Classifications of Adsorptive Ultrafiltration Membrane

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Adsorptive ultrafiltration mixed matrix membranes (MMMs) are a new strategy, developed in recent years, to remove harmful cations and small-molecule organics from wastewater and drinking water, which achieve ultrafiltration and adsorption functions in one unit and are considered to be among the promising technologies that have exhibited efficiency and competence in water reuse.

Keywords: adsorptive ultrafiltration membrane ; water reuse ; harmful cations

1. Introduction

Water is the source of life. Without water, there is no future [1]. There are plenty of water resources on earth, however, due to low per capita freshwater resources, unbalanced temporal and spatial distribution of water resources, and poor utilization efficiency of water resources, human beings have a serious situation of insufficient or even a shortage of water resources [2][3]. At the same time, with the rapid development of some industries, such as the electroplating industry, mining industry, battery industry, paper industry, and the agricultural pharmaceutical industry, more and more heavy metals (such as zinc, copper, nickel, mercury, cadmium, lead, and chromium, etc.) are directly or indirectly discharged into the environment. In addition, small-molecule organics (such as bisphenol A, polychlorinated biphenyls, industrial synthetic substances, phthalate lipids, acetochlor, and other pesticide substances) are harmful chemicals that are also released into the environment due to human production and life. These trace heavy metals and small-molecule organics cause irreversible damage to the ecological environment and to human beings [4][5][6]. Water resources are necessary for human development, especially the safety of drinking water, which is directly related to people's life, health, and safety. Therefore, it is very important to remove heavy metals and small-molecule organics from wastewater and drinking water.

Membrane-based water treatment processes have great potential in sustainable water purification and provide a viable avenue for producing potable water due to their high flux, good performance, and low negative effects. In the field of water treatment, although reverse osmosis and nanofiltration can remove small-molecular organics and heavy metal ions, it is difficult to apply them to urban water supply treatment on a large scale because of the high operating pressure and high energy consumption [7]. Ultrafiltration has the characteristics of good treatment effect, low energy consumption, high reliability, and stable operation. It can almost completely remove protozoa, bacteria, and some viruses from water. The commonly used ultrafiltration membrane manufacturing materials in the market are polysulfone (PSF), polyacrylonitrile (Pan), polyvinylidene fluoride (PVDF), and polyethersulfone (PES). In addition, there are polytetrafluoroethylene (PTFE), polyvinyl chloride (PVC), polypropylene (PP), polyethylene (PE), etc., but these membranes have poor pollution resistance and cannot intercept some small-molecular organics and heavy metal ions.

Adsorbents are promising materials for capturing pollutants, such as low-molecular organics and heavy metal ions, because of their abundant sorption sites, large surface area, and fast adsorption kinetics [8][9][10][11][12][13][14]. However, adsorbents are usually synthesized in the form of powders, which give rise to some problems in the separation and regeneration processes [15][16] and potential safety issues may occur due to leaching into water bodies [17][18][19]. Furthermore, it is difficult to use particles directly to retain macro-molecules and particulates. Therefore, there is an urgent need to develop the next generation ultrafiltration membrane technology with both interception and adsorption performance in order to achieve economic and efficient water treatment.

Adsorptive ultrafiltration MMMs appear when polymers and adsorbents with adsorption capacity are fixed in the membrane instead of being added into the wastewater. It is still a challenge to combine the advantages of adsorbent and ultrafiltration membranes successfully and to overcome their respective shortcomings in water treatment.

2. Classifications of Adsorptive Ultrafiltration Membrane

Ultrafiltration membranes with adsorption function have been reported in literature. Based on the type of adsorbent added to the membrane, adsorption ultrafiltration MMMs can be divided into the following four categories: inorganic filler, organic filler, biomaterial, and mixed filler membrane. **Table 1** lists the removal results of these four adsorptive ultrafiltration MMMs.

