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WATER POLLUTION (G TOOR AND L NGHIEM, SECTION EDITORS)

High-Performance Ultrafiltration Membrane: Recent Progress and Its Application for Wastewater Treatment

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Abstract

Purpose of Review This review presents an overview of high-performance ultrafiltration (UF) membranes, including fouling resistant, micellar-enhanced, tight, adsorptive, and catalytic UF. The review discusses recent advances in the development of these membranes, focusing on their preparation method, performances, and applications. Then, the review concludes with a discussion of the challenges and future outlooks of these UF membranes in wastewater treatment.

Recent Findings Recently, the development of UF membranes has resulted in membranes with high performances in wastewater treatment. For instance, fouling-resistant membranes synthesized through surface modification show significant improvement in terms of fouling reduction and flux recovery. In addition, coupling with complexation reaction, tightening membrane pore structure, endowing membrane with adsorption ability, and functionalizing UF membrane with catalytic properties, greatly improve the performance of UF in removing pollutants. Highly selective UF membranes can achieve remarkable various pollutant removals (e.g., organic compounds and heavy metals) from wastewater.

Summary UF membrane has been widely applied in wastewater treatment due to its low-pressure operation, relatively low energy consumption, high product quality, and simple operation. Significant efforts have been dedicated to improve UF membrane performance. Fouling resistant and highly selective UF membranes have been developed successfully, which showed remarkable performance in various pollutant removals. These high-performance UF membranes provide the possibility of process simplification in wastewater treatment since they can remove a more wide range of pollutant types, and thus post-treatment step may be reduced.

Keywords Adsorption · Catalysis · Fouling · Organic matter · Ultrafiltration

Introduction

Ultrafiltration (UF) is a pressure-driven membrane, which has been widely applied in wastewater treatment and various industrial applications. UF offers a high removal rate of macromolecules, with less energy consumption, lower footprint, and mild condition than conventional processes. In addition, membranes are easy to scale-up and need lower cost, which make them favorable for large-scale applications [1–3].

Wastewater contains various complex components. Some components, such as organic substances, may cause

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fouling formation. Fouling is a major problem in membrane operation, including UF [4–8]. To maintain its effective lifetime, the membrane needs chemical cleaning. Furthermore, membrane operation requires higher transmembrane pressure than operating pressure used in the initial operation for achieving the same productivity. Therefore, the fouling phenomenon results in high operational and capital costs [9, 10]. One of the effective approaches to mitigate fouling impact is by modifying membrane properties. Numerous studies have been devoted to preparing antifouling UF membrane, as shown in Fig. 1. The reported anti-fouling membranes showed significant reduction of fouling propensity.

Furthermore, the complex composition of wastewater may need multiple treatment methods for meeting target water quality. Variations in the molecular weight of pollutants are difficult to remove by a single UF membrane. Therefore, some research has proposed improving UF selectivity towards various components that cannot be removed by filtration only. Micellar enhanced UF (MEUF) [11, 12], tight UF [13–15], adsorptive UF [16, 17], and catalytic UF [18, 19] are advanced UF membranes that have been developed to increase the removal rate of pollutants. As shown in Fig. 1, these types of membranes have gained increasing interest of the researcher to study and develop these membranes for wastewater treatment. It is evidenced by several studies that engineering membrane structure, combining with chemical agents, and introducing new functionalities can obtain higher removal of pollutant than conventional UF membrane [20, 21]. This improvement offers the possibility of system simplification by reducing post-treatment steps of UF membrane permeate.

Some excellent reviews of UF membranes, which focus on fouling [22, 23], specific wastewater treatment and separation [24–26], and advanced UF membranes [27–30] can be found in the literature. However, a review of high performance UF membrane for wastewater treatment, which focuses on the improvement of pollutant removal and fouling resistance, is rarely reported. Therefore, this paper would be the complement of previous studies, by providing discussion on recent development and applications of high-performance UF for wastewater treatment. This paper reviews high-performance UF membranes, including fouling-resistant membrane, MEUF, tight UF, and UF membranes with adsorptive and catalytic functionality. The preparation methods of these membranes are discussed, and their performances in wastewater treatment are also analyzed. Then, the review concludes with a discussion of the challenges and future outlooks of the high-performance UF membranes in wastewater treatment.

Fouling-Resistant UF Membrane

In general, membrane fouling occurs through one or more of the following mechanisms: adsorption of feed components, clogging of pores, chemical interaction between solutes and membrane material, gel formation, and bacterial growth [31]. The interaction between foulants and membrane is attributed to several parameters, such as the characteristic of foulants [32], morphology or characteristic of the membrane [33], and operating condition [34]. For industrial wastewater that contains high organic compounds, fouling is

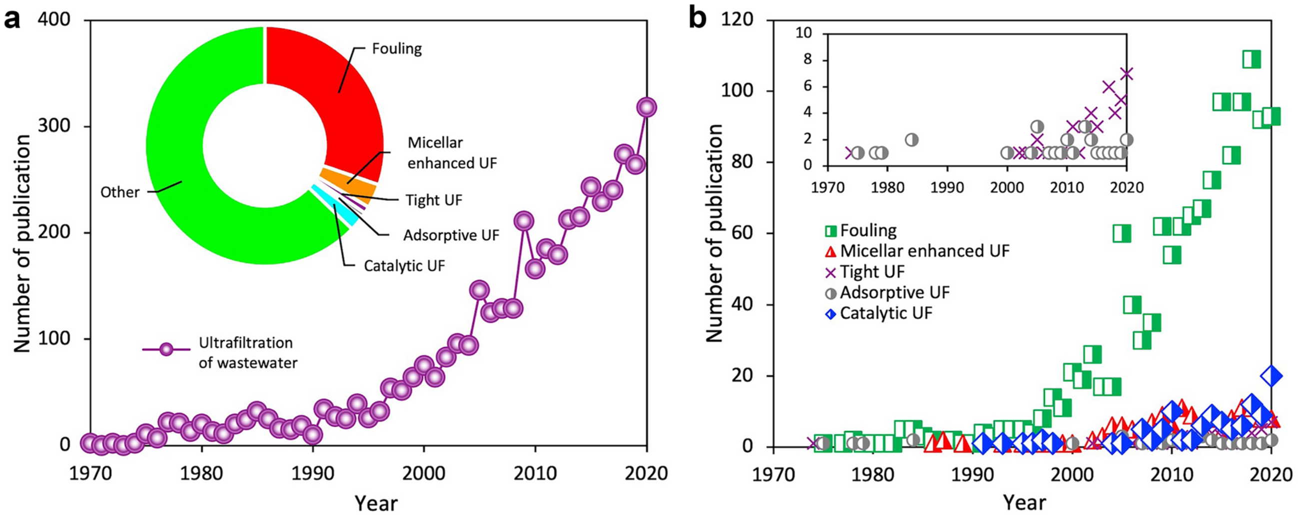

Fig. 1 Number of publications related to **a** UF of wastewater and **b** specific topics. Number of publications indexed by Scopus (queries: TITLE-ABS-KEY(terms))

