible light, which makes photocatalysis more effective and applicable.

To make any semiconductors work in a visible region various modification techniques are used by surface modification, doping, and other methods. Some of the common dopants for semiconductors are Fe, V, Cr, Mn, Co, Bi, Ni, Cu, Pt, etc. The visible light activity of photocatalysts should be considered in the view of economy and reliability.

Membrane fabrication:

The fabrication of membrane involves coating of selective elements on the porous substructure. Fabrication of the membrane will be significantly affected by the uniformity and thickness of the membrane. Some commonly used coating techniques are layer-by-layer (LbL), dip-coating, spinning, and spraying, chemical vapor deposition (CVD).

Studies on a comparison between LbL and CVD have been done to evaluate methylene blue as a probe compound. LbL assembly is done by applying plying polyelectrolytes (PE) to the surface and then exposing that electrode to nanoparticle suspension for particle adhesion on the surface. In the CVD method, titanium dioxide is oxidized using plasma to coat it on the surface of the reactor. The binding of the photocatalyst on the surface is the same for both methods. Both show similar normalized reactive fluxes and rate constant but in concern of pollutant degradation LbL shows high efficiency and it does not depend on the number of layers[5].

The most commonly used membrane fabrication method is phase inversion method in which the membrane solution will be mixed with the photocatalyst particles and after the formation of a homogeneous solution, the doped solution was cast on a smooth glass plate with the required thickness of the membrane and then it will be immersed in solvent for a required time followed by drying of a membrane in different temperature[6,7].

In case of the electrospinning method of membrane preparation, the photocatalyst will be mixed with membrane materials and other solvents, after that solution will be loaded in a syringe of electrospinning instrument. The needle of a syringe which is connected to the power supply, distance between needle and collection plate is monitored with a flow

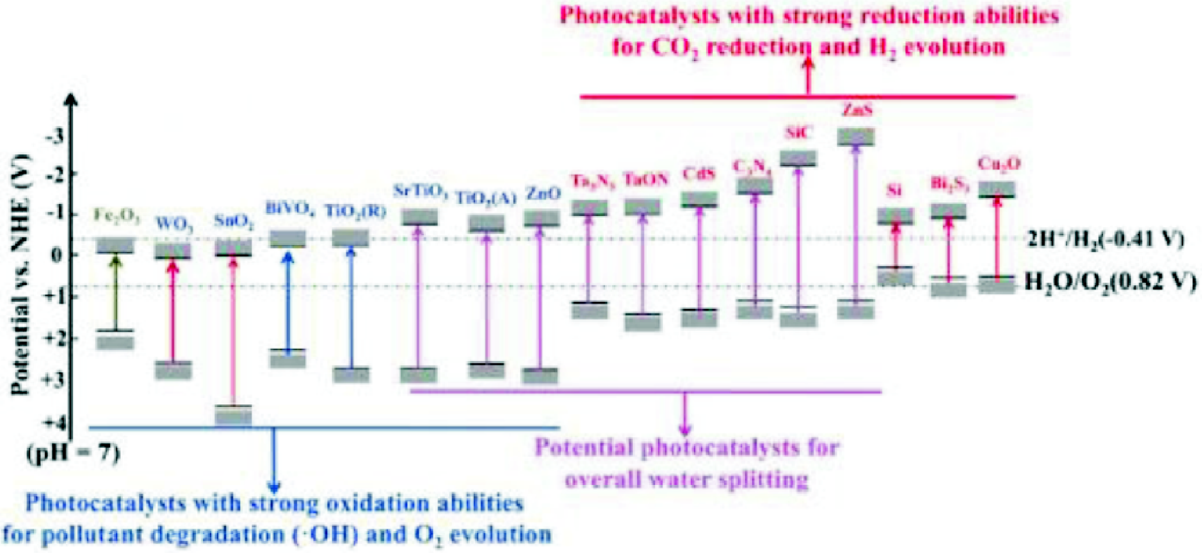

Fig. 2. Schematic illustration of band gaps of different photocatalysts[4].

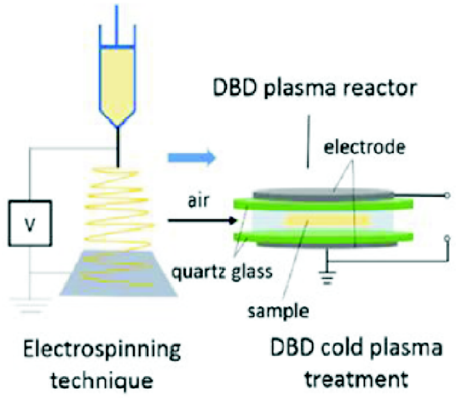

Fig. 3. Schematic illustration of electrospinning method[9].

rate of a syringe which plays the main role in the membrane properties[8]. Electrospinning followed by cold plasma treatment and hydrothermal treatment to prepare with electrospinning apparatus, a homogenous photocatalytic membrane is obtained then plasma treatment is done for that membrane[9].

Fig. 4 represents the semantic representation of the spray system, where synthesized ultra-fine powder of photocatalyst mixed with other solvents, the solution is passed to pump with dry gas with fixed speed using a nozzle. Liquid mist is sprayed on the substrate plate.

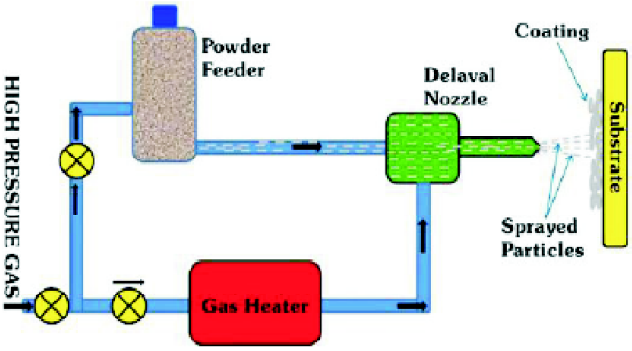

Fig. 4. The architecture of cold spray system[10].

Photocatalytic membrane reactor setup:

PMRs configurations based on the state of photocatalyst:

PMRs are of two types: (i) immobilized photocatalyst reactor, and (ii) suspended photocatalyst reactor. The main difference is in the case of an immobilized photocatalyst reactor photocatalyst will be fixed to the membrane, but in the case of a suspended photocatalyst reactor it will be in suspension from with pollutant and there will be a membrane to recover the photocatalyst[11].

An immobilized photocatalytic reactor with TiO_2 induced

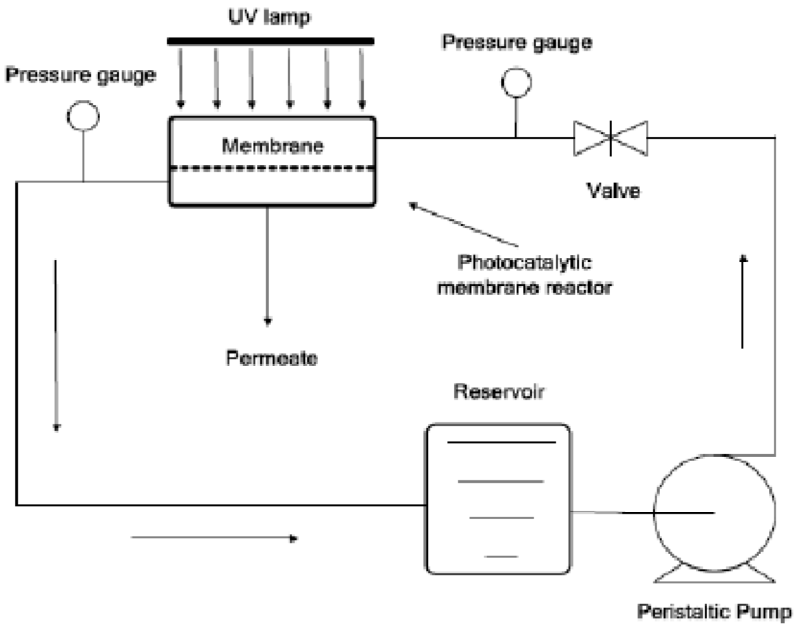

Fig. 5. A immobilized photocatalyst reactor with TiO_2 photocatalysts.

on the membrane by a surface modification to polypropylene macroporous membranes has been studied. The reactor setup is as shown in Fig. 5. It is done to the photocatalytic decomposition of phenol in water, water is pumped to membrane unit, cross-flow reactor setup is done and UV light is used as a source of illumination on the top of the membrane. Permitted water is collected for analysis and the remaining water is made to recirculate within the system.

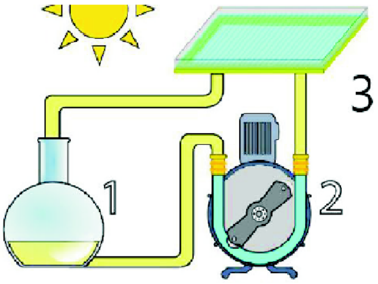

Fig. 6. Schematic illustration of immobilized solar photoreactor with solution flask (1), pump (2) and photoreacter (3)[12].

Fig. 6 is an immobilized photocatalyst reactor where TiO_2 particles are bounded into the poly(vinylidene fluoride-trifluoroethylene) membrane to conduct the photocatalytic reaction and the membrane is kept in sunlight as a source of illumination. Pollutants are recirculated in the system with a pump. The membrane is placed at the surface of the photoreactor which is fabricated with glass materials. The flow rate is adjusted between 9.8 mL/s to 28 mL/s. The study was also done under UV light which given a better result than that of sunlight. This is due to the use of TiO_2 as a photocatalyst which works effectively in UV light[12].

Fig. 7 depicts the treatment of fulvic acid using submerged PMR and TiO_2 as photocatalyst. Some amount of TiO_2 will settle in reactor bottom automatically due to gravity, then the remaining will be separated with the help of microfilter membrane. Continuous airflow is maintained in the reactor. A small baffle wall is placed between the photocatalytic oxidation and the membrane separation zones. UV lap is used as the source of illumination for photoreaction.

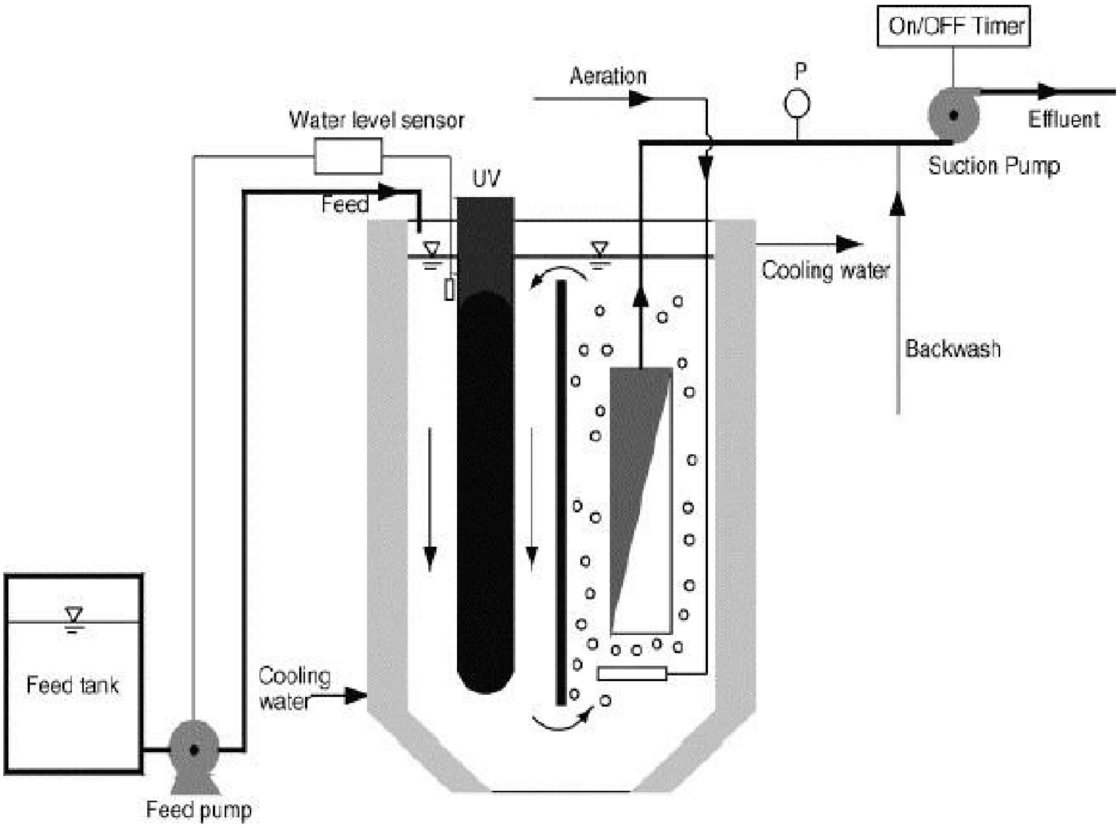

Fig. 7. Submerged membrane photocatalysis reactor system[13].