2.1. Inorganic Filler-Based MMMs

These advanced adsorptive ultrafiltration membranes contain inorganic fillers, such as Al_2O_3 [20], ZnO [21], MWCNT [22], carbon nanotubes [23], graphene oxide [24], zeolite [25], and activated carbon [26]. These inorganic fillers significantly improve the adsorption performance of the membrane. For example, copper ion removal efficiency improved from 25% to 60% just by adding small amounts of Al_2O_3 nanoparticles (≤1.0 wt.%) into polyethersulfone (PES) membranes [20]. Shah and Murthy [22] added functionalized multi-walled carbon nanotubes (MWCNT) into polysulfone (PSF) membranes through the phase inversion method, using DMF as a solvent and water with isopropanol as a coagulant. The functionalized MWCNT/PSF composite membranes displayed 94.2% removal for Cr(VI) and 78.2% removal for Cd(II), however, the unblended plain polysulfone membranes only displayed 10.2% removal for Cr(VI) and 9.9% removal for Cd(II), respectively. In addition, using zeolite nanoparticles impregnated polysulfone membranes for the removal of heavy metals in wastewater [25]. After 60 min of filtration at a transmembrane pressure of one bar, the maximum adsorption capacities of the mixed membrane for lead and nickel ions were 682 and 122 mg/g, respectively. The addition of hydrophilic inorganic fillers into the polymeric membranes mainly resulted in a significant improvement of water flux, which was attributed to an increase in hydrophilic properties that decreased the contact angle, coupled with greater surface roughness and overall porosity [27][28][29]. Using this type of adsorptive ultrafiltration MMM not only improves the flux and rejection, but also prevents membrane fouling due to the increased hydrophilicity [30].

2.2. Organic Filler-Based MMMs

In this case, organic fillers, such as polyvinyl tetrazole (PVT) [31], polyaniline (PANI) [32], hyperbranched polyester [33], and 2-aminobenzothiazole [34], are added by the methods of blending and phase inversion. Kumar et al. [31] manufactured polyvinyl tetrazole−co−polyacrylonitrile (PVT−co−PAN) membranes by nonsolvent induced phase separation (NIPS). After adding the PVT segment, the prepared adsorption ultrafiltration MMMs became more negatively charged and hydrophilic due to the existence of -NH- functional groups. The PVT segment in the membrane is the main binding site for adsorbing Cu (II) ions in aqueous solution, and the adsorption capacity can reach 44.3 mg g^{-1}, which is higher than the other membranes reported in the literature. In addition, Ding et al. [32] prepared a charged UF membrane composite (PANI/PVDF) that was regulated via an electrochemically reversible control in portions of amine (-N^+=:)/imine (-NH-) functional groups of PANI. The permeability of treated water and rejection ratios of Congo red anion on charged PANI/PVDF, compared with pristine a PVDF membrane, increased from 19.6 to a maximum of 183.3 Lm^{-2} h^{-1} bar^{-1} and from 3.4% to 74%, respectively. Moreover, through electrochemical regulation, the rejection ratio of Congo red on PANI/PVDF reached up to 93%. In addition, hyperbranched polyester that was cross-linked with PVC was used to form a PVC–UF composite membrane, which has a high permeate flux of 237.6 L m^{-2} h^{-1} and a good sunset yellow anion rejection rate of 96.4% at 0.4 Mpa [33]. This type of membrane is preferred over the inorganics as they have more functional groups, which makes them more adaptable and capable to attach cations and small-molecule organics to the substrate through molecular interactions.