mainly caused by hydrophobic interaction [35]. Therefore, hydrophilization of UF membrane still received great attention from researchers to prevent the adsorption of foulants on the membrane surface. Each method of surface membrane modification will be discussed in the following sub-section.

Surface Functionalization

Surface functionalization is one of the preferred strategies to improve anti-fouling properties of UF membrane. It can be achieved through polar group introduction on the membrane surface by plasma treatment, sulfonation, etc. The addition of a polar group to the membrane leads to higher percentage of hydrogen bond donor such as oxygen, nitrogen, and fluorine on the membrane surface. They are able to form a strong hydrogen bond with water molecules, and thus produce water layer on the membrane surface. The presence of the water layer is able to prevent or reduce the undesirable adsorption or adhesion of foulants on the membrane surface [36], and thus enhances water permeate flux as well as mitigate membrane fouling [37].

Plasma treatment has been widely used to increase the hydrophilicity and reduce UF membrane fouling. The process is started by cleaning and drying the membrane, and then placed in a plasma reactor. Gas molecules in a plasma reactor are then activated by the collision with electrons, positive ions, or metastable species that subsequently attack the membrane surface; thus, new polar functional groups are apparent on the surface of the membrane [38]. Plasma treatment time should not be too long in order to prevent the membrane pore blocking due to the material deposition. Surface modification by plasma treatment can be achieved using gases such as air, oxygen, nitrogen, ammonia, argon [39–43]. Some gases, especially oxygen containing gases, provided outstanding results with low water contact angle and high flux recovery ratio. Hydrophilic modification of the membrane surface by plasma polymerization also showed the effect of reducing organic absorption [44]. However, hydrophilicity and anti-fouling characteristic gained by plasma treatment is not stable [39, 45]. The effect of plasma treatment can get lower and even disappear due to the mobility of surface functionalities.

Another modification can be achieved by a grafting method. This method is very effective to obtain membranes with stable hydrophilicity. In grafting, the monomers are covalently bonded in the polymer chain with the help of chemical treatment, photo-irradiation, plasma treatment, or high energy radiation. The desirable polymer can be easily tethered on membrane materials with reactive groups on the surface through the free radical graft polymerization of a monomer or the chemical reaction of a membrane surface with functional end groups. Meanwhile, materials without reactive groups on the surface require plasma, ozone, γ-ray irradiation, or UV induction to introduce functional groups to the membrane surface [46]. The characteristics of grafted membranes mainly depend on the grafting degree. The higher degree of graft polymerization provides a strong driving force to reduce the interfacial free energy by migrating and reorienting of the hydrophilic monomers [47]. Therefore, a higher grafting degree increases the hydrophilicity as well as anti-fouling property of the membrane.

The major limitations to scale up both plasma treatment and graft polymerization are the process complexity and high energy requirement. Plasma treatment and plasma-induced graft polymerization require plasma reactor with vacuum condition and high energy to activate the plasma. Irradiation-induced graft polymerization also needs high energy to induce UV or γ-rays to the membrane surface. Therefore, several researchers tried to develop physical modification methods, such as coating, dispersion, atomic layer deposition. These methods use simple equipment with low energy requirement. However, hydrophilic stability still becomes the main issue. Hydrophilic property of the modified membrane through physical treatment can only be temporarily increased. The hydrophilic layer can be easily degraded after being operated or stored for a period of time. Hence, there is an urgent need to develop the best method that renders stability on the hydrophilic property of the modified membrane with a simple process and low energy requirement.

Zwitterionic-Based Membrane

In the last decade, the development of zwitterionic based membrane has attracted attention as a promising alternative to obtain fouling resistance UF membrane. Various types of zwitterionic polymer have been utilized, including zwitterionic chitosan [48], zwitterionic cellulose acetate [49], zwitterionic polyvinyl chloride [50], zwitterionic polyimides [51], polyacrylonitrile-based zwitterionic copolymers [52–54], polymethylmethacrylate-based zwitterionic copolymers [55], zwitterionic tertiary amine–modified polyethersulfone [56], zwitterionic sulfobetaine poly(arylene ether sulfone) (PES-SB), and carboxybetaine poly(arylene ether sulfone) (PES-CB) [56] etc. Zwitterionic polymers typically contain the same number of anionic and cationic groups; thus, the overall charge is zero under normal condition. The chemical structures of zwitterionic polymers are commonly hydrophilic with overall electrically neutral, hydrogen-bond acceptors but not hydrogen-bond donors [57, 58]. These unique characteristics allow zwitterionic polymers to form a hydration layer near the membrane surface to avoid the adsorption of solutes and resistance to non-specific protein adsorption, bacterial adhesion, and biofouling [59]. In overall, zwitterionic-based UF membranes have a very high water flux recovery ratio and BSA rejection.

Micellar Enhanced UF

In MEUF, a surfactant is added to the wastewater to promote the complexation between the ions/solutes and the surfactant. The surfactant molecules will attach to each other to form amphiphilic aggregates with large molecular sizes, named as micelles (Fig. 2a). The solutes are then adsorbed in the structure of the micelles by ionic or hydrophobic interaction, and thus increase the solute molecular size, which then are retained by the UF [60, 61].

Effect of Surfactant, Membrane, and Operating Conditions

Amphiphilic molecules consisting of a hydrophobic chain and a hydrophilic head group are mostly used as surfactant in MEUF. The head group can be anionic, cationic, non-ionic, or amphoteric [27]. For removal of ionic substances, surfactant with the opposite charge to the ions is required to form an ion-pair complex. On the other hand, non-ionic surfactants could be applied to remove hydrophobic non-charged solutes.

The effectiveness of MEUF is also affected by the concentration of the surfactant. The micelles cannot be formed when the surfactant concentration is below critical micellar concentration (CMC). The surfactant remains present

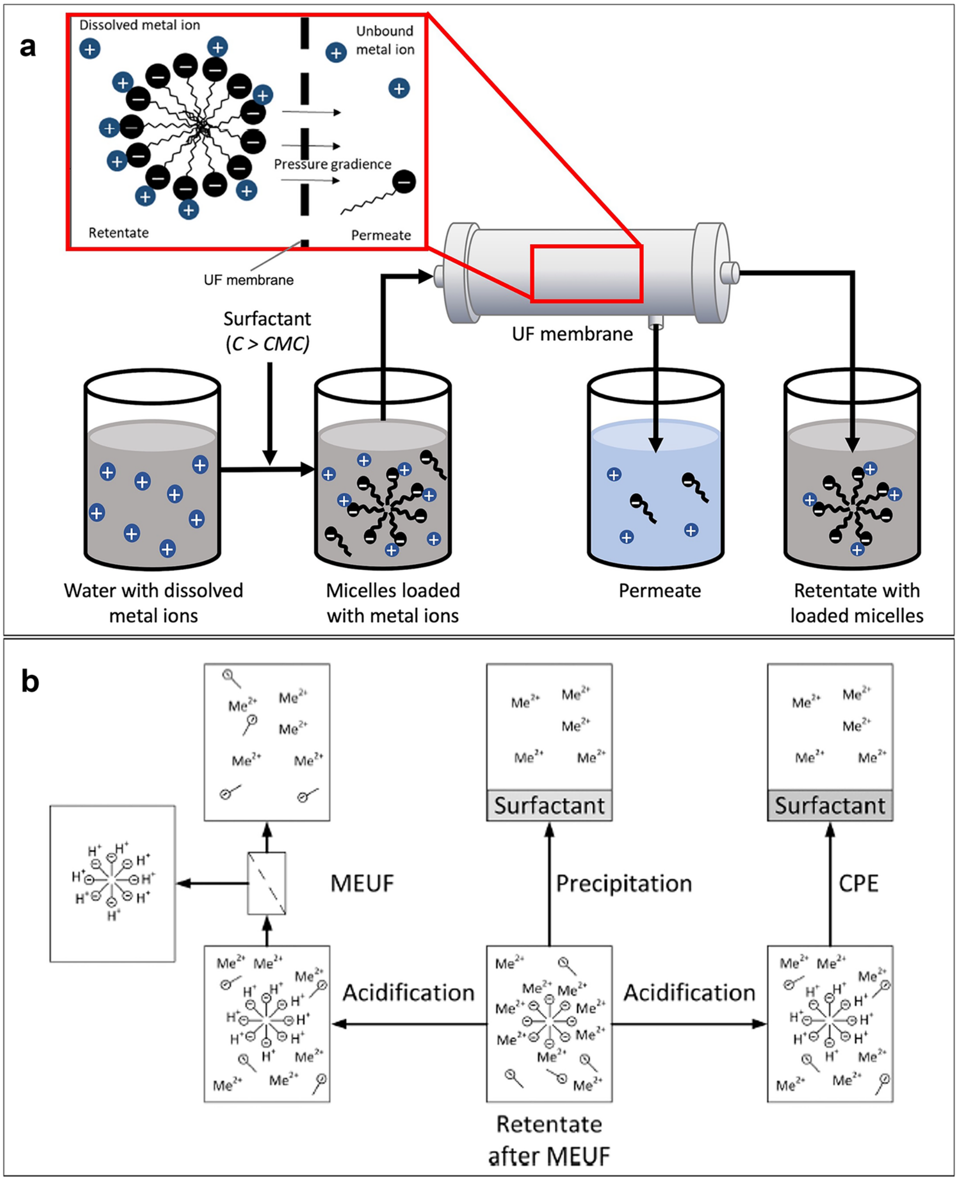

Fig. 2 Schematic of **a** MEUF process and **b** surfactant recovery. **b** is reprinted from [27] with permission, Royal Society of Chemistry, 2018©

as its monomer and can easily pass through the membrane [62]. When the surfactant concentration increases up to its CMC, the surfactant monomers spontaneously aggregate into micelles that provide sites for ions/solutes to attach. However, further increase of the surfactant concentration leads to micelles breaking into smaller molecules and forms of surfactant aggregates of smaller size, which can easily pass through the membrane [27].

Membrane material, surface properties, and molecular weight cut-off (MWCO) also determine the separation performance of MEUF. Hydrophobic membranes tend to have lower flux than hydrophilic membranes due to higher surfactant adsorption. In addition, the MWCO of the membrane has to be selected based on the size of the micelles. Most of the used surfactants produce micelles with hydrodynamic radius of 2–10 nm; thus, membranes with MWCO lower than 10 kDa are mostly applied.

The operating conditions including transmembrane pressure, pH, temperature, and characteristics of the feed solution should also affect the performance of MEUF. In the presence of the surfactant and the solute, the flux increases with the pressure only until a certain pressure is reached [63]. The pH is responsible for the interaction of solute and micelles. For example, the protons of anionic surfactants are coordinated to the micelles and the cations adsorption is hindered at lower pH values, while more "free" groups are available to bind cations at higher pH values [108]. Temperature also plays important role in MEUF processes that determine CMC of the surfactants. At higher temperature, CMC of the surfactant increases due to the de-micellization process [62]. Furthermore, the ionic strength of the solution is also responsible to the performance of MEUF. Chaudhari and Marathe [64] showed that the addition of ionic strength to the solution by the addition of salts led to the salting out effect where the water was more attracted to salt ions, and organics were encouraged to move toward the micelles.

Applications of MEUF in Wastewater Treatment

MEUF has been widely used to remove various heavy metals from wastewater containing single metal, mixture of metals, or mixture of metals and organic substances (Table 1). In general, a single ionic surfactant is effective to remove both organic and inorganic compounds simultaneously. It can be seen from Table 1 where MEUF with various types of surfactants can remove up to 99% of various metals in wastewater. The performance of MEUF in metal removal depends on metal ion concentration in the feed. At the beginning of operation, metal ion retention increases as the metal ion concentration increased since higher metal concentration promoted more surfactant molecule present in micelle form [62]. However, after a period of time, metal ion retention decreases quickly due to the saturation of the micelles. Therefore, the right choice of the ratio between surfactant and metal ions concentration is very important to obtain optimum metal ions retention. Therefore, some researchers proposed the use of mixed surfactant system to solve this problem. Li et al. [12] used a mix of non-ionic surfactant (poly-oxyethylene octyl phenyl ether (Triton-X)) and an anionic surfactant (SDS) to remove copper. The maximum rejection of the copper was 99.9%. The addition of Triton-X could reduce the dosage of SDS as well as minimize the permeation of SDS monomers. The use of mixed surfactant also provides better rejection of the metal ions from the

Table 1 Performance of MEUF in wastewater treatment

Element removed	Surfactant	Rejection (%)	Ref
Single metal			
Arsenic	CPC	93–100	[68, 69]
Cadmium	SDS and Triton X-100	85–90	[69]
Chromate	SDS and NPE	< 99.5	[70, 71]
Copper	CPC	99.2–99.8	[72, 73]
Lead	SDS	91–99	[74]
Lead	SDS, Triton X-100, and NP12	> 98.4	[75]
Zinc	SDS	97–99	[76, 77]
Mixture of metals			
Cobalt, copper, manganese, nickel, zinc	Triton X-100	> 90	[78]
Copper, lead, nickel, and zinc	Rhamnolipid	> 99	[79]
Mixture of metals and organic substances			
Cadmium and phenol	SDS	< 91.3	[80]
Chromate and ferric cyanide	ODA	> 98	[63]
Copper and TCE	CPC and Tween-80	< 93.7	[81]

TCE, Trichloroethylene; *CPC*, Cetylpyridinium chloride; *SDS*, Sodium dodecyl sulfate; *NPE*, Nonylphenol Ethoxylates; *NP12* , Nonylphenol-12; *ODA*, Octadecylamine

Bold text shows the category of the feed wastewater containing mixture of metals as well as mixture of organics and metals. The presence of non-ionic surfactant helps to form complex with organic solutes or competitor metals, which then solubilize within the micelle formed while the targeted metal ions tend to bind on the outer surface of the micelle due to electrostatic attraction [62].

Recovery of Surfactant from MEUF Retentate

In MEUF processes, the production of secondary pollutants from the complexations of the solute and the surfactant still becomes the major drawback. Therefore, the surfactant recovery after MEUF also needs attention for the economic realization of the process. One of the most used strategies for separating the solute and the surfactant is the change of pH or micelle chelation, followed by precipitation or ultrafiltration (Fig. 2b). Purkait et al. [65] utilized two-step chemical treatment procedure for surfactant recovery. In the first step, the surfactant was precipitated by potassium iodide, and in the second step, the surfactant was recovered from the precipitate by the addition of cupric chloride. The results showed 90% of surfactant was successfully recovered. Kim et al. [65] used nitric acid, sulfuric acid, and hydrochloric acid to treat the MEUF retentate and successfully removed 95% of cadmium and copper. Meanwhile, Li et al. [66] used chelation by EDTA followed by ultrafiltration and acidification followed by ultrafiltration for separation of cadmium or zinc from SDS micelles. These methods had proven to be effective which is shown by removal efficiencies of cadmium and zinc more than 90%. Another strategy to recover the surfactant in the retentate stream is decreasing the solution temperature below the Krafft point. When the solution is cooled below the Krafft point, the solubility of the surfactant in water will be disturbed. Hence, the surfactant can be easily precipitated [67].

Tight UF Membrane

Tight ultrafiltration (tight-UF) membrane is developed to overcome the disadvantage of conventional UF membranes, which have a low rejection of low molecular weight compounds. The tight-UF membrane has a pore size between UF and nanofiltration, i.e. between 300 and 510.000 Da, to bridge the gap between nanofiltration and UF [82]. Both ceramic and polymeric tight UF membranes have successfully been used to remove soluble contaminants from the wastewater, either single or integrated with other separation units [13–15, 83]. Among these applications, the tight UF membrane is mainly used for dye removal in textile wastewater, which resulted in more than 95% dyes rejection.

Up to this time, numerous methods have been extensively explored to prepare tight UF membranes, including phase inversion [84], surface modification by dip-coating [13], and interfacial polymerization [85]. In the phase separation process, a high concentration of polymers (above 17 wt.%) is used to create a tight structure in the surface layer or along with the thickness of the UF membrane [15]. Since there is a trade-off between the selectivity and permeability of the membrane, hydrophilic fillers, particularly nanoparticles, are added to the membrane structure [82]. The hydrophilic fillers are blended in the polymer solution or impregnated on the UF surface layer [82]. Recently, metal organic framework (MOF) has been considered as one of the promising fillers in membrane fabrication [86], such as cerium (Ce) [15], Ferric (Fe) [86], and zirconium (Zr)-based [87] MOF. The Fe-MOF/PES membranes provided excellent rejections (> 98.5%) for cationic and anionic dyes [86]. Despite it showed good performances, both in permeability and selectivity, the compatibility between MOF or other inorganic fillers and polymers is still a challenge to keep the particles inside the membrane structure during long-term application [88].

To increase the selectivity of the tight UF membrane, an ordered pore structure in the membrane surface layer is required to induce uniform mass transfer routes. Covalent organic frameworks (COFs) were proposed by Banerjee and coworkers in 2017, with pore sizes ranging from 1.4 to 2.6 nm [89]. The COFs tight UF membranes showed simultaneously high water permeance and selectivity [90]. Fang et al. [85] synthesized large-pore COFs tight UF with a pore size of ~ 3.6 nm on the microporous substrate. The COF membrane provides a permeate flux of ~ 3147 L m^{-2} h^{-1} and Congo rejection of almost 93%.

The application of tight-UF membranes for industrial wastewater treatment is shown in Table 2. The separation performance of tight UF is not only affected by the molecular weight of the solute but also the size sieving, steric hindrance, and charge effect during the membrane separation process [91]. Surface charge plays an important role when the tight UF is used to separate charged pollutants, such as dyes and salts [92]. Several studies focused on synthesized charged tight-UF, and its application on wastewater treatments has been performed. The charge can generally be introduced on the membrane surface by several methods, such as sulfonation [93], polycondensation, and quaternary amination [51]. Some researchers use conductive polymer materials, such as PANI [92]. The charge of the membrane influences the pH of the solution when the pH is increased due to the presence of free hydroxyl group (OH–) from the aqueous solution [94]. In general, the membrane surface can be protonated below the isoelectric point of the polymers. Up to this time, the development of tight UF membranes still faces a great challenge, particularly in balancing the selectivity and permeability.

Adsorptive UF

Adsorption has become one of the well-established technologies for a wide range of applications, which is based on

Table 2 Development of tight-UF membranes for industrial wastewater treatment

Membrane types	Materials	Applications	Membrane Performances	Ref
Polymer	Polysulfone/poly (styrene-co-maleic anhydride) coated with rimesoyl chloride/β-cyclodextrin	BSA and Congo red dye removal from water	Permeate flux: 127 LMH BSA removal: 94% Congo red dye rejection: 96%	[95]
	PES mixed with Fe-MOF	Dye removal from wastewater	Dye rejection: 98.5% Permeate flux: 165.68 LMH TSS removal: 100% COD removal: 92%	[86]
	PES-mixed with Ce-anthranilic acid, (Ce-AnthMOF)	Cheese whey wastewater treatment	Pore size: 1.1 nm (1800 Da) Permeate flux: 19 LMH Humic acid rejection: 99% COD removal: 99.8% BOD removal: 99.7% TSS removal: 99.8% Turbidity removal: 99.6%	[15]
	PES mixed with polydopamine (PDA) modified 3% wt.% of MoS_2 (MoS2@PDA) and PVP	Dye separation	Pore size: 2.62 nm Permeate flux: 42 LMH Dyes rejection: 98.17–99.88% Na_2SO_4 rejection: 10.52%	[96]
	Polysulfone mixed with zwitterionic graphene oxide nanohybrid	Dye removal	Permeate flux: 49.6 LMH Dye removal: 74–99% Na_2SO_4 rejection: $< 5\%$	[97]
Ceramic	Chromium-nitrate (CrN)	Dyes removal	Pore size: 1500 Da Permeate flux: 121 LMH Dyes rejection: 90–100%	[98]
	ZrO_2	Protein separation	Pore size: 25–66 kDa (or 7–10.9 nm) Permeate flux: 135–225 LMH BSA rejection: 100%	[99]
	ZrO_2 bilayer	Dyes separation	Permeate flux: 110.5 LMH BSA rejection: 97.5% Dyes removal: 65–99%	[100]
	Al_2O_3-doped TiO_2	Alizarin Red-S removal	Permeate flux: 9.6–11.1 LMH Pore size: 4650 Da (3.5 nm) Dye removal: 96.8%	[13]
	TiO_2/ZrO_2 membrane on α-Al_2O_3 support	Fractionation of dyes and salts mixture (NaCl/Na_2SO_4)	rejection of dye molecules: $> 98\%$ rejection of NaCl: $< 10\%$ and rejection of Na_2SO_4: $< 30\%$	[101]

BOD biological oxygen demand, *BSA* bovine serum albumin, *COD* chemical oxygen demand, *PES* polyethersulfone, *TSS* total suspended solids, *LMH* L m^{-2} h^{-1}

physical/chemical mechanisms for removing inorganic and organic pollutants from water and wastewater. Therefore, adding a specific adsorption capability to UF membranes has attracted attention in recent years. Progress and achievement in the development of adsorptive UF membranes for heavy metal ions and some organic pollutants removal are summarized in Table 3. The adsorptive functionality can be introduced by incorporating additives, such as carbon, multiwalled carbon nanotubes (MWCNTs); graphene; titanium oxide; polydopamine (PDA); and polyvinyltetrazole (see Table 3). With adsorption capability, adsorptive UF shows superior performance in metal ion removal and organics than the convectional UF.

Several promising results of pollutant removal by adsorptive membrane have been reported in the literature. Adsorptive membrane could remove metal ions, such as copper [16, 102–105], lead and chromium [17, 20, 21, 106, 107], zinc (Zn), arsenic (As), nickel (Ni), and phosphate reported [108–110], and organics [111–115]. Polyacrylonitrile membrane modified by polyvinyltetrazole could adsorb Cu^{2+} up to 134.4 mg/g [104]. The adsorption was ascribed as the electrostatic interaction between Cu^{2+} and the grafted polyvinyltetrazole [104]. The adsorption capacity increased with the degree of functionalization (or the degree of grafted polyvinyltetrazole) [104]. Another adsorptive UF with remarkable Cu^{2+} adsorption capacity is 0.05 wt%-A-MWCNTs/PVDF membrane [103]. The introduction of organosilane-functionalized MWCNT significantly improves the adsorption of PVDF membrane from 0.516 to 2.067 mg/g [103].

Table 3 Some adsorptive ultrafiltration membranes with additional function of adsorption

Membrane	Permeability	Performance				Ref
		Rejection (%)		Adsorption		
HPAMAM-grafted PTFE	635 L/(m^2·h) at 25 kPa	Polystyrene nanoparticles	93–99.9%	Cu^{2+}	1.42 g/m^2	[16]
PVDF – PAMAM	427 L/(m^2·h) at 2 bar			Cu^{2+}	19–21 g/m^2	[102]
0.05 wt%-A-MWCNTs/PVDF	121.93 L/(m^2·h·bar)	BSA	93.67%	Cu^{2+}	2.067 mg/g	[103]
PVT-co-PAN	158–358 L/(m^2·h·bar) for flat sheet 14.8–17.6 L/(m^2·h·bar) for hollow fiber			Cu^{2+}		[104]
TAP/GMA@CN MCM	283 L/(m^2·h) at 0.2 MPa	BSA	> 95%	Cu^{2+}	110.83 mg/g	[105]
PSF/HFO NPs UF MMM	942.1 L/(m^2·h·bar)			Pb^{2+}	13.2 mg/g	[17]
HPZNs-loaded PES	~ 180 L/(m^2·h·bar)	BSA	95.3%	Pb^{2+}		[106]
PES/PDA	166 L/(m^2·h·bar)	BSA	92.9%	Pb^{2+}	20.23 mg/g (static) and 0.95 mg/g (dynamic)	[107]
PSf/PAN-GO/ZnO-NPs	26.52 – 54.67 L/(m^2.h) at 1.5 kg cm^{-2}			Pb^{2+}	147.33 – 279.63 mg/g	[119]
α-Al_2O_3/γAl_2O_3/TiO_2 multilayer	56.4 L/(m^2.h) at ~ 3 bar			Cr^{3+}		[120]
PVDF/2-aminobenzothiazole	231.27 L/(m^2·h·bar)	BSA	91.71%	Cr^{6+}	157.75 µg/cm^2	[121]
GO-coated	308–363 L/(m^2·h) with pressure increase from 2 to 5 bar			As^{3+}		[109]
PAA/ZIF-8/PVDF	460 L/(m^2·h·bar)			Ni^{2+}	219.09 mg/g	[110]
Plasma-modified MWCNT	44.4 L/(m^2·h)			Zn^{2+}		[108]
CSMM blended PES	< 30 L/(m^2·h·bar)			EDCs, PPCPs		[111]
ZrePES	1.72 × 10 – 8 m/(s kPa)	HA	97%	HA	50.5 mg/g	[112]
Carbon NPs PSF	~ 8 × 107 m^3/(m^2·s) at 69 kPa			BTP	53–85 mg/g	[113]
PDA-coated modified PSF	28–338 L/(m^2·h·bar)	27 nm particles	89–96%	MB	~ 5–10 mg/g	[114]
MWCNTs-PSF composite	208.54 L/m^2 at 20 psi			BPA	20.76–23.48 mg/g	[115]

Several adsorptive membranes were examined in the separation of various ions. For instance, polyethersulfone membrane decorated by polydopamine (PDA) nanoparticles from reverse direction (PES/PDA-R) exhibited adsorption capacities of 10.42 mg/g, 17.01 mg/g, and 20.23 mg/g, for Cu, Cd, and Pb, respectively [107]. However, the adsorption test was conducted separately, and therefore, the competitive sorption among the ions was not observed. Adsorption is also potential for removing specific organics [111–115] and anion [116, 117] pollutants from wastewater. For instance, MWCNTs-PSF composite membranes could adsorb bisphenol A (BPA) up to 20.76–23.48 mg/g [115]. Polyethersulfone membrane incorporated with 0.4 wt% iron-doped TiO_2 nanotubes or FeTNT displayed a maximum rhodamine B removal and rejection of 97% [118].

Moreover, the introduction of adsorptive function into UF membrane also positively impacts the overall membrane properties such as pure water permeability (Table 3). The introduction of additives usually improves membrane hydrophilicity, which leads to the increased pure water flux. PAA/ZIF-8, which was incorporated into the PVDF membrane, decreased water contact angle of the membrane from 83.2° to 43.7° [106]. The hydrophilicity increased due to the presence of –COOH functional groups at PAA [106]. As a result, the pure water flux rose from ~ 410 to ~ 480 L/m^2 h [106]. However, it is not always true, as reported in [110]. Polysulfone membrane modified by polydopamine had a lower water contact angle (~ 43°) than the pristine polysulfone membrane (~ 53°) but with < 1/10 pure water permeability (or about 24 L/m^2 h bar) than the pristine one (338 L/m^2 h bar) [110]. This might be associated with the change of the membrane structure after modification. The membrane pore size might become smaller after modification, but showing high pollutant rejection.

Abidin et al. [117] fabricated flat sheet polysulfone/iron oxide nanoparticles (PSf/IONPs) UF membranes to remove phosphate from aqueous solution. Pure water flux and maximum phosphate adsorption capacity of the membrane were 55.2 L/(m^2 h bar) and 73.5 mg/g, respectively. Filtration using feed solution with 10 mg/L calcium phosphate concentration showed that the flux declined rapidly and was stable after 130 min at ~ 28 L/m^2/h. Although phosphate rejection was only about 37% after 3 h of filtration carried out, they claimed that the PSf/IONPs membrane was better than the PVDF/La(OH)$_3$ membrane developed by Chen et al. [116].

Because the adsorption function of an adsorptive UF membrane cannot be continuously maintained in the long-term operation, the regeneration is a key point. For instance, PAA/ZIF-8/PVDF membrane developed by Li et al. [110] could be reused by regeneration in a HCl–NaCl solution under a direct current electric field. However, investigation of the reusability of the adsorptive function is rarely reported, especially after membrane cleaning. Therefore, further efforts should be put into the development of adsorptive membrane with low-frequency regeneration. Strategies for simultaneous membrane cleaning and fast regeneration and their parameters are necessary to be developed. The cost of this adsorptive UF technology also needs to be further assessed.

Catalytic UF

Preparation of Catalytic UF Membrane

Nanoparticles, such as TiO$_2$ [18], Fe$_3$O$_4$ [19], Fe$_3$O$_4$@SiO$_2$ [122], iron (II) phthalocyanine (FePc) [123], Au nanoparticles [124], silver nanoparticles [125], zirconium hydroxide [126], FeOCl nanoparticles [127], are examples of materials that have been used extensively to introduce catalytic function into UF membrane. These materials can be introduced, for example, by additive blending [123], heat treatment or mineralization [128], and layer-by-layer [129]. The additive blending method consists of mixing additive with membrane solution and casting the membrane solution. This method is relatively simple and extensively used to prepare mixed-matrix membranes. In heat treatment or mineralization, a solution containing additive is placed on the membrane surface, followed by heating the membrane in an oven [128]. Heat treatment changes the additive in the solution into minerals. Layer-by-layer method coats the membrane with a solution containing additive several times. The coatings can be conducted by dipping the nascent membrane into one or more additive solutions [129]. Multi-layer coatings ensure the mechanical strength of the additive layer on the membrane surface. These methods can incorporate catalytic function into the membrane matrix, pore, and surface.

Poor interaction between inorganic catalytic materials and membrane matrix usually negatively impacts the membrane structure, membrane separation performance, and the permeate quality. Inorganic particles may leach from the membrane during wastewater treatment. For instance, ceramic/MnO$_2$–Co$_3$O$_4$ membrane contaminated its permeate by 0.002–0.04 mg/L Mn and 0.008–0.1 mg/L Co [130]. Another example is silver nanoparticle leaching observed from PES/silver membrane [125]. About 8% of silver nanoparticles leached the PES/silver membrane after 7 (seven) filtration cycles. Additive-membrane matrix incompatibility also leads to membrane defects and eventually to low membrane selectivity. Therefore, better linkage or interaction between the additive and the membrane matrix is needed. One of the effective approaches to solve this problem is by using functionalized additives [131]. Functional groups of the additive may interact with the functional groups of the membrane matrix and creates a linkage [128].

