Preparation of Antifouling Biomimetic Membrane in Water Treatment

Jiyu Hu1, Liqing Zhang1,2,*, Zhiqiang Zhang1 and Zhenhao Yang1

1 School of Civil Engineering and Architecture, University of Jinan, Jinan250022, China
2 State Key Laboratory of Green Building in Western China, Xian University of Architecture & Technology, 13 central Yanta road, Beilin district, Xi'an, Shanxi province, China

Corresponding author’s e-mail: cca_zhanglq@ujn.edu.cn

Abstract. In this paper, the preparation of antifouling biomimetic membrane in water treatment was reviewed from three aspects: superhydrophobic antifouling surface, hydrophilic antifouling surface and reactive self-cleaning surface. The antifouling biomimetic membrane has higher water flux and separation performance, and has broad application prospects in water treatment such as oily wastewater, dye wastewater and protein wastewater. Finally, based on the current research on antifouling biomimetic membrane, the future research directions of biomimetic membranes are proposed, and the development and prospects of antifouling biomimetic membrane in water treatment are prospected.

1. Introduction
Membrane separation technology mainly includes microfiltration, ultrafiltration, nanofiltration, reverse osmosis and electrodialysis.[1] Compared with the traditional water purification technology, the membrane separation process has more and more applications because of its simple technology, good water purification effect, low energy consumption, and no secondary pollution. Biomimetic membranes have potential applications in enhancing water flux and salt rejection.

In recent years, people have gradually recognized the value of new materials for biomimetic membranes. Along with this, new biomimetic membrane materials with special properties have been rapidly developed. Shengjie Ling et al. [2], a filtration system in bionic nature, has realized a multi-layer nanoporous membrane based on biomaterials, which is suitable for large-scale production of low-cost water purification membranes. Silk nanofibers (SNFs) and hydroxyapatite (HAP) materials are membrane materials. These SNF/HAP membranes have a highly ordered multilayer structure. Compared with membranes of similar size and thickness, the multilayer structure of membranes has more high water flux. Both the SNF and HAP components exhibit good absorption properties for the absorption of heavy metal ions. Moreover, the cost is low, there is no secondary pollution, and it is expected to achieve large-scale production.

However, the adsorption and deposition of contaminants on the membrane surface during the separation process lead to serious membrane fouling, resulting in frequent membrane replacement and increased production costs, which seriously restricts the development of membrane technology. It is a huge challenge to prepare biomimetic membranes with excellent antifouling properties without reducing water flux and salt rejection. Many researchers have considered this issue and have done some related research. In this paper, the antifouling mechanism of biomimetic membranes is...
introduced, and the preparation methods and properties of current antifouling biomimetic membranes summarized. Finally, we discuss the challenges and development prospects of antifouling biomimetic membranes based on the deficiency of current research.

2. Membrane fouling

Membrane fouling refers to the adsorption or deposition of particles, colloidal particles or solute macromolecules in the treated material due to physical or chemical interaction or mechanical interaction with the membrane, resulting in pore size reduction or clogging. An irreversible change in the transmitted flow and separation characteristics occurs [3]. Typical soils that cause membrane fouling include oils, microorganisms, biomacromolecules, natