Ultrafiltration Integrated Photocatalytic Treatment Systems for Water and Wastewater

C. Nirmala Rani and S. Karthikeyan

Abstract Advanced wastewater treatment and reclamation is a sustainable strategy to address the issues related to emerging contaminants (ECs) present in aqueous solutions. Conventional treatment methods are found to remove ECs only partially. Low-pressure membrane separation processes have received extensive attention from researchers worldwide due to their simplicity, eco-friendliness, continuous separation, easy scaling up, the possibility of hybrid processing, low fabrication, and operating costs. However, these processes are limited due to low membrane lifetime, low selectivity, flux decline, linear up-scaling, and fouling. Heterogeneous photocatalytic systems using TiO_2 photocatalyst had been intensively investigated and found to be efficient, economical and environmentally friendly, and sustainable for the degradation of ECs from aqueous solutions owing to the various advantages it possesses including (i) an increase in photocatalytic potential, (ii) stability (chemical and thermal), (iii) energy efficiency, (iv) cost-effectiveness, and (v) nontoxicity. However, these systems have the drawbacks of catalyst separation after treatment and incomplete mineralization. Photocatalysis (PCO) has been integrated with low-pressure membrane systems to address this issue. This chapter provides an overview of ultrafiltration (UF) integrated photocatalytic oxidation (PCO) systems in aqueous solutions, especially for the removal of emerging contaminants (ECs). The mechanisms, merits, and demerits of UF separation, PCO process, and integrated ultrafiltration-photocatalytic oxidation (UF-PCO) processes are discussed in detail. The key influencing factors/operating variables on the performance of UF-PCO systems such as; photocatalyst loading, structure, and properties of photocatalyst, light wavelength, light intensity, initial concentration of pollutant, pH of feedwater, temperature, aeration, inorganic ions, membrane material, membrane pore size, transmembrane pressure (TMP), membrane packing density, and cross-flow velocity (CFV) are discussed elaborately. Furthermore, the removal of ECs had been

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explored with respect to its characteristics and the same of the membrane. A discussion on the economic aspects of UF-PCO systems in water and wastewater treatment is also included.

Keywords Ultrafiltration · Photocatalytic oxidation · Permeate flux · Membrane fouling · Emerging contaminants

1 Introduction

Emerging contaminants (ECs) are chemicals, including pharmaceuticals, personal care products, hormones, pesticides, persistent organic pollutants (POPs), disinfection by-products, etc., that impact humans or ecology. The occurrence of ECs may be from anthropogenic and natural substances, and their concentrations in water generally range from nanograms to micrograms per litre (Luo et al. 2014). ECs in surface water would be a serious concern while using the ECs contaminated surface water for drinking purposes (Riva et al. 2018).

Membrane separation (MS) processes have become a new innovative emerging technology in treating aqueous solutions (Lau et al. 2020, Khan et al. 2021). During MS, the membrane identifies and recovers particles from aqueous solutions (Sirkar 2008). The pressure-driven (PD) membrane processes are more popular and extensively used than non-pressure-driven (NPD) processes. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) is novel, attractive, and alternative methods to conventional treatment for treating both water and wastewater (Baker 1991; Ahmad 2005) due to their various advantages viz., (i) high-quality permeate, (ii) could be operated under moderate temperatures, (iii) low energy requirements, (iv) non-necessity of adding chemicals, (v) reusability of water, (vi) some valuable waste constituents, and (vii) could be easily coupled with other processes. During the MS process, depending upon the membrane's pore size, the contaminants/pollutants are removed, and water passes through the membrane. However, the main drawback in these systems is membrane fouling (Wiesner and Apel 1996; Scholz and Lucas 2003; Padaki et al. 2015) which leads to flux decline that can be reversible or irreversible.

UF membranes with an operating pressure of 2–8 bars can remove macromolecules with a molecular weight (MW) ranging from 1000–100,000 Da, bacteria, and viruses and fail to remove soluble and low MW compounds. However, UF membranes have successfully been applied for drinking water treatment over the past 15 years in the recently upgraded treatment plants (Huang et al. 2009).

The Photocatalytic oxidation (PCO) method is one of the advanced oxidation processes (AOPs) in which various light sources such as; ultraviolet (UV), visible (VIS), and infrared (IR) radiations are used to produce an oxidizing/reducing species ($OH^{\bullet}$ and $O_2^{\bullet-}$) (Palmisano et al. 2007; Molinari et al. 2017, 2021). In this PCO system, hydroxyl radicals (reactive species) mineralize the hazardous, toxic organic compounds into simpler, harmless end products (Damodar et al. 2009; Rani and

Karthikeyan 2021). Heterogeneous photocatalysis has become more popular among the AOPs and found successful for the treatment of degrading hazardous pollutants due to; (i) the usage of safer and greener catalysts (particularly TiO_2), in contrast to the thermally induced catalysis that occurs in heavy metal catalysts (Guo et al. 2019; Riaz and Park 2020), (ii) mineralization of non-biodegradable organic compounds into non-toxic by-products with the help of molecular oxygen, (iii) high versatility due to its applicability in all three phases including liquid, solid and gaseous, (iv) usage of renewable solar energy and (v) could be coupled easily with other technologies (Tufail et al. 2020; Molinari et al. 2021). Despite its various advantages, the application of PCO processes in the treatment of both municipal and industrial wastewater is limited owing to; (i) the cost-related to the recovery and reuse of heterogeneous photocatalyst and (ii) poor process selectivity (Loddo et al. 2009; Molinari et al. 2017, 2021). To overcome these limitations, PCO processes are coupled with MS processes.

Coupling membrane filtration with advanced oxidation processes is an effective technique because of the technical feasibility of MS processes (Ganiyu et al. 2015). Combining classical photoreactors with membrane processes is a helpful method to meet green technology's environmental and economic benefits (Molinari et al. 2017).

Many of the organic compounds present in the water/wastewater are recalcitrant, endocrine-disrupting, and genotoxic. They directly impact ecosystems and will be a serious concern for both humans and the environment even though they are much lower in concentration up to ng/L. Recent research focused more on integrated UF-PCO systems, and the same was implemented in water and wastewater treatment (Mozia 2010). UF-PCO systems are found to be highly effective for the removal of organic compounds (Molinari et al. 2008; Sarasidis et al. 2014) due to the various advantages viz., (i) ambient temperature operation, (ii) no change in phase, and (iii) up to 90% removal of organic compounds (Rani et al. 2021).

Therefore this book chapter explores the applicability of UF-PCO systems in wastewater treatment. UF and PCO processes are overviewed separately regarding their features, mechanisms, and applications. The operating parameters that affect the integrated UF-PCO processes have been discussed elaborately. The types of UF-PCO systems and their operational limitations, such as membrane fouling and its control measures, are discussed in detail. In addition, the removal of emerging contaminants that are of great environmental concern has been discussed in detail with respect to the characteristics of ECs and membrane properties.

2 UF Membrane Process

2.1 An Overview

Ultrafiltration (UF) is a type of most widely used low pressure-driven membrane process in which molecular weight cut-off (MWCO) is used as an important tool to characterize the membrane. High molecular weight (HMW) compounds are retained

by the UF membrane, while low molecular weight compounds (LMW) are less retained/rejected or pass through the membrane (Mozia and Morawski 2009; Rani et al. 2021). The application of UF membranes is not only limited to treating industrial wastewaters, including wastewaters from food, dairy, beverage, and pharmaceutical industries, but also as an advanced method in treating municipal water and wastewater. Recovery, purification, and concentration of products are the added advantages of providing UF membranes in wastewater treatment. UF membrane was also employed in oily wastewater treatment due to: (i) the non-necessity of chemical additives and (ii) low energy cost (He and Jiang 2008). In oily wastewaters, heavy metals such as Cu and Zn have been removed up to 95% (Bilstad and Espedal 1996; Padaki et al. 2015), while benzene, toluene, and xylene (BTX) removal was only 54% (Bilstad and Espedal 1996) using UF membranes.