Uneven distribution of additives in the membrane matrix is one of the critical problems that should be addressed in preparing catalytic UF. Agglomeration may occur due to poor dispersion of the additive in the membrane solution. The introduction of additive, which can dissolve in the membrane solution's solvent, is one of the effective strategies to solve this issue. Chen et al. [123] prepared poly(vinylidene fluoride) (PVDF)/iron (II) phthalocyanine (FePc) membrane by using this approach. FePc is soluble in *N*,*N*-dimethylacetamide (DMAc); thus, it can disperse in PVDF/DMAc solution homogeneously. The resulted membrane shows uniform distribution of FePc particles. Better nanoparticle dispersion can also be achieved by the functionalization of the additives. Functionalized additive can easily disperse in organic solvent [131].

Pollutant Removal by Catalytic UF

Figure 3 shows several mechanisms of pollutant degradation in catalytic UF. Pollutant degradation can take place under light irradiation or photocatalysis system. For instance, to remove sulfadiazine from a wastewater, PVDF/PVP-TiO$_2$-dopamine membrane was assisted by UV light (at 365 nm wavelength irradiation [18]. After 2 h irradiation and at pH 7.5, the PVDF/PVP-TiO$_2$-dopamine membrane could remove > 90% sulfadiazine [18]. The removal rate increased with irradiation time [18]. Photocatalysis can be performed under visible-light, as reported by Yang et al. [132]. Figure 3a shows the mechanism of bisphenol-A removal by using PVDF/Fe(III)-TiO$_2$ membrane and visible light irradiation. Under solar irradiation, PVDF/Fe(III)-TiO$_2$ membrane successfully removed 69.9% bisphenol-A through catalytic degradation, and the removal rate was higher than the pristine PVDF membrane [132]. Similarly, a higher removal rate was obtained at longer irradiation time. In addition, the PVDF/Fe(III)-TiO$_2$ membrane showed

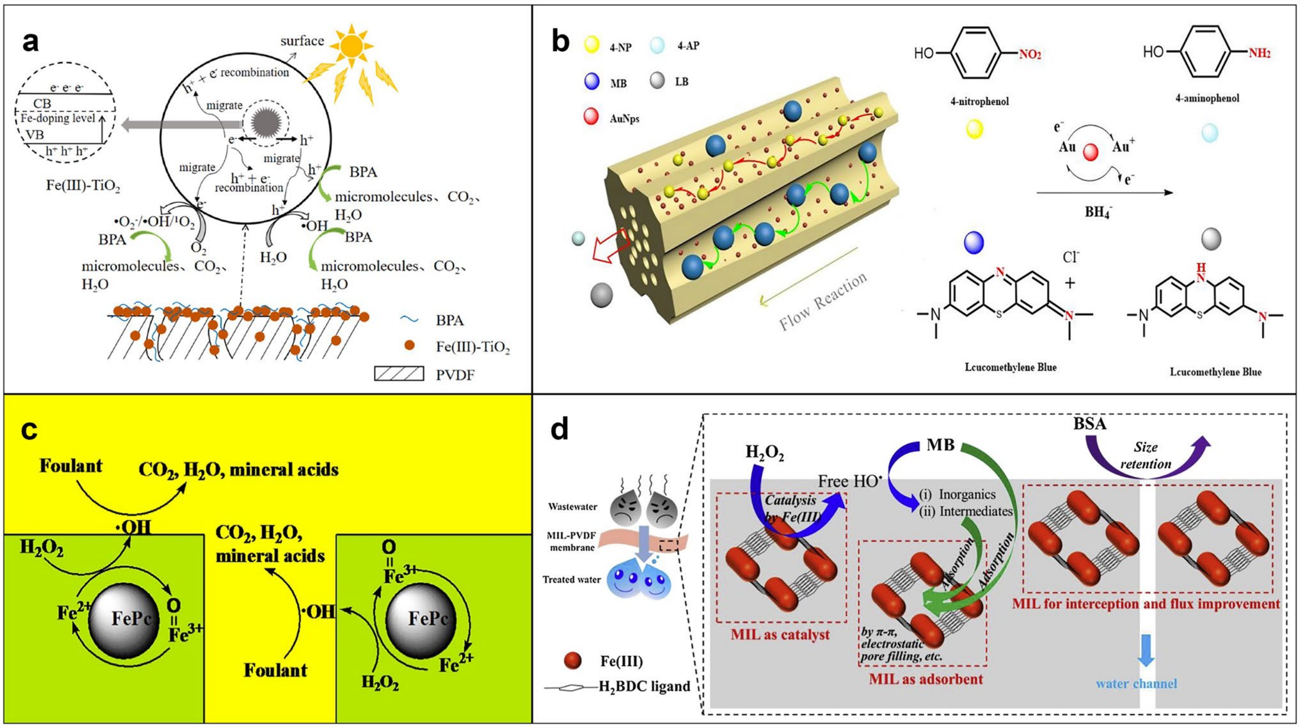

Fig. 3 Mechanisms of the pollutant degradation process. **a** Catalytic degradation under solar irradiation (reprinted from [132] with permission, ©Elsevier, 2021). **b** Degradation in the membrane pore assisted by BH_4– (reprinted from [124]with permission, ©Elsevier, 2018). **c** Radical generation assisted by peroxide (reprinted from [123] with permission, ©Elsevier, 2018). **d** Catalytic degradation and adsorption by PVDF/MIL-53(Fe) membrane (reprinted from [137] with permission, ©Elsevier, 2019)

excellent durability with less than 4% efficiency loss after 9 times membrane usage [132].