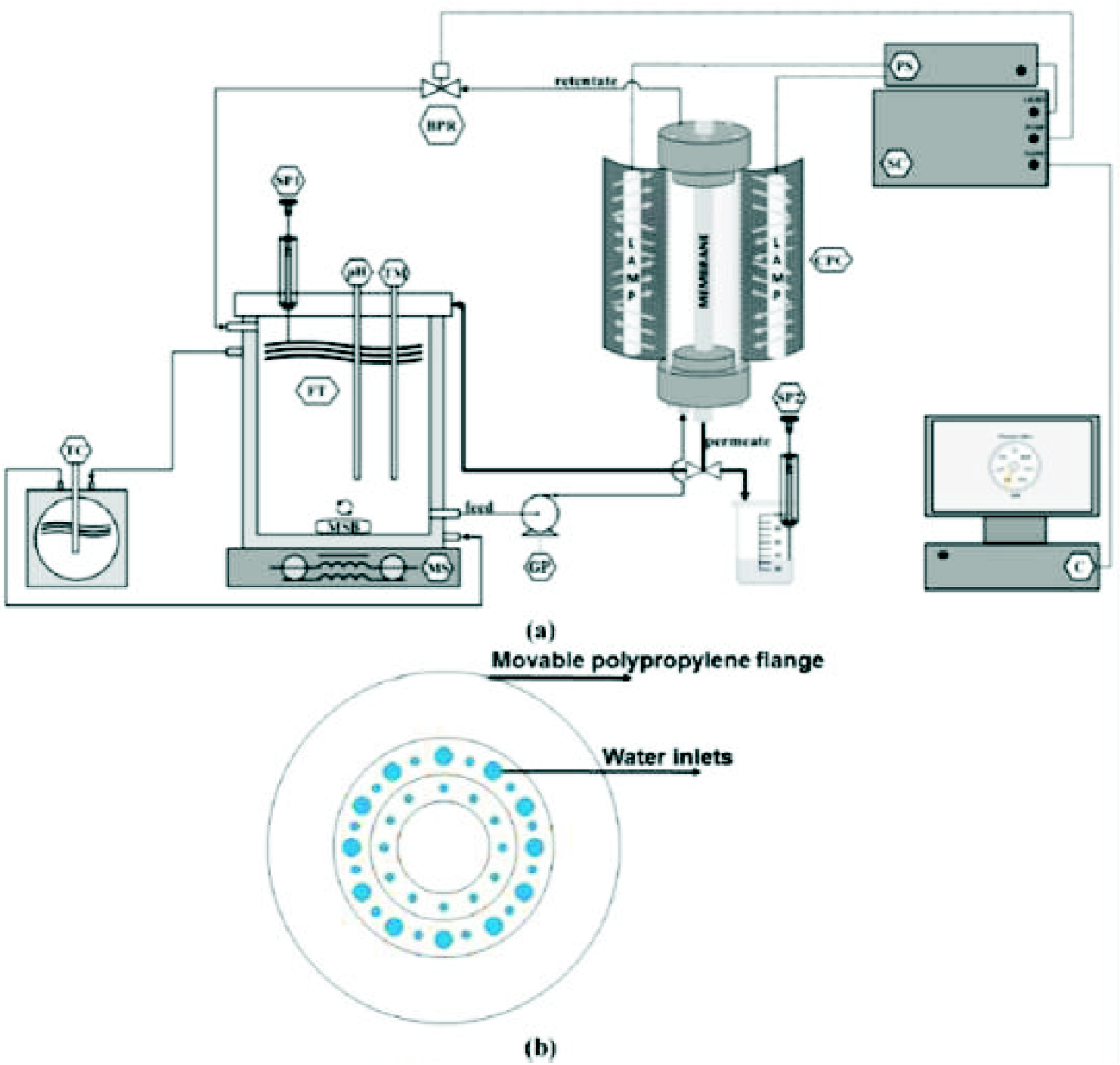

Fig. 8. A pictorial depiction of PMR consisting of microfiltration with UVA photolysis[14].