2.2 Membrane Materials

Membranes that treat aqueous solutions may be polymeric and inorganic (ceramic). Researchers in exploring new membrane materials have made intensive efforts.

2.2.1 Polymeric Membranes

The polymeric membrane materials could be cellulose acetate (CA), polypropylene (PP), polyacrylonitrile (PAN), polyethersulfone (PSU) and polysulfone (PSU), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF) (Ochoa et al. 2003; Rahimpour and Madaeni 2007; Mansourizadeh and Azad 2014) among which polyethersulfone (PSU) and polysulfone (PSU) are low UV resistant owing to the presence of sulfone groups. Similarly, polypropylene (PP), polyacrylonitrile (PAN), and cellulose acetate (CA) had also shown less resistance due to the breakage of chemical bonds of the methyl group (-CH-) when exposed to UV light. Meanwhile, polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE) exhibited good UV resistance.

When polymeric membranes are applied in slurry UF-PCO systems, the membranes have the limitations such as; (i) low UV light resistance (Lee et al. 2001; Chin et al. 2006), (ii) damage in the structure of the membrane due to the generation of hydroxyl radicals (Chin et al. 2006; Mozia 2010) (Chin et al. 2006; Mozia 2010) and (iii) stability to resist the penetration of photocatalyst particles (Mozia et al. 2014, 2015). Photocatalytic membranes have direct exposure to the light source and get irradiated. The exposure of UV light for 10 days of 200 Mm H_2O_2 condition cracked the membrane surface. After 30 $_{days}$ of UV exposure and 3 wt% of TiO_2 nanoparticles, TiO_2/PVDF dual-layer membrane revealed a decrease in tensile strength from 28–23 MPa owing to the cracks formed on the surface of the membrane (Dzinun et al. 2017). However, UV light resistance of the membrane is based upon both the source materials and formulation of polymer (Chin et al.

2006). Hence the polymeric membranes were chosen for the water, and wastewater treatment should be better UV resistant.

2.2.2 Ceramic Membranes

A better substitute for polymeric membranes is ceramic membranes due to; (i) the high-water recovery rate, (ii) extended backwash intervals, (iii) less damage of membrane structure (Azrague et al. 2007), (iv) chemical resistance, (v) thermal stability, (vi) superior physical integrity, (vii) less chemical need, (viii) less membrane cleaning frequency, and (ix) longer membrane lifetime. In addition, the application of advanced oxidation processes could significantly reduce membrane fouling by organic compounds as a pre-treatment step, which improves the quality of water and reduces the operating costs. Ceramic membranes can withstand high backwash pressure and provide excellent backwash efficiency (Reguero et al. 2013).

Ceramic membranes are more advantageous than polymeric membranes due to; (i) great affinity between the membrane and photocatalyst, (ii) sustainability at elevated temperatures, and (iii) feasibility for transforming amorphous TiO_2 precursor to the photocatalytically active phase (e.g. anatase).

3 Photocatalyst

For photocatalytic processes, the light sources may be artificial lamps or solar irradiation (Alfano et al. 2000). The redox potential of an efficient semiconductor photocatalyst must lie within its bandgap (Li et al. 2005). Semiconductors such as; Fe_2O_3, GaP, and GaAs have narrow bandgaps of 2.3 eV, 2.23 eV, and 1.4 eV, respectively, and can absorb visible light. TiO_2 has been widely used among semiconductor photocatalysts due to its chemical stability, low cost, and harmless nature (Fujishima et al. 2000), even though it has a broad bandgap of 3.2 eV. TiO_2 photocatalyst is not driven by visible light (Miyauchi et al. 2002) and can only be activated upon irradiation in the UV domain ($\lambda \leq 387$ nm for anatase) (Irie et al. 2003; Pelaez et al. 2012). Since 5% of the solar spectrum is occupied with UV and 95% of UV are in the UV-A range, researchers had focussed their work on the preparation of novel photocatalysts that can be activated upon the solar spectrum of the visible range (Rehman et al. 2009). In the recently developed UF-PCO systems, visible-light photocatalysts (Gao et al. 2014; Athanasekou et al. 2014) had been applied. To lower the bandgap of TiO_2 and to increase the photocatalytic activity visible light active solar spectrum, photocatalysts have been modified by composite photocatalysis with carbon nanotubes (Yu et al. 2005; Ahmed et al. 2021) noble metals or metal ions (Ni et al. 2007), dye sensitizers (Tabei et al. 2012), and non-metal doping (Fujishima et al. 2008). The graphical representations of bandgaps of photocatalyst subjected to UV and visible light are graphically illustrated in Fig. 1a. Chong et al. (2010) and Malato et al. (2009) had discussed the same in detail in their studies. Modification of photocatalyst with
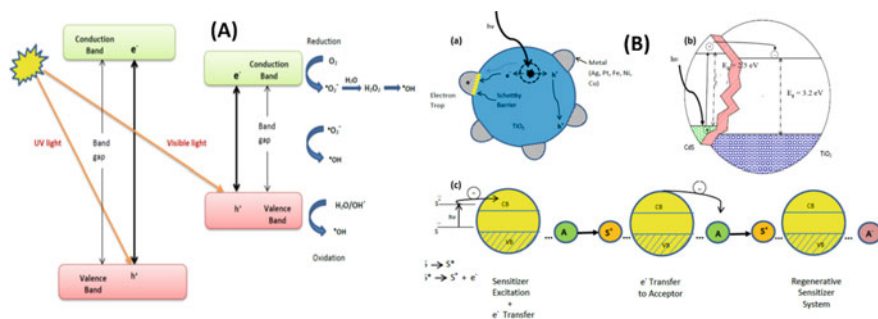
Fig. 1 **A** Graphical illustration of bandgaps of photocatalyst subjected to UV and visible light; **B** **a** Modified metal photocatalyst, **b** TiO$_2$ coupled semiconductor, **c** Dye sensitizer—excitation steps (Rani et al. 2021)

metal, coupling TiO$_2$ with semiconductor, and the excitation steps of a dye sensitizer are graphically illustrated in Fig. 1b. Even though visible light active photocatalysts are cost-effective, for the practical applicability of the process, the process should promote extensive usage of photons and high quantum efficiency (Argurio et al. 2018).

4   UF Membranes Integrated PCO (UF-PCO) Systems

The schematic diagram of a UF-PCO system is graphically illustrated in Fig. 2. The configurations of UF-PCO systems could be of two types, namely; (i) systems with immobilized photocatalyst (photocatalyst is supported on a carrier material) and (ii) systems with suspended photocatalyst (photocatalytic particles remain in suspension). Immobilized UF-PCO systems could be further divided into three types, namely; (i) membrane surface coated with photocatalyst, (ii) membrane with photocatalyst blended, and (iii) stand-alone photocatalytic membrane. In the first two types of Immobilized UF-PCO systems, photocatalysts are initially manufactured and then coated/blended with the membrane, while in the third type of system, the membrane itself is fabricated with a photocatalyst in pure form. Based upon the position of the PCO unit and UF module, UF-PCO systems with photocatalyst in suspension were further divided into two types as (i) split type and (ii) integrative type. In integrative type UF-PCO systems, the UF module and PCO unit are merged in one apparatus, and both UF separation and PCO processes occur simultaneously in the same reactor vessel, while in the split type UF-PCO systems, two processes occur separately in two different apparatuses. The merits and demerits of both types of UF-PCO systems are represented in Tables 1 and 2.