Several catalytic UF membranes perform the oxidation process in chemical system, such as peroxide system [127]. Catalytic UF can generate •OH radicals from the peroxide solution as observed in PVDF/FeOCl membrane [127]. The generated •OH radicals helped the membrane to increase the BSA removal from 82 to 96% [127]. The removal rate of BSA increased with FeOCl concentration in the membrane matrix and peroxide dose in the chemical system. With the assistance of peroxide system, PVDF/Fe_3O_4 membrane could remove 97.6% methylene blue from a synthetic wastewater containing 100 ppm methylene blue [19]. Another chemical system that can assist the chemical oxidation is peroxymonosulfate (PMS) system [133]. A membrane doped with $SrCu_xCo_{1-x}O_{3-\lambda}$ (SCC37, $\lambda \geq 0.5$)-MCM-41 hybrid catalyst (SCCM-40%) could generate $^1O_2$ and SO_4• – from the PMS system, which degraded rhodamine B (RhB) [133]. Here, $^1O_2$ was the main contributor to the degradation process, and the removal rate was affected by temperature. In another study, SO_4• – generated from PMS was the dominant oxidant that contributed to the catalytic process [130]. A ceramic/MnO_2–Co_3O_4 membrane assisted by SO_4• – generated from the PMS system could remove 60% natural organic matter (NOM) from a wastewater compared to a sole filtration [130]. The degradation reaction also can take place in the membrane pores as the pollutant permeating across the membrane (Fig. 3b). The catalyst should be anchored in the membrane pores, such as by employing adhesive [124]. PVDF membrane loaded by Au nanoparticles in the membrane pores could obtain 18.35 s^{-1} kinetic reaction constant and > 99% removal of *p*-nitrophenol [124]. The results indicate that catalytic UF shows significant improvement in various pollutant removal compared to the sole wastewater filtration by conventional UF membrane. However, the reaction rate would still need further improvement to speed up the reaction and the retention time of pollutants in the membrane.

Self-Cleaning Ability, Improved Hydrophilicity, and Other Functions

Another interesting feature of catalytic UF is a self-cleaning ability by employing the oxidation reaction. In the membrane cleaning or regeneration process, some foulants can hardly be removed by a simple backwashing process, and thus, chemical cleanings are required. Catalytic UF can utilize the oxidation reaction to degrade pollutants attached to the membrane surface or pores. In this way, the chemical cleaning can be more effective. For instance, FePc/PVDF composite membrane soaked in 0.02 M H_2O_2 solution could recover 97.7% of the initial flux, which was almost two times from those obtained by PVDF membrane (< 40% flux recovery) [123]. Figure 3c shows the mechanism of foulant removal by catalytic reaction in FePc/PVDF composite membrane. It may imply that catalytic UF can perform better pollutant removal and performance stability.

The cleaning efficiency of catalytic membrane is also associated with the improved membrane hydrophilicity. Additives such as metal oxides have high hydrophilicity [134–136]. Therefore, the incorporation of catalytic materials made of metal oxides can also improve the membrane hydrophilicity. Polyethersulfone membrane modified by $Fe_3O_4@SiO_2$ nanoparticles displayed significant WCA reduction from 80.8° to 54.6° [122]. Then, the membrane pure water flux increases almost sevenfold, compared to the unmodified polyethersulfone membrane [122]. In addition to higher productivity or flux, a membrane with lower hydrophobicity usually has a lower fouling tendency [6].

Sometimes, the inorganic additive that is introduced into UF membrane creates several functions, as reported by Ren et al. [137]. MIL-53(Fe), which was used as catalyst, can adsorb the organic compounds as well, leading to the increased pollutant removal. It creates multiple processes during the pollutant removal and degradation, as shown in Fig. 3d. Another interesting result is the interaction between the catalyst particles or the additive with the membrane matrix. For instance, interaction of MIL-53(Fe) and PVDF matrix leads to decreasing pore size, hydrophilicity, and surface roughness [137]. These synergetic effects that change the membrane structure lead to improved pollutant rejection.

Concluding Remarks

Recently, the development of UF membranes has resulted in membranes with improved performances in wastewater treatment. UF membranes with fouling tendency are desired to obtain stable productivity under long-term operation. Fouling-resistant membranes are also expected to decrease operational costs associated with fouling control. A number of studies have reported the successful preparation of fouling-resistant membranes by various methods. Surface modification has been considered as one of the most effective strategies to improve the fouling resistance of the UF membrane. It can be conducted through polar group introduction on the membrane surface by plasma treatment, graft polymerization, coating, etc. Various polymers, additives, and zwitterionic materials have been utilized and have successfully increased water flux recovery ratio and decreased fouling formation.

Meanwhile, the performance of UF membrane in pollutant removals is greatly improved, such as by coupling membrane with complexation reaction, tightening the membrane pore structure, endowing membrane with adsorption ability, and functionalization of UF membrane with catalytic properties. These developments provide the possibility of process simplification in the wastewater process since the UF membrane can remove more wide range of pollutant types. Post-treatment process of UF membrane may be reduced.

To improve the performance of UF for separation of organic and heavy metal containing wastewater, MEUF has been developed. In MEUF, a surfactant is added to promote the complexation between the ions/solutes and the surfactant to form amphiphilic micelles. The ions/solutes are then adsorbed in the structure of the micelles by ionic or hydrophobic interaction, thus increasing the solute molecular size, which can then be retained by the UF. Performances of MEUF are influenced by type and concentration of surfactant, membrane type, and operating conditions. Numerous studies reported that MEUF was able to remove more than 90% of heavy metals from wastewater containing single metal, mixture of metals, or mixture of metals and organic substances.

However, some developed membranes may need more improvement. After being saturated by pollutants, the adsorptive UF membrane will need regeneration for recovering its ability. Adsorptive membrane with low-frequency regeneration should be developed in the future to improve its durability. Moreover, strategies for simultaneous membrane cleaning and fast regeneration and their parameters are necessary to be developed. Furthermore, the cost of this adsorptive UF technology also needs to be further assessed for providing the feasibility of adsorptive UF application.

Catalytic membrane needs an appropriate system to perform pollutant degradation. The catalytic membrane can be assisted with chemical agents or light irradiation. These systems may need optimization to satisfy both technical and economic points of catalytic UF membrane applications. Performance improvement of catalytic degradation is also required, especially when other pollutants are present. Usually, the catalytic activity of the membrane is examined with a single pollutant. Meanwhile, the presence of other pollutants may decrease the effectiveness of membrane performance.

The addition of nanoparticles can produce a membrane with new functionality, increased hydrophilicity, and better pore membrane structure owing to the intrinsic properties of the nanoparticles. Nanoparticles leaching from membrane matrix may occur during wastewater treatment, which can contaminate UF permeate. In the future, membrane preparation, which is able to create chemical linkage between inorganic materials with polymeric membrane matrix, is therefore needed.

Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

Human and Animal Rights and Informed Consent This article does not contain any studies with human or animal subjects performed by any of the authors.

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