2.3. Biomaterial-Based MMMs

Recently, because biomaterial-based adsorbents have the advantages of eco-friendliness, accessibility, and low cost (or even free of expense), research studies have particularly focused on the biomaterial-based adsorbents that stem from plant wastes, such as hulls, tea leaves, fruit peels, plant seeds, and so on. [35]. Usually, plant wastes, including some groups of COOH, OH, or phenolics, can provide charge interaction and hydrogen-bonding interaction with cations and small-molecule organics [35][36]. For instance, Aquaporin Z was incorporated into a triblock copolymer with symmetric poly-(2-methyloxazoline)-poly-(dimethylsiloxane)-poly-(2-methyloxazoline) (PMOXA15-PDMS110-PMOXA15) vesicles and the performance of the adsorptive ultrafiltration MMMs were investigated for the removal of urea, glucose, glycerol, and salt from water. The results showed that these solutes were completely rejected [37]. Lin et al. [38] reported an adsorptive ultrafiltration MMM using plant waste (including banana peel, tea waste, and shaddock peel) as biofiller in polyethersulfone and evaluated the removal performance of cationic dyes from water. The rejection of dye molecules reached up to 95%.

2.4. Hybrid Filler-Based MMMs

Hybrid filler-based MMMs contain two organic–inorganic adsorbents (independently or in composite) and metal–organic framework (MOF) materials are added to the polymer solutions, which represent the latest adsorptive ultrafiltration MMMs technology [39][40][41][42]. For example, Daraei et al. [39] added iron (II, III) oxide and polyaniline into a PSF matrix, with which the removal of Cu (II) can be 85% from water, and this membrane can be reused after four cycles with only about 3% decrease in the rejection capability. In the study of Parsamanesh et al. [40], polyethersulfone-based MMMs incorporated with citric acid–amylose-decorated multiwall carbon nanotubes (Am–MWCNTs–CA) were fabricated. The humic acid removal capability of the prepared membranes was also calculated to be as high as 97.4% for the membrane that was embedded with 0.5 *w*/*v*% Am–MWCNTs–CA. Furthermore, Zhang et al. [41] presented the MIL-PVDF multifunctional ultrafiltration membrane with ultra-high MIL loading through a new method of predispersion and thermally induced phase separation in acetone. Compared with the traditional mixed ultrafiltration membrane, the effective treatment volume of 67-MIL-PVDF membrane increased by nine times, and the MB removal rate was more than 75%. In addition, Zhang et al. [42] prepared a new MOF-based hybrid ultrafiltration MMM (PAA/ZIF-8/PVDF membrane), which is superior to other adsorption materials and has the first and highest nickel ion (Ni (II)) adsorption capacity of 219.09 mg/g in high salinity wastewater.

Table 1. Summary for fabrication techniques.

Type of MMMs	Membrane	Adsorbent	Pollutants	Rejection	Ref.
Inorganic filler-based MMMs	PES	Al_2O_3	Cu^{2+}	60.0%	[20]
	PVDF	ZnO	Cu^{2+}	83.3%	[21]
	PSf	MWNTs	Cr^{5+}	94.2%	[22]
	PVC	CNT	Fe^{2+}	95.1%	[23]
	PES	GO	Pb^{2+}	98.0%	[24]
	PSF	NaX	Pb^{2+}	91.0%	[25]
	PES	Carbonaceous materials	Cu^{2+}	79.1%	[26]
Organic filler-based MMMs	PAN	PVT	Cu^{2+} Pb^{2+}	98.5% 51.0%	[31]
	PVDF	PANI	Congo red	74.0%	[32]
	PVC	Hyperbranched polyester	Sunset yellow	96.4%	[33]
	PVDF	2-aminobenzothiazole	Cr^{5+}	82.1%	[34]
Biomaterial-based MMMs	PMOXA15-PDMS110-PMOXA15	Aquaporin Z	Urea, glucose, glycerol	100%	[37]
	PES	Banana peel, tea waste, and shaddock peel	Methylene blue Methyl violet 2B	95.0% 96.0%	[38]
Hybrid filler-based MMMs	PES	Iron (II, III) oxide and polyaniline	Cu^{2+}	85.0%	[39]
	PES	Citric acid–amylose-decorated multiwall carbon nanotubes	Humic acid	97.4%	[40]
	PVDF	MIL	MB	75.0%	[41]
	PVDF	PAA/ZIF-8	Ni^{2+}	99.0%	[42]

References

1. Cosgrove, W.J.; Loucks, D.P. Water management: Current and future challenges and research directions. Water Resour. Res. 2015, 51, 4823–4839.