Integrated UF and PCO technology has attracted many recent researchers and has been declared an effective method of treating both water and wastewater. PCO units may be employed pre-or post-treatment with UF systems. While degrading
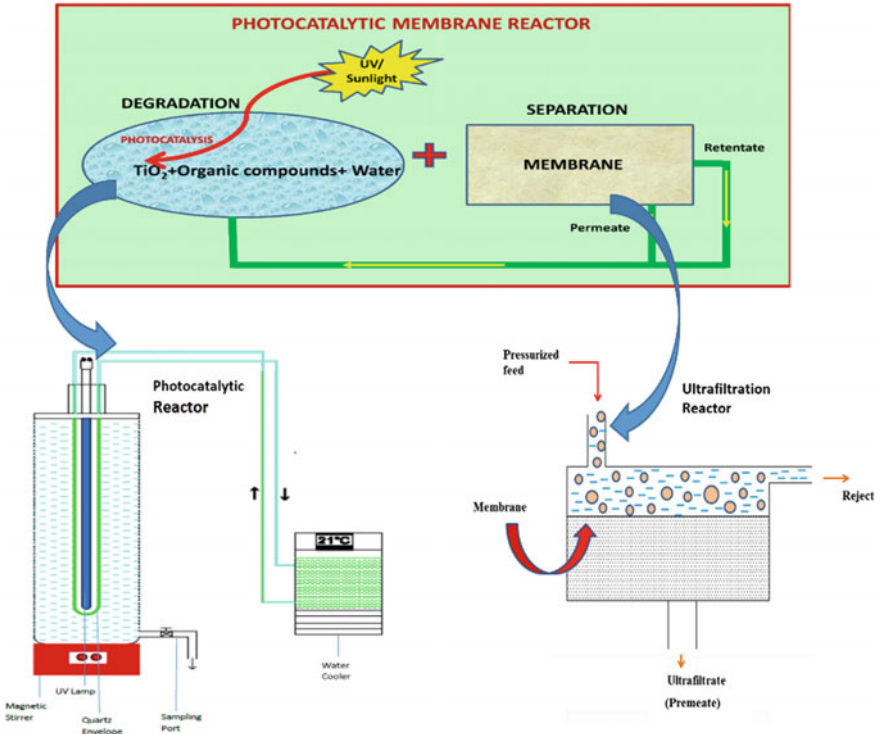
Fig. 2 A typical integrated UF-PCO system

Table 1 The characteristics of UF membrane

| Type of membrane material	polymeric, metallic, ceramic
membrane pores	1 to 100 nm
Type of driving force applied	Pressure (1 to 10 bar)
Mechanism of transport	Flow through pores
Mechanism of separation	Size exclusion or sieving
Permeate flux	50 to 1000 L/m^{2}h
Energy requirement	10 to 150 W/m^3

organic compounds, the PCO system could be used as a pre-treatment system in the feedwater. In contrast, in the integrated UF-PCO system, PCO could be used as a post-treatment system during the mineralisation of contaminants in permeate and retentate. (Rani et al. 2021) (Fig. 3).

The application PCO unit with the UF system may be either as a (i) pre-treatment system or as a (ii) post-treatment system. During degradation of organic compounds in the feed water, the UF-PCO system could be used as a pre-treatment system. In contrast, the integrated system could be used as a post-treatment system during the

Table 2 Merits and demerits of UF-PCO systems with photocatalysts in suspension and immobilized

	UF-PCO systems with photocatalysts in suspension	UF-PCO systems with immobilized photocatalyst
Advantages	1. Due to more active surface area for adsorption, high photocatalytic activity, and degradation efficiency 2. Photocatalyst loadings can be easily varied to the required value 3. Destruction of membrane structure due to UV light and hydroxyl radicals could be avoided 4. Exhausted catalysts can be replaced without replacing the membrane	1. Non-necessity of photocatalyst separation after treatment 2. Degradation of compounds occurs in both the feed and permeate sides 3. Less membrane fouling owing to the increase in hydrophilicity and degradation of organic compounds 4. Catalyst separation and recycling are not needed
Disadvantages	1. Due to the presence of suspended photocatalyst nanoparticles, a light scattering effect is observed 2. Membrane fouling is caused by photocatalysts and pollutants, which leads to permeate flux decline 3. Higher operating cost 4. An additional process is needed to separate photocatalyst particles from the treated solution	1. Due to the less surface area available for photodegradation, photocatalytic efficiency is less 2. According to the wastewater composition, photocatalyst concentration cannot be adjusted 3. Destruction of polymeric membrane structure by UV light and the reactive species (hydroxyl radicals) 4. The membrane has to be exchanged when the photocatalyst loses its activity
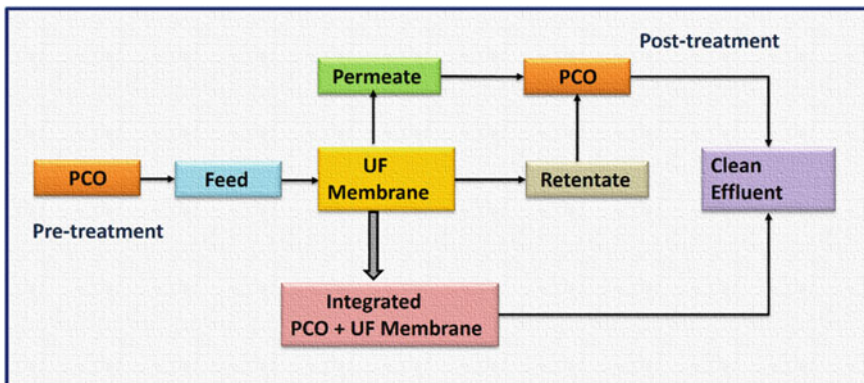
Fig. 3 The graphical illustration of the scheme UF process with PCO used for wastewater treatment (Rani et al. 2021)
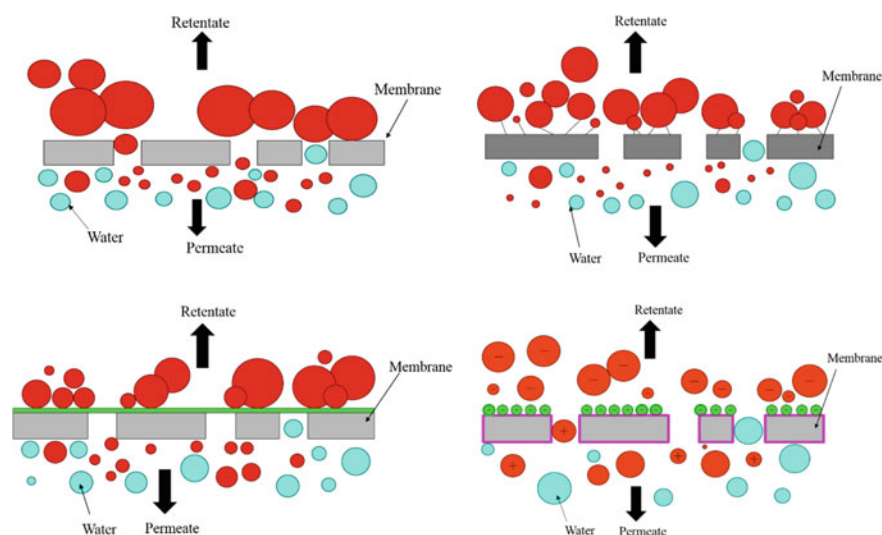
Fig. 4 ECs removal mechanisms through membrane separation; **a** size exclusion, **b** hydrophobic interactions, **c** adsorption, and **d** electrostatic interactions (Rani et al. 2021)

mineralisation of contaminants in permeate and retentate. (Rani et al. 2021). The flow diagram illustrating the scheme of the UF process with PCO used for wastewater treatment is illustrated in Fig. 4.

Even though many literature studies on UF integrated PCO processes are available with different configurations (Fernandez et al. 2014; Sarasidis et al. 2014; Rani and Karthikeyan 2018) and all cannot be discussed in order to get a complete understanding of the configurations, a thorough reading of each literature is needed.