Hybrid systems coupling microfiltration (MF) with TiO_2 photocatalyst was invested for the removal of oxytetracycline (OTC) as shown in Fig. 8. PMR apparatus consists of a glass feed tank with a coolant system and magnetic stirrer arrangement from which the solution will be transferred to the photoreactor through a pump, water is uniformly distributed with help of lower flange holes. Two UV lamps are placed near the membrane module. The membrane is a cross-flow type, it is placed axially to flow direction in the inner tube. The top flange is similar to the bottom one but it has one outlet with a back-pressure regulator. Flow recirculation arrangement is also done in the system. The membrane system is studied under both immobilized and suspended photocatalyst. An increase in the dose of the photocatalyst, the slurry will lead to the formation of the TiO_2 cake layer. So the optimum amount of the photocatalyst is important for PMR. The removal of pollutant efficiency in suspended photocatalyst is higher then that of the immobilized photocatalyst is

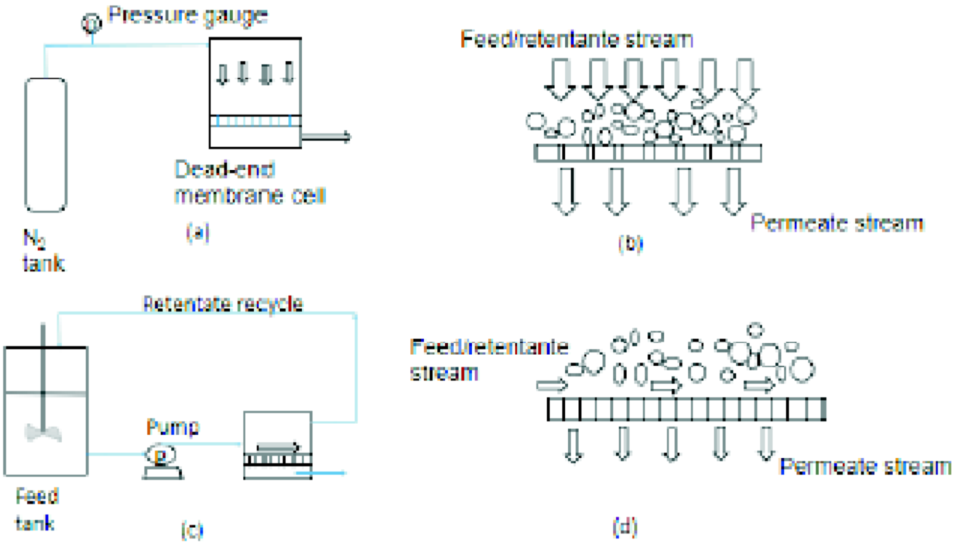

Fig. 9. Schematic representation of (a and b) Direct flow filtration or Deadened Filtration (DFF), (c and d) Cross-flow Filtration or Tangential Flow Filtration (TFF) membrane filtration test system[15].

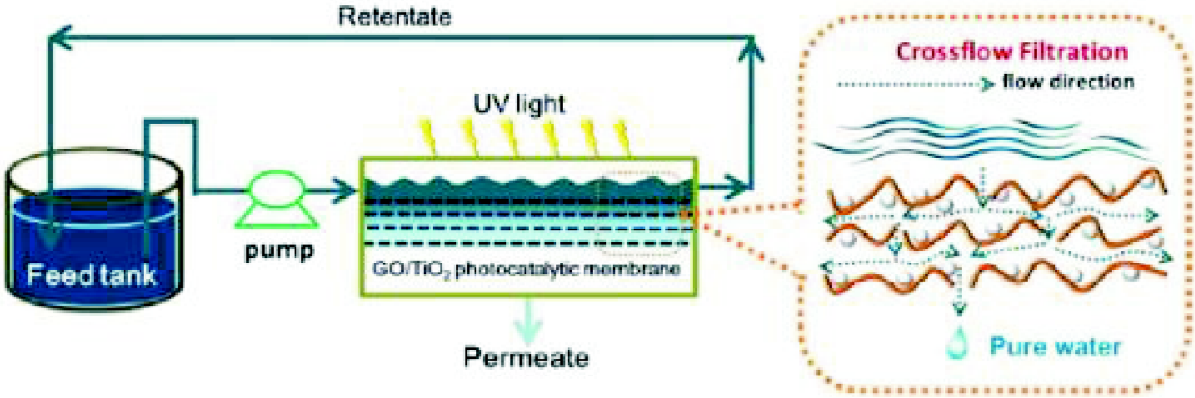

Fig. 10. Crossflow membrane system with GO/TiO_2 photocatalyst[16].