2. Song, M.L.; Wang, R.; Zeng, X.Q. Water resources utilization efficiency and influence factors under environmental restrictions. J. Clean. Prod. 2018, 184, 611–621.
3. Gao, X.R.; Zhao, Y.; Lu, S.B. Impact of coal power production on sustainable water resources management in the coal-fired power energy bases of Northern China. Appl. Energ. 2019, 250, 821–833.
4. Jagdish, G.P.; Sanjay, S.; Shi, W. Heavy metal associated health hazards: An interplay of oxidative stress and signal transduction. Chemosphere 2021, 262, 128350.
5. Wu, H.Y.; Xu, B.; Guan, Y.S. A metabolomic study on the association of exposure to heavy metals in the first trimester with primary tooth eruption. Sci. Total. Environ. 2020, 723, 138107.
6. Feng, L.; Hullebusch, E.D.; Rodrigo, M.A. Removal of residual anti-inflammatory and analgesic pharmaceuticals from aqueous systems by electrochemical advanced oxidation processes. Chem. Eng. J. 2013, 228, 944–964.
7. Wu, C.R.; Wang, Z.Y.; Liu, S.H. Simultaneous permeability, selectivity and antibacterial property improvement of ultrafiltration membranes via in-situ quaternization. J. Membr. Sci. 2018, 548, 50–58.
8. Peng, Q.; Guo, J.; Zhang, Q.; Xiang, J.; Liu, B.; Zhou, A.; Liu, R.; Tian, Y. Unique lead adsorption behavior of activated hydroxyl group in two-dimensional titanium carbide. J. Am. Chem. Soc. 2014, 136, 4113–4116.
9. Cao, C.Y.; Qu, J.; Yan, W.S.; Zhu, J.-F.; Wu, Z.-Y.; Song, W.-G. Low-cost synthesis of flowerlike α-Fe2O3 nanostructures for heavy metal ion removal: Adsorption property and mechanism. Langmuir 2012, 28, 4573–4579.
10. Khajeh, M.; Laurent, S.; Dastafkan, K. Nanoadsorbents: Classification, preparation, and applications (with emphasis on aqueous media). Chem. Rev. 2013, 113, 7728–7768.
11. Zhao, Y.; Xu, J.; Wang, J. Adsorptive Separation of Furfural/5-Hydroxymethylfurfural in MAF-5 with Ellipsoidal Pores. Ind. Eng. Chem. Res. 2020, 59, 11734–11742.
12. Wang, X.M.; Wang, J.; Du, T.T. Zn (II)-imidazole derived metal azolate framework as an effective adsorbent for double coated solid-phase micro-extraction of sixteen polycyclic aromatic hydrocarbons. Talanta 2020, 214, 120866.
13. Ana, M.C.; Jose, G.S.; David, D. Using Aliphatic Alcohols to Tune Benzene Adsorption in MAF-6. Adv. Theor. Simul. 2019, 11, 1900112.
14. Ehsan, B.E.; Sina, M.; Nazanin, M. Study on the performance of Cd2+ sorption using dimethylethylenediamine-modified zinc-based MOF (ZIF-8-mmen): Optimization of the process by RSM technique. Sep. Purif. Technol. 2020, 15, 2713–2728.
15. Qu, X.; Brame, J.; Li, Q.; Alvarez, P.J. Nanotechnology for a safe and sustainable water supply: Enabling integrated water treatment and reuse. Acc. Chem. Res. 2012, 46, 834–843.
16. Tang, W.; Su, Y.; Li, Q.; Gao, S.; Shang, J.K. Superparamagnetic magnesium ferrite nanoadsorbent for effective arsenic (III, V) removal and easy magnetic separation. Water Res. 2013, 47, 3624–3634.
17. Tong, T.; Wilke, C.M.; Wu, J.; Binh, C.T.T.; Kelly, J.J.; Gaillard, J.-F.; Gray, K.A. Combined toxicity of Nano-ZnO and Nano-TiO2: From single-to multinanomaterial systems. Environ. Sci. Technol. 2015, 49, 8113–8123.
18. Magrez, A.; Kasas, S.; Salicio, V.; Pasquier, N.; Seo, J.W.; Celio, M.; Catsicas, S.; Schwaller, B.; Forró, L. Cellular toxicity of carbonbased nanomaterials. Nano Lett. 2006, 6, 1121–1125.
19. Zhang, Q.R.; Du, Q.; Hua, M.; Jiao, T.F.; Gao, F.M.; Pan, B.C. Sorption Enhancement of Lead Ions from Water by Surface Charged Polystyrene-Supported Nano-Zirconium Oxide Composites. Environ. Sci. Technol. 2013, 47, 6536–6544.
20. Ghaemi, N. A new approach to copper ion removal from water by polymeric nanocomposite membrane embedded with γ-alumina nanoparticles. Appl. Surf. Sci. 2016, 364, 221–228.
21. Zhang, X.; Wang, Y.; Liu, Y.; Xu, J.; Han, Y.; Xu, X. Preparation, performances of PVDF/ZnO hybrid membranes and their applications in the removal of copper ions. Appl. Surf. Sci. 2014, 316, 333–342.
22. Shah, P.; Murthy, C.N. Studies on the porosity control of MWCNT/polysulfone composite membrane and its effect on metal removal. J. Membr. Sci. 2013, 437, 90–98.
23. Farid, M.U.; Luan, H.Y.; Wang, Y.; Huang, H. Increased adsorption of aqueous zinc species by Ar/O2 plasma-treated carbon nanotubes immobilized in hollow-fiber ultrafiltration membrane. Chem. Eng. J. 2017, 325, 239–248.
24. Zinadini, S.; Zinatizadeh, A.A.; Rahimi, M.; Vatanpour, V.; Zangeneh, H. Preparation of a novel antifouling mixed matrix PES membrane by embedding graphene oxide nanoplates. J. Membr. Sci. 2014, 453, 292–301.
25. Yurekli, Y. Removal of heavy metals in wastewater by using zeolite nano-particles impregnated polysulfone membranes. J. Hazard. Mater. 2016, 309, 53–64.