5 Operating Variables of Integrated UF-PCO Systems and Their Effect on Degradation

While fabricating the economically viable and technically feasible UF-PCO system, selecting appropriate operating parameters is vital. The parameters that affect the UF-PCO systems are; (i) structure, properties, and loading of photocatalyst, (ii) light wavelength and intensity, (iii) initial concentration of pollutant (iv) feedwater pH (v) temperature, (vi) inorganic ions, (vii) aeration, (viii) membrane material, (ix) membrane pore size, (x) aeration, (xi) transmembrane pressure (TMP), and (xii) membrane module packing density.

5.1   Effect of Photocatalyst Loading on Pollutant Degradation

In slurry UF-PCO systems, the increase in photocatalyst loading results in increased surface area for catalyst adsorption and photodegradation up to a certain extent and a further increase in the concentration of photocatalyst reduced the degradation rate. It hence decreased the removal efficiency (Gaya and Abdullah 2008). The decrease in removal efficiency may be due to excess photocatalyst concentration, which leads to higher solution opacity, increased solution turbidity, and reduced photons' penetration through the reaction mixture. In addition, the agglomeration of photocatalyst also reduces the total surface area of photocatalyst (Mozia 2010; Zhang et al. 2016) and hence reduces the photocatalytic activity in UF-PCO systems.

In immobilized UF-PCO systems, photocatalyst concentration increases the photodegradation rate. Excessive addition of photocatalyst would diminish the photocatalytic activity of photocatalyst at the bottom layer through absorption, light scattering, reflection, and blockage of UV light. In addition, adding more amounts of photocatalyst will also decrease the membrane pores and porosity (Xiao et al. 2010). Furthermore, an optical thickness that considers both geometrical thicknesses of the photoreactor and photocatalysts concentration is identified as one of the elemental parameters of a photocatalytic reactor (Zheng et al. 2017).

5.2   Effect of Properties and Structure of Photocatalyst on Pollutant Degradation

The properties and structure of photocatalysts that include bandgap energy, active surface area, crystal composition, and particle size have a greater impact on its efficiency (Zheng et al. 2017). The bandgap is an important property that must be considered while selecting a photocatalyst. The photocatalyst can achieve visible light response when it has lower bandgap energy, due to which it needs less energy for the excitation of electrons from the valence band (VB) to the conduction band (CB). Due to more photocatalytic activity, less toxicity, and chemical stability, TiO_2 based photocatalysts have become more popular. However, photocatalysts with a greater bandgap could be modified in order to make them responsive to visible light.

5.3   Effect of Light Wavelength on Pollutant Degradation

The UV electromagnetic spectrum can be divided into three types namely; UV-A (λ_{max} = 315–400 nm) (3.10 eV to 3.94 eV), UV-B (λ_{max} = 280–315 nm) (3.94 eV to 4.43 eV) and UV-C (λ_{max} = 100–280 nm) (4.43 eV to 12.4 eV) (Chong et al. 2010; Zheng et al. 2017). The UV flux near the earth's surface is 20–30 W/m². This range of UV flux corresponds to 0.2–0.3 mol photons/m²h (300–400 nm) provided

by the sun is more efficient for the degradation of pollutants in the aqueous phase. Both UV-A and UV-C lamps are widely used due to their ability to obtain higher photon fluxes. An increase in light wavelength decreased photocatalytic degradation (Zhang et al. 2008). Shorter wavelengths caused higher energy illumination (Zertal et al. 2001; Han et al. 2004). However, the utilization of solar lights is limited during cloudy days. Hence recent studies have been focused on modifying photocatalysts to the visible solar range of the spectrum (Rehman et al. 2009). A UF-PCO system was evaluated by Kertèsz et al. (2014) for the removal of Acid Red 1 employing 365 nm and 254 nm irradiation intensities and reported that the degradation rate was rapid and greater at 254 nm.

5.4 Effect of Light Intensity on Pollutant Degradation

The effect of light intensity on pollutant removal could be divided into three stages (Mozia et al. 2010; Zhang et al. 2013) as (i) low intensities in the range of 0–20 mW/cm^2; Due to negligible electron–hole recombination, the degradation rate of pollutant increases linearly with the intensity of light (Wang et al. 2013), (ii) High light intensities of >25 mW/cm^2; Since electron–hole pair separation competes with recombination, the degradation rate of pollutant is related to the intensity of light, (iii) High light intensities of >25 mW/cm^2; degradation rate of pollutant is independent of light intensity (Argurio et al. 2018). Increasing the light intensity increases the volumetric reaction rate until the mass transfer limit is obtained (Ollis et al. 1991). When the irradiation intensity of light is high, there is a transfer of electrons from the photocatalyst to oxygen in water, forming $O_2 \cdot^-$. This limits the degradation rate when the size of the photocatalyst particles is more or when it agglomerates (Doll and Frimmel 2005).

5.5 Effect of Initial Pollutant Concentration on Pollutant Degradation

The initial concentration of compound/pollutant is a key parameter that affects the performance of UF-PCO systems. An increase in the pollutant concentration imparts a negative impact on degradation efficiency due to the loss of solution opacity, less transmission of UV light, and occupation of active sites of photocatalyst by the pollutants (Damodar et al. 2010; Kertèsz et al. 2014). In addition, at high initial pollutant concentration, a thick fouling layer was observed on the surface of the membrane, which severely affected the compound degradation rate due to the availability of a lesser surface area. At lower initial concentrations, the degradation was more (Ong et al. 2014).

5.6 Effect of Feedwater pH on Pollutant Degradation

The feed solution pH significantly impacts degradation, and it is very complex. The impact of variations in feedwater pH on the photocatalytic degradation of organic compounds in aqueous solution depends upon (i) the ionization state of photocatalyst surface, (ii) generation of hydroxyl radicals, (iii) agglomeration of photocatalyst particles, (iv) position of valence and conduction band of photocatalyst, and (iv) hydroxyl radical generation.

For the membrane separation process, the difference in pH leads to a change in zeta potential values of photocatalyst particles. The change in pH will increase the particle size of the photocatalyst due to the photocatalyst particles' dispersion and agglomeration and has a significant impact on membrane permeate flux (Huang et al. 2007). In addition, electrostatic attraction between pollutants and the photocatalytic layer on the membrane surface varies at different pH conditions (Ma et al. 2009) and influences the adsorption of pollutant molecules on the membrane surface.

Wang et al. (2013) investigated the degradation of carbamazepine (CBZ) using C-N-S doped TiO_2 and reported that the degradation of CBZ was maximum at alkaline pH. This result contradicts the results obtained by Fu et al. (2006) (for fulvic acid degradation) and Chin et al. (2007b) (for Bisphenol A degradation), in which the authors reported the maximum degradation at acidic pH. Khan et al. (2015) reported that HA degradation was twice more at low pH than at high pH. Since contradictory results are available, more research needs to focus on the effect of pH on photocatalytic degradation.

5.7 Effect of Temperature

The ideal temperature for photodegradation studies falls between 20 ºC and 80 ºC (Herrmann 1995, 2005; Gogate and Pandit 2004). At low temperature (below 0 ºC) there is an increase in apparent activation energy due to which the degradation products desorb from the catalyst surface, and hence the process emerges as a rate-limiting step (Chong et al. 2010). At high temperatures >80 ºC, electron–hole recombination is enhanced that diminishes photodegradation and hence low degradation efficiency. For the temperature range of 20 ºC–60 ºC, an increase in the photodecomposition rate was observed (Mozia et al. 2005; Thiruvenkatachari et al. 2008).

In UF-PCO systems, the temperature substantially influences solution viscosity and affects the permeate flux of the membrane. At high temperatures, feed solution viscosity decreases, and induced turbulence disperses the fouling cake and concentration polarization layers on the membrane surface. This increases the permeate flux of the membrane.

5.8 Effect of Inorganic Ions

The impacts of the presence of inorganic salts such as $NaHCO_3$, Na_2HPO_4, and Na_2SO_4 in the feed solution on fouling and stability of UF membranes applied in the UF-PCO system was investigated by Darowna et al. (2014). The authors observed a remarkable decrease in membrane flux when salt content was high. Severe permeate flux decrease was noticed when HCO_3^- ions were present, which may be owing to increased pH and a dense fouling layer formed on the membrane surface. It was also observed that the maximum permeate flux (even greater than the permeate flux obtained in UF-PCO systems with fresh photocatalyst) was observed when SO_4^{2-} ions were present. The increased permeate flux was owing to the repulsion of TiO_2 photocatalyst particles over the membrane surface and produced lower fouling layer thickness.

5.9 Effect of Aeration

In PCO-UF systems, aeration serves three important purposes; (i) enhances photo-oxidation of organic molecules by providing dissolved oxygen (DO) for suppressing electron–hole recombination reactions (Asha and Kumar 2015), (ii) facilitates homogeneous mixing and fluidize the system, and (iii) induces turbulence in submerged membrane systems and reduces membrane fouling. An increase in aeration rates generates more shear rates, keeps the photocatalyst particles in suspension, and prevents agglomeration. Lesser the agglomeration, the greater the degradation rate of the compounds due to the availability of more surface area (Chin et al. 2007a). However, excessive aeration prevents the adsorption of pollutants onto the photocatalytic surface and decreases the removal efficiency. Aeration provided in the form of the coarse bubble (Huang et al. 2009) or bubbly flow (Du et al. 2017) generated turbulent flow, induced shearing effect, removed fouling layer, and concentration polarization onto membrane surface (Zheng et al. 2017).

5.9.1 Effect of Membrane Material

The membrane material is an important parameter that affects pollutant removal efficiency. UV light greatly influences polymeric membranes, and UV light exposure could damage the membrane material (Chin et al. 2006). The breakage of the chemical bonds of the methyl group (-CH-) was found to be responsible for membrane damage in PAN, polypropylene (PP) and, cellulose acetate (CA) membranes, while the presence of sulfone groups in polyethersulfone (PES) and polysulfone (PSU) membranes caused for the damage in membrane structure. However, PTFE and PVDF membranes are the least affected polymeric membranes by UV light. In addition to

this, it was also observed that ceramic and metallic membranes exhibited higher resistance to UV lights. Though ceramic membranes consist of different materials such as; TiO_2, Al_2O_3, and ZrO_2, TiO_2 membranes are mostly employed in ultrafiltration (UF) systems since they possess excellent hydrophilic properties and better fouling resistance (Wang et al. 2007). Due to chemical stability and increased mechanical strength, ceramic membranes were the best suitable for UF-PCO systems (Zhang et al. 2016; Horovitz et al. 2019).

5.9.2 Effect of Membrane Pore Size on Compound Removal

The chosen pore size of the selected membrane must exhibit (i) a high retention rate for the target pollutants, (ii) high photocatalytic separation efficiency (Zheng et al. 2017) and greater membrane permeate flux (Xiao et al. 2010). For the efficient applications of UF membranes in UF- PCO systems, the membrane pores' size is greater to reduce membrane resistance and increase the permeate flux (Xiao et al. 2010). Low-pressure UF membranes can retain particles over 10 nm and hence could be able to separate the photocatalyst more efficiently. However, it is to be noted that when high-quality permeate is required, high-pressure membranes are of good choice. High-pressure membranes exhibit high separation efficiency, retain pollutants and their intermediates for further treatment, and promote removal efficiency.

5.9.3 Effect of Transmembrane Pressure (TMP) and Cross Flow Velocity (CFV) on Compound Removal

Choo et al. (2008) observed a reduction in permeability while CFV decreases from 1.45 to 0.19 m/s. Without backwashing, higher TMP and lower CFV intensified the deposition of TiO_2 particles on the membrane surface, which resulted in membrane fouling and a decrease in compound removal efficiency (Wang and Lim 2012). The cake resistance decreased with an increase in CFV. Higher values of CFV and shear rates could dislodge the photocatalyst particles on the membrane surface, lessen the cake layer thickness and reduce membrane fouling (Wang 2016). When TMP is increased, the permeation rate of the reaction mixture is accelerated. This increases cake and fouling resistances and may cause less membrane life (Zhang et al. 2007). In general, to achieve guaranteed flux, the TMP should be kept as low as possible.

5.9.4 Effect of Membrane Packing Density on Compound Removal

The voids in the fibers not only allow water to flow through but also promote mass transfer between the feedwater and the surface of the membrane (Yeo et al. 2006; Günther et al. 2010; Ren et al. 2013). Small diameter hollow fibers with high packing density contribute to more filtration area and promote profound inter-fiber fouling within the fibers (Yoon et al. 2004; Günther et al. 2010; Ong et al. 2015). Membrane

with high fiber packing density caused the foulant to accumulate inside the fiber module and adversely affected photoactivity. This observation was in line with the observations made by Günther et al. (2010). In this study, the author noticed an increase in permeate flux by 25% when fiber packing density decreased from 80 to 40%. An increase in packing density decreased the mass transfer coefficient up to 50% of the total volume fraction, and a further packing density increased the mass transfer coefficient (Wu and Chen 2000).

6 Recovery and Reuse of Photocatalyst Particles in UF-PCO Systems

The major advantage of integrating membrane processes with photocatalysis is the recovery of photocatalyst particles from the treated solution and the reuse of recovered photocatalyst particles. All types of pressure-driven membrane processes, including MF processes even with the pore sizes of 0.1 μm (Huang et al. 2007; Choo et al. 2008) and 0.4 μm (Meng et al. 2005) were found to be very effective in retaining photocatalyst particles.

By synergistically coupling MS with PCO systems and continuously operating the reactor, the photocatalyst particles were effectively recovered and reused (Jiang et al. 2010; Rani and Karthikeyan 2018; Espindola et al. 2019), which was confirmed by the low turbidity detected in the permeate. Jiang et al. (2010) reported the permeate turbidity <0.3 NTU after continuously recirculating the solution and operating the UF-PCO system for 120 min. Rani and Karthikeyan (2018) utilized the same slurry for the seven cycles and found that the degradation and mineralization efficiencies remained almost the same after running the reactor for seventh cycles when the photocatalyst was fresh and used. Due to the deposition of photocatalyst particles over the membrane surface, a small drop in removal efficiencies was noticed during the second cycle.

UF membranes were proved to be highly effective in dislodging photocatalyst particles and removing the dense cake layer formed on the membrane surface (dynamic membrane). TiO_2 photocatalyst particles are nm in size (the size lesser than the pore size of UF membrane) and hence could not be rejected by UF membranes. However, when they are dispersed into the feedwater solution, the size of the photocatalyst particles increases from nm to μm due to agglomeration and hence easily retained by low-pressure UF membranes.

Sopajaree et al. (1999) employed a UF-PCO system with a TiO_2 concentration of 1 g/L and reported the permeate turbidity of 0.22–0.45 NTU while the feedwater turbidity measured during this study was 5200 NTU. Similarly, the studies conducted by Mozia and coworkers on UF-PCO systems with TiO_2 concentrations of 0.1–0.5 g/L reported a significant reduction in permeate turbidity. The permeate turbidity ranged 0.07–0.08 NTU TiO_2 concentrations of 0.1–0.5 g/L) confirms the effective separation efficiency of the UF membrane (Mozia et al. 2006, 2009). During their

study, Espindola et al. (2019) noticed that the UF-PCO system was highly efficient in separating photocatalyst particles from the treated water. The permeate turbidity noticed was 4100 times lower than feedwater turbidity, having a value of <0.1 NTU. The results obtained from the studies conducted on UF-PCO systems demonstrated the excellent separating efficiency of UF membranes.

7 Membrane Fouling and Its Control Measures in UF-PCO Systems

Modern UF-PCO systems and their applications have spanned various water and wastewater treatment fields. However, fouling on the membrane surface is a major drawback that reduces the potential of this technology. Due to high energy demand, membrane fouling may increase operational costs, additional labour needed for maintenance, the cost of chemicals needed for membrane cleaning, and reduced membrane life. More challenging and effective methods had been developed and found successful in controlling and minimizing fouling. Membrane fouling could be prevented by various methods such as; feedwater pre-treatment, surface modification of membrane, aeration, UV irradiation, optimization of operational conditions, and periodic membrane cleaning (Williams and Wakeman 2000; Hilal et al. 2005; Rani et al. 2021).

7.1 Membrane Cleaning

Among the membrane cleaning methods, periodical membrane cleaning is one of the methods applied for cleaning the membrane and reducing membrane fouling (D'Souza and Mawson 2005). The membrane could be cleaned by means of washing it with pure water or with chemicals. The chemicals used for membrane cleaning may be NaClO, NaOH, or HCl (Huang et al. 2007; Yue et al. 2021). Automatic periodic backwashing effectively controlled fouling (Molinari et al. 2000; Sarasidis et al. 2014). Backwashing displaces the photocatalyst particles from the membrane pores and loosens filtration cakes (Gao et al. 2011). The working flux required for backwashing is at least two times greater than the normal filtration flux. In UF-PCO systems, the fouling observed was reversible since even 2 min of distilled water backwashing at a flow rate of 150 cm^3/h (Damszel et al. 2009) and after 15 min filtration with moderate permeate flux and 1 min of backwashing dislodged (Patsios et al. 2013) photocatalyst particles on the membrane surface and mitigated membrane fouling.

Furthermore, the membrane could be washed with either water or chemicals. If we compare both types of washing while washing the membrane with chemicals, the flux recovery rate was high. While washing plain PVDF membrane and modified

PVDF membrane with nano TiO_2/Al_2O_3 with pure water, the flux recovery rates were 88% and 94%, respectively, for which the flux recovery rates were 95% and 100% when washed with NaClO solution (Yi et al. 2011).

7.2 Aeration

In slurry PCO-UF systems, photocatalyst particles remained in suspension by providing aeration due to the turbulence created. Air sparging is one method that could enhance membrane flux and control membrane fouling (Cui and Taha 2003). This method could also reduce concentration polarization and perform as a good control for colloidal settlements (Laborie et al. 1997; Cabassud et al. 1997). Coarse bubble aeration was found to be a more efficient technique than fine bubble aeration, maintained the photocatalyst particles in suspension, and prevented catalyst entrapment over the membrane surface (Huang et al. 2007) in slurry UF-PCO systems.

Cleaning the membrane by the method of air sparging after 5 days of operation sustained the permeability of the membrane up to 50% of the original initial value, which was almost 30% more than that obtained by conventional backwashing. In addition, no flux decline was observed when sequentially applying air sparging along with backwashing at low TMP (Psoch and Schiewer 2006). However, the air sparging method of membrane cleaning may be applied only to the cross-flow mode of UF filtration and not to the dead-end mode (Guigui et al. 2003). In order to supply oxygen and to keep the photocatalyst particles in suspension to prevent membrane fouling during batch operations, an air blower was also provided beneath the membrane module during batch operations in UF systems (Choi et al. 2006). Continuous air bubbly flow was also proved to be an advantageous method to prevent fouling on the membrane surface. Du et al. (2017) reported that with an increase in aeration, there is a decrease in fouling rate ($\frac{dTMP}{dt}$) from 0.0908 to 0.0069 kPa/min. In addition, there is also an increase in the mean shear stress from 0.505–2.111 Pa while increasing the airflow rate from 0–3.2 L/min (Du et al. 2017).

7.3 UV Light Irradiation

Irradiation of UV light source could effectively control fouling and increase permeates flux in UF-PCO systems (Shon et al. 2005; Ma et al. 2009; Ganiyu et al. 2015; Peyravi et al. 2017). Others observed similar results in UF-PCO systems. Compared with the flux in the dark, a remarkable increase in the flux of 71.7% was observed after the illumination of UV light for an hour (Ma et al. 2009). After irradiating the PVDF-PEG-TiO_2 membrane with UV light, a decline in permeate flux from 56% to 28% was noticed while filtration duration was 100 min (Song et al. 2014). The authors also reported the flux decline of 66 and 48% on PVDF-LiCl-TiO_2 membrane

without and with UV irradiation, respectively. In UF-PCO systems, the PVDF-LiCl-TiO_2 membranes effectively decreased flux decline during the cross-flow mode of filtration.

In the WO_3-1% membrane, the fouling ratio was 53.6% and 92.4% with or without UV irradiation, respectively, and this significant difference in fouling ratio may be due to pore blocking by WO_3 photocatalyst particles on the membrane surface, which led to the reduction in pore size and hence higher rejection than fresh membrane (Peyravi et al. 2017). The study conducted by Yu et al. (2016) revealed that for a permeate flux of 20 L/m²h, the pulsed UV of 1 min with 31 min cycle at 3.17×10^{-2} W/cm² effectively prevented TMP increase over a period of 32 days. However, there was a fourfold increase in TMP for the conventional UF system without UV.

7.4 Surface Modification of Membrane

Membranes are modified via five methods in order to increase their hydrophilicity and mitigate fouling. They are; (i) plasma treatment, (ii) physical coating/adsorption, (iii) photo-assisted and miscellaneous grafting, (iv) by means of a chemical reaction, and (v) via impregnation of nanoparticles (Bet-moushoul et al. 2016). Among these methods, developing new polymeric membranes using TiO_2 nanoparticles had attracted many recent researchers, and impregnation of nanoparticles on the membrane surface could be developed through; (i) the addition of nanoparticles into casting solution (phase inversion method) (Zhao et al. 2011) and (ii) immersion of the porous membrane into nanoparticles suspension (Xu et al. 2013). The phase inversion method was used to prepare the asymmetric polymeric UF membrane (Rahimpour et al. 2011; Gao et al. 2018).

While adding TiO_2 nanoparticles into the casting solution, there was an increase in hydrophilicity and a decrease in contact angle and the coated membrane (Rahimpour et al. 2008; Song et al. 2012; You et al. 2012). Increasing the hydrophilicity of the membrane will result in an increase in fouling resistance and enhancement in flux (Madaeni et al. 2011; Song et al. 2012). PES UF membranes modified with nanoparticles improved permeate flux from 60–84% at 2 wt% loadings of TiO_2 (Razmjou et al. 2011). Studies also revealed that nano-sized TiO_2/Al_2O_3 modified PVDF membrane imparted better antifouling properties than the unmodified membrane with the same operational conditions (Yi et al. 2011).

7.5 Pre-Treatment of Feed Water

Treating feed water before it reaches the membrane is one of the fouling control strategies adopted for UF-PCO systems. Coagulation as a pre-treatment removed hydrophobic organics and increased permeate flux. Coagulated flocs efficiently absorb hydrophilic neutral organic compounds and improve flux (Chen et al. 2007).

Controlling the feedwater pH and application of aluminium chloride coagulant reduce fouling and enhance membrane permeate flux (Erdei et al. 2008; Gerrity et al. 2009). However, the application of coagulation as a pre-treatment for UF-PCO systems is restricted due to the requirement of post-treatment needed to remove foulants after the process, which may lead to an increase in the operational cost.

Employing magnetic ion exchange resin (MIEX) as a pre-treatment is another method to reduce membrane fouling (Gilbert et al. 2016; Chen et al. 2019). Chen et al. (2019) reported that even though MIEX had limitations of non-removal of suspended particles and creating secondary pollution due to the presence of some quantity of resin beads (Kabsch-Korbutowicz et al. 2018), MIEX was potentially effective in membrane fouling control.