seen in the results, this is due to lower surface area availability for a pollutant to react with a photocatalyst is high.

PMRs configurations based on the passion of membrane:

Membrane filtration configuration can be divided into, (i) Direct flow filtration or Deadened Filtration (DFF) and (ii) Cross-flow Filtration or Tangential Flow Filtration (TFF). In DFF the flow of solution is arranged perpendicular to the membrane surface. Whereas in the case of TFF the flow will be in parallel to the membrane surface.

A crossflow photocatalytic membrane reactor fabricated with GO/TiO_2 as a photocatalyst by a one-step facile approach for eradication of methylene blue under UV illumination.

The membrane with high flux recoverability of 96% was observed even after 100 min of filtration and 92% of degradation of pollutant. PMR setup contains a feed tank of pollutant which is pupped to membrane block where the cross-flow filtration takes place then filtered water is collected at the end beaker of rector[16].

Another typical direct flow PMR is shown in Fig. 11. The PMR is used to remove the dyes from industrial waste using TiO_2 as a photocatalyst. The system is built by coupling the

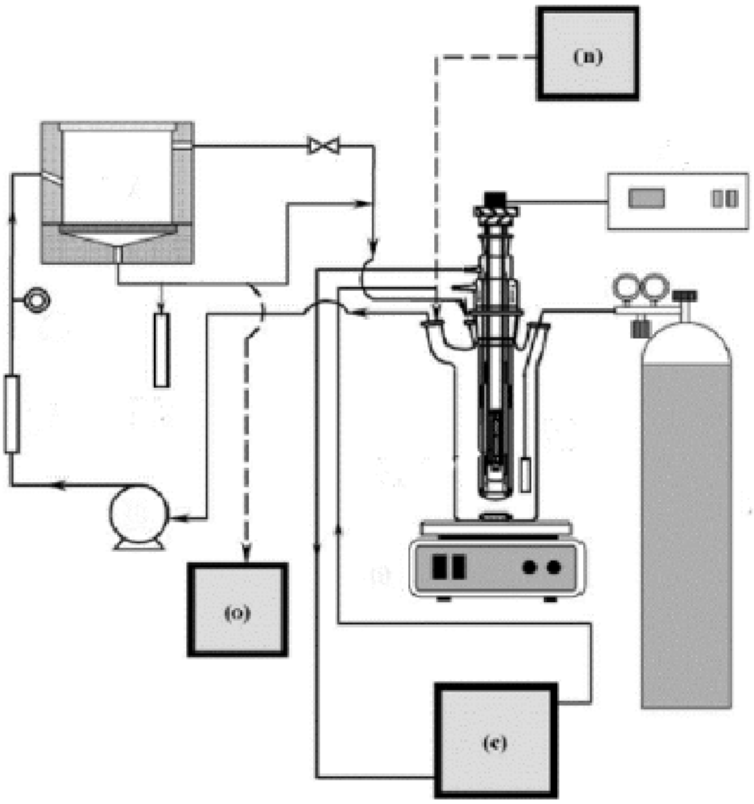

Fig. 11. Diagram of PMR with suspended catalyst comprising of irradiation source, gas and power supply[17].

membrane cell to photoreactor, membrane cell was pressurized with the help of diaphragm pump. A pollutant sample is placed in a tank, then pumped to a photoreactor where the light source is placed, oxygen is supplied to the system. Then photo reacted solution is passed to a pressurized cell containing the membrane where direct flow filtration is performed. The experiment is done in both suspended and immobilized photocatalyst, results conclude that the suspended photocatalyst is more efficient than that of the entrapped one.