26. Hofman, M.; Pietrzak, R. Copper ions removal from liquid phase by polyethersulfone (PES) membranes functionalized by introduction of carbonaceous materials. Chem. Eng. J. 2013, 215, 216–221.

27. Abdullah, N.; Gohari, R.J.; Yusof, N.; Ismail, A.F.; Juhana, J.; Lau, W.J.; Matsuura, T. Polysulfone/hydrous ferric oxide ultrafiltration mixed matrix membrane: Preparation, characterization and its adsorptive removal of lead (II) from aqueous solution. Chem. Eng. J. 2016, 289, 28–37.

28. Chan, K.H.; Wong, E.T.; Idris, A.; Yusof, N.M. Modification of PES membrane by PEG-coated cobalt doped iron oxide for improved Cu(II) removal. J. Ind. Eng. Chem. 2015, 27, 283–290.

29. Mondal, M.; Dutta, M.; De, S. A novel ultrafiltration grade nickel iron oxide doped hollow fiber mixed matrix membrane: Spinning, characterization and application in heavy metal removal. Sep. Purif. Technol. 2017, 188, 155–166.

30. Qadir, D.; Mukhtar, H.; Keong, L.K. Mixed matrix membranes for water purification applications. Separ. Purif. Rev. 2017, 46, 62–80.