7.6 Non-Conventional Methods of Fouling Control

The methods adopted to control membrane fouling other than non-conventional methods are ultrasonic and electrical cleaning. During the ultrasonic method, high-frequency sound waves are introduced to act on the foulant, and the aqueous solution is agitated (Shi et al. 2014). It is demonstrated that during the ultrasonic cleaning method, the filtration process is continuous while backwashing with water or chemical needs a break during operation. The ultrasonic method is also more advantageous due to; (i) the non-usage of chemicals and water for backwashing and (ii) preventing the problems pertaining to the disposal of waste and environmental concerns. For the dairy whey solutions fouled PS membranes, ultrasound had increased the cleaning efficiency by 5–10%. Optimum cleaning results were obtained at 10 min sonication period (Muthukumaran et al. 2005), and intermittent operation was carried out instead of continuous operation. Furthermore, the addition of surfactants during ultrasonic cleaning can significantly improve the flux recovery rate (Muthukumaran et al. 2004).

The transverse vibration produces shear and secondary flows and mitigates membrane fouling in the reactors. The low displacements of <5 mm and frequencies of <21 Hz contributed significantly to fouling reduction (Kola et al. 2012). An intermittent vibration with a 120 s non-vibration time interval was found to be sufficient to mitigate irreversible membrane fouling (Bilad et al. 2012). An electric field created across the membrane by placing two electrodes on either side of the membrane during electrical cleaning increase permeate flux and mitigates fouling in UF membranes (Rioss et al. 1988). The deposits on the membrane surface were lifted and carried away by electrostatic force (Saxena et al. 2009). The remarkable drawback of this method is the necessity of high energy needed for the continuous application of electric field, which may be 10 kWh/m^3 of permeate (Bowen et al. 1989). The energy requirement could be reduced by introducing intermittent (pulsed) operation that can make the process more effective and reduce the energy requirement <1 kWh/m^3 (Liu et al. 2012).

8 Removal of Emerging Contaminants (ECs) in UF-PCO Systems

The removal of ECs in UF-PCO systems depend upon (i) the kind of membrane process, (ii) characteristics (physico-chemical) of compounds, (iii) operational conditions, (iv) properties of membrane materials, and (iv) membrane fouling (Kumari et al. 2020; Vander Bruggen and Manttari 2008). Various ECs, including pharmaceutical compounds, diclofenac (DCF) and oxytetracycline (OTC), were found to be effectively degraded in UF-PCO systems (Reguero et al. 2013; Sarasidis et al. 2014; Asha et al. 2018; Espindola et al. 2019). Fernandez et al. (2014) explored the removal of 33 trace organic compounds (TrOCs) (drugs, analgesics, antibiotics surfactants) and reported that after 1 h reaction, 18 compounds of hydrophilic nature were completely degraded while hydrophobic tris (2-chloroethyl) phosphate (TCEP) was not degraded. Reguero et al. reported 86% trihalomethanes (THMs) removal in UF-PCO systems. Sarasidis et al. (2014) reported >96% diclofenac (DCF) degradation in the integrated UF photocatalytic systems. However, the studies also reveal that 100% degradation of oxytetracycline was obtained in UF-PCO systems in 5 h of reaction (Espindola et al. 2019).

8.1 Characteristics of ECs and Their Impacts

The characteristics of ECs have a significant impact on their removal efficiencies. The key characteristics such as; molecular weight (MW), size (length and width), acid dissociation constant (pK_a), diffusion coefficient (D_p), octanol_water partition coefficient (log K_{ow}) that determines hydrophobicity/hydrophilicity, chemical structure, and charge characteristics (i.e. electron-donating or withdrawing functional group) were revealed to have a remarkable impact on ECs rejection during membrane separation process (Nghiem and Hawkes 2007; Tadkaew et al. 2011; Chon et al. 2012). The mechanisms for the removal of ECs during the UF membrane separation may be; (i) size-exclusion mechanism, (ii) adsorption phenomenon, (iii) hydrophobic interactions, and (iv) electrostatic interactions (Schafer et al. 2011). The mechanisms for ECs removal have been graphically depicted in Fig. 4.

Adsorption is one of the removal mechanisms that contribute more to the removal of ECs, while other mechanisms contribute a bit (Fernandez et al. 2014). The adsorption mechanism is responsible for the removal of ECs initially till the equilibrium is attained, and later the other mechanisms contribute. Hydrophobicity of the membrane determined the adsorption of ECs on the membrane surface (Schafer et al. 2011) and hydrophobicity depended upon its log K_{ow} value (Fernandez et al. 2014; Ojajun et al. 2015). ECs with log $K_{ow} > 2.5$ are hydrophobic and tend to adsorb more onto the hydrophobic membrane surface (Xu et al. 2006; Hajibabania et al. 2011), while hydrophobic adsorption causes for retaining ECs. These results are in converse with the observations made by other researchers (Yoon et al. 2007; Camerton et al. 2007;

Khanzada et al. 2020), in which the authors reported that the ECs with log $K_{ow < 3}$ (hydrophilic) were adsorbed more while ECs with log $K_{ow} > 3$ (hydrophobic) had reflected the opposite behaviour during the UF process. Since contradictory results are available in the literature explaining the mechanisms of ECs removal, further investigations are needed in this aspect.

The removal of 33 TrOCs in a UF-PCO system was investigated by Fernandez et al. (2014). The studies revealed that the log Kow > 4 (hydrophobic) compounds were more adsorbed and highly retained on the membrane surface, while the hydrophilic compounds were less adsorbed and, hence, less retained. Secondes et al. (2014) investigated the pharmaceutical compounds and reported that the retention characteristics were due to log K_{ow} values. The authors also observed that diclofenac (DIC) was the highly retained compound among the three investigated pharmaceutical compounds, and the next was carbamazepine (CBZ). Amoxicillin (AMX) was the least of all.

The charge of ECs also affects the adsorption process due to electrostatic interactions. The compounds with charges as negative, similar values of log K_{ow} and MWCO were less adsorbed because of electrostatic repulsion with the negatively charged membrane. However, while computing percentage adsorption, along with feed and permeate concentrations, the amount of time taken to attain the equilibrium must also be duly considered (Fernandez et al. 2014).

The size of the ECs depends upon their molecular weight, length, and width (Tadkaew et al. 2011; Chon et al. 2012), which was more observed in the uncharged ECs (Ozaki and Li 2002). Even though Log D, molecular weight (MW), and charge-neutral pH are important variables during UF membrane separation, there was no well-defined relationship between the ECs removal by the UF membrane and their specified properties (Chon et al. 2012).

8.2 Membrane Properties and Their Effects

The membrane characteristics, such as; membrane pore size, MWCO of UF membrane, contact angle, zeta potential, and membrane surface roughness, contribute significantly to the removal of ECs (Evans et al. 2008; Wray et al. 2014). Due to the large pore size of UF membranes (10-100 kDa) relative to the size of many ECs (<1 kDa), the retention is reported to be less than 30% (Jermann et al. 2009; Schafer et al. 2011). Pharmaceutical compounds such as triclosan, oxybenzene, estrone, progesterone, and erythromycin having log $K_{ow} > 3$ were less retained by UF membrane with a retention percentage of <30% (Yoon et al. 2007).

UF membrane separation processes have been commonly utilized for the removal of ECs. Most of the ECs have MW < 1 kDa, and their MW is at least an order of magnitude lesser than the MWCO of membranes (10–100 kDa) (Yoon et al. 2006; Dharupaneedi et al. 2019) and hence size-exclusion mechanism does not contribute for ECs removal. However, adsorption is the major mechanism for ECs removal.