TFF is more efficient than DFF because the solution passes directly through the membrane of DFF leading to a clogging problem by which reduction in the pore size and it leads to decrease flux and rejection efficiency. In TFF the flow of polluted water is parallel with respect to membrane surface, this will cause turbulence on the membrane surface and reduces clogging by increasing the efficiency of the membrane.

Conclusion

PMRs shows promising result pollution degradation in aqueous media. The composite photocatalyst shows high efficiency and can be utilized under visible range. PMR efficiency also depends on the membrane preparation method, which is decided by the uniformity in the distribution of photocatalyst. PMRs with suspended photocatalyst reactor shows higher efficiency than that of immobilized photocatalyst reactor. But immobilized photocatalyst reactor has high durability, higher flux, and rejection efficiency. TFF has high efficiency than DFF due to fewer clogging problems in the membrane.

References

1. A. Boretti and L. Rosa, *npj Clean Water*, 2019, **2(1)**. doi: 10.1038/s41545-019-0039-9.
2. S. Zhu and D. Wang, *Adv. Energy Mater.*, 2017, **7(23)**, 1. doi: 10.1002/aenm.201700841.
3. W. Zhang, X. Xiao, L. Zheng and C. Wan, *Appl. Surf. Sci.*, 2015, **358**, 468. doi: 10.1016/j.apsusc.2015.08.054.

4. X. Li, J. Yu and M. Jaroniec, *Chem. Soc. Rev.*, 2016, **45(9)**, 2603. doi: 10.1039/c5cs00838g.
5. B. J. Starr, V. V. Tarabara, M. Zhou, S. Roualdès and A. Ayral, *J. Memb. Sci.*, 2016, **514**, 340. doi: 10.1016/j.memsci.2016.04.050.
6. Y. Mansourpanah, S. S. Madaeni, A. Rahimpour, A. Farhadian and A. H. Taheri, *J. Memb. Sci.*, 2009, **330(1-2)**, 297. doi: 10.1016/j.memsci.2009.01.001.
7. R. Singh, V. S. K. Yadav and M. K. Purkait, *Sep. Purif. Technol.*, 2019, **212**, 191. doi: 10.1016/j.seppur.2018.11.029.
8. B. Xu *et al.*, *Chem. Eng. J.*, 2020, **399(5)** 125749. doi: 10.1016/j.cej.2020.125749.
9. P. Dong, Z. Huang, X. Nie, X. Cheng, Z. Jin and X. Zhang, *Mater. Res. Bull.*, 2019, **111(11)**, 102. doi: 10.1016/j.materresbull.2018.11.007.
10. Y. Shen *et al.*, *Mater. Res. Express*, 2019, **6(9)**. doi: 10.1088/2053-1591/ab3028.
11. D. Klauson, M. Šakarašvili, N. Pronina, M. Krichevskaya, E. Kärber and V. Mikli, *Environ. Technol. (United Kingdom)*, 2017, **38(7)**, 860. doi: 10.1080/09593330.2016.1214185.
12. L. Aoudjit, P. M. Martins, F. Madjene, D. Y. Petrovykh and S. Lanceros-Mendez, *J. Hazard. Mater.*, 2018, **344**, 408. doi: 10.1016/j.jhazmat.2017.10.053.
13. J. Fu, M. Ji, Z. Wang, L. Jin and D. An, *J. Hazard. Mater.*, 2006, **131(1-3)**, 238. doi: 10.1016/j.jhazmat.2005.09.039.
14. J. C. Espíndola, R. O. Cristóvão, A. Mendes, R. A. R. Boaventura and V. J. P. Vilar, *Chem. Eng. J.*, 2019, **378(6)**, 122114. doi: 10.1016/j.cej.2019.122114.
15. Darunee Bhongsuwan, Tripob Bhongsuwan, and Jamras Na-Suwan, *Songklanakarin J. Sci. Technol.*, 2002, **24**, 999.
16. C. Zhu, G. Liu, K. Han, H. Ye, S. Wei and Y. Zhou, *Chem. Eng. Process. Process Intensif.*, 2017, **120(3)**, 20. doi: 10.1016/j.cep.2017.06.012.
17. R. Molinari, F. Pirillo, M. Falco, V. Loddo and L. Palmisano, *Chem. Eng. Process. Process Intensif.*, 2004, **43(9)**, 1103. doi: 10.1016/j.cep.2004.01.008.