31. Kumar, M.; Shevate, R.; Hilke, R.; Peinemann, K.V. Novel adsorptive ultrafiltration membranes derived from polyvinyltetrazole-co-polyacrylonitrile for Cu(II) ions removal. Chem. Eng. J. 2016, 301, 306–314.

32. Ding, J.; Pu, L.T.; Zou, D.; Cao, M.; Shan, C.; Zhang, Q.X.; Gao, G.D.; Pan, B.C. Removal of model dyes on charged UF membranes: Experiment and Simulation. Chemosphere 2020, 240, 124940.

33. Qiu, Z.L.; Kong, X.; Yuan, J.J.; Shen, Y.J.; Zhu, B.K.; Zhu, L.P.; Yao, Z.K.; Tang, C.Y. Cross-linked PVC/hyperbranched polyester composite hollow fiber. membranes for dye removal. React. Funct. Polym. 2018, 122, 51–59.

34. Wang, X.; Zhou, K.; Ma, Z.; Lu, X.; Wang, L.; Wang, Z.; Gao, X. Preparation and characterization of novel polyvinylidene fluoride/2-aminobenzothiazole modified ultrafiltration membrane for the removal of Cr(VI) in wastewater. Polymers 2018, 10, 19.

35. Salleh, M.A.M.; Mahmoud, D.K.; Karim, W.A. Cationic and anionic dye adsorption by agricultural solid wastes:acomprehensive review. Desalination 2011, 280, 1–13.

36. Castro, R.S.D.; Caetano, L.; Ferreira, G.; Padilha, P.M.; Saeki, M.J.; Zara, L.F.; Martines, M.A.; Castro, G.R. Banana peel applied to the solid phase extraction of copper and lead from river water: Preconcentration of metalions with a fruit waste. Ind. Eng. Chem. Res. 2011, 50, 3446–3451.

37. Kumar, M.; Grzelakowski, M.; Zilles, J.; Clark, M.; Meier, W. Highly permeable polymeric membranes based on the incorporation of the functional water channel protein Aquaporin Z. Proc. Natl. Acad. Sci. USA 2007, 104, 20719–20724.

38. Lin, C.H.; Gung, C.H.; Sun, J.J.; Suen, S.Y. Preparation of polyethersulfone/plantwaste-particles mixed matrix membranes for adsorptive removal of cationic dyes from water. J. Membr. Sci. 2014, 471, 285–298.

39. Daraei, P.; Madaeni, S.S.; Ghaemi, N.; Salehi, E.; Khadivi, M.A.; Moradian, R.; Astinchap, B.; Daraei, P.; Madaeni, S.S.; Ghaemi, N.; et al. Novel polyethersulfone nanocomposite membrane prepared by PANI/Fe3O4 nanoparticles with enhanced performance for Cu(II) removal from water. J. Membr. Sci. 2012, 415, 250–259.

40. Parsamanesh, M.; Mansourpanah, Y.; Tehrani, A.D. Improving the efficacy of PES-based mixed matrix membranes incorporated with citric acid-amylose-modified MWCNTs for HA removal from water. Polym. Bull. 2021, 78, 1293–1311.

41. Ren, Y.; Li, T.; Zhang, W.M.; Wang, S.; Shi, M.Q.; Shan, C.; Zhang, W.B.; Guan, X.H.; Lv, L.; Hua, M.; et al. MIL-PVDF blend ultrafiltration membranes with ultrahigh MOF loading for simultaneous adsorption and catalytic oxidation of methylene blue. J. Hazard. Mater. 2019, 365, 312–321.

42. Li, T.; Zhang, W.; Zhai, S.; Gao, G.; Ding, J.; Zhang, W.; Liu, Y.; Zhao, X.; Pan, B.; Lv, L. Efficient removal of nickel(II) from high salinity wastewater by a novel PAA/ZIF-8/PVDF hybrid ultrafiltration membrane. Water Res. 2018, 143, 87–98.