Adsorption occurs both on the membrane surface and the pore structure of the membrane, while pore structure depends upon pore radius (Camerton et al. 2007). More porous the membrane, more ECs removal efficiency since more compounds are adsorbed within the membrane's pores. If we compare UF membranes with the tight NF/RO membranes, the pores are more in UF, and more ECs are adsorbed on both the surface of the membrane and its pores (Khanzada et al. 2020). The removal efficiencies of perfluorooctanoic acid, perfluorooctane sulfonate, and dissolved organic compound (DOC) of $\approx 45\%$, $\approx 28\%$ and, 36%, respectively, were obtained using PVDF hollow fiber UF membranes (Kim et al. 2018). The lower removals were owing to the greater pore size of the UF membrane failed to act as a barrier for the retention of ECs (Kim et al. 2018). After the UF process, ECs having the concentration of 1000 ng/L showed <5% retention owing to adsorption alone. Size exclusion will not be responsible for its removal since the MW/size of the compounds (MW < 300 g/mol) was lesser than the size of membrane pores which is 0.04 μm (Pramanik et al. 2017).

During UF membrane filtration, the initial adsorption resulted in the retention of ECs, and after equilibrium is attained, the size exclusion mechanism contributes to its removal. The studies conducted by the researchers reveal that adsorption could not alone be the mechanism for ECs removal. Hydrophobic adsorption, size exclusion, and electrostatic repulsion are also mechanisms for ECs removal. The removal depends upon feedwater characteristics (Nghiem et al. 2005; Camerton et al. 2007; Jin et al. 2007).

Zeta potential is another important parameter that contributes to the retention of ECs during the UF process. Lower the zeta potential value, the greater the removal efficiencies. Bellona et al. (2004) investigated the removal of nitrate ions employing two membranes with different MWCO and zeta potentials; MWCO 350 Da (-24.1 mV) and MWCO 1000 Da (-20.4 mV). The studies revealed that the nitrate ions removal efficiency for the membrane with MWCO 350 Da was 8% lower than that of the membrane with MWCO 1000 Da.

The contact angle of the membrane is an index that determines the hydrophilicity/hydrophobicity of a membrane surface. The contact angle < 90º indicates the hydrophilic nature, and the contact angle >90º indicates the hydrophobic nature of the membrane surface. The greater the contact angle, the more hydrophilic is the membrane surface (Camerton et al. 2007).

UF membranes with 1–3 kDa have almost the same separation efficiency as NF membranes with MWCO 350–400 kDa. The separation efficiency of UF membranes with 1–3 kDa is almost similar to the separation efficiency of NF membranes with MWCO 350–400 kDa. Low molecular weights (1–3 kDa) UF membranes were very effective in separating low MW proteins, sugars, and peptides in the range of NF membranes (Rohricht et al. 2009). Even though the MWCO of the membrane is greater than the MW of target pharmaceutical compounds, the UF membrane was having MWCO 8000 Da showed a greater removal of 25–95% pharmaceutical compounds (Ibuprofen) with an MW of 206 g/mol (Park et al. 2004). UF membranes

effectively eliminate high molecular weight NOM. However, the size/MW of most of the pharmaceutical compounds are smaller than the MWCO of UF membranes, and hence UF was employed as a pre-treatment system for NF/RO (Huang et al. 2011; Jarusutthirak et al. 2002). In addition, the adsorption capacity of hydrophobic UF membranes is in the range of hundreds of mg/m^3 membranes (Galanakis 2015).

In UF-PCO systems, low MW compounds with MW < 360 Da were not retained by the UF membrane. The compounds detected in permeate confirm their passage through the membrane (Rajca et al. 2016). Despite the passage of low MW compounds through the membrane, the lower compound removal efficiency was observed owing to the partial adsorption of low MW compounds on the membrane surface (Choi et al. 2007; Rajca 2016). There is no catalyst loss in this UF-PCO system, and it could also be used for disinfection purposes.

9 Economic Aspects of Integrated UF-PCO Systems

While upscaling UF with PCO systems, the economic and costs of the system should be an important aspect that has to be given due consideration since the cost of the membrane seems to be high. The technical realization of the integrated system has to be rigorously considered.

The applied pressures have an influence on the operational costs. Lower pressure systems are more cost advantages than high-pressure systems. Based on the practical experiences in UF-PCO systems, the rough costs for permeate fluxes have to be identified before the systems will be designed for realization. Membrane fouling reduces the permeate flux. Better fouling control strategies need to be adopted to improve the permeate flux. A good UF-PCO system will have better fouling control and constant flux throughout the reactor run.

The operational cost of photocatalysts is primarily based on the cost of energy which is mainly obtained from the light source. The economic and feasibility of the process seems to be better for immobilized photocatalytic reactors than slurry reactors due to the energy costs needed for the dispersion of photocatalyst and transmission of UV light (Dostanić et al. 2013).

Even though many UF-PCO systems had been developed and evaluated by many researchers technically, only a few studies demonstrated the economic aspects and feasibility of UF-PCO systems. The energy consumption of slurry UF-PCO systems was evaluated by Eq. (1).

$$\text{Energy Consumption} = \text{EC(kWh/I)} = \frac{w \times \text{HRT}}{v} \tag{1}$$

In which EC—energy consumption, W—output energy of the light source, HRT—hydraulic retention time, and V—reactor volume (Damodar et al. 2010; Laohaprapanon et al. 2015).

Laohaprapanon et al. (2015) computed the cost of electricity to remove the colour from wastewater in a photocatalytic membrane reactor equipped with a PVDF membrane (pore size 0.45 μm). During this study, the electrical cost was calculated as approximately 0.15 USD/g (30 W UV light, time of exposure = 4 h, $[RB_5]$ = 75 mg/L, colour removal = 95% and energy consumption = 0.12 kWh/l or 1.62 kWh/g). The cost for membrane filtration was excluded since the reactor was run with a low TMP, and no significant fouling was observed on the membrane surface during 110 h. However, utilizing higher concentrations of the catalyst may increase TMP and decrease permeate flux, leading to an increase in treatment cost. This reveals that the operating variables have to be optimized to reduce the operating cost.

In the very few recent studies, the cost estimation was carried out separately for the photocatalytic and membrane parts (Dostanic et al. 2013; Samhaber and Nguyen 2014; Rani and Karthikeyan 2021). Rani and Karthikeyan (2021) estimated the operating cost for a UF-PCO system by considering the UF unit and PCO system separately. In this study, the authors estimated the treatment cost to treat 1 m³ of effluent, and the cost was ranged from $10.4 to $13.6 or ₹728 to ₹952. In this integrated UF-PCO system, the area required for the installation was only 16.5 m² which is almost doubled when UF was used as a pre or post-treatment system. Despite the higher treatment cost of the integrated UF-PCO systems than the systems with the individual processes (UF system and PCO system), the synergies of the integrated systems will ascertain the significance of the process.

10   Conclusions and Future Scope

The studies on UF-PCO systems have made significant progress over the last twenty years of research. Among the two types of UF-PCO (slurry and immobilized systems), slurry systems are more advantageous owing to the larger surface area for the adsorption of photocatalyst and reaction. Split-type UF-PCO systems are more suitable for large-scale applications since both processes could be independently optimized. Though many types of research are available on the utilization of UV light, visible light active solar-driven photocatalytic conversion with the modified photocatalysts has become more attractive due to adsorption of visible light enhanced degradation and mineralization of compounds in UF-PCO systems.

The UV light exposure for 10 days with 200 μm H_2O_2 damaged the membrane structure (Chin et al. 2006) and 30 days with 3 wt% of TiO_2 cracked the polymeric membrane surface (decreased the tensile strength from 28 to 23 MPa) (Dzinum et al. 2017). Therefore, various challenges, including long-term stability and anti-fouling property of membrane, need to be focused on further research. Furthermore, real wastewater as feedwater, removal mechanisms of ECs, and degradation of intermediate products in UF-PCO systems need further investigation. However, applying real wastewater as a feed to the membrane reduced the membrane flux from 247 L/m²h to 82 L/m²h, indicating the fouling of the membrane by the feed constituents (Vatanpour et al. 2020). Hence while using real wastewater as feedwater, care should

be taken to address the influence of wastewater constituents. Though many UF-PCO systems were developed on a lab-scale so as to successfully scale up and implement the integrated system, more studies at the pilot scale are needed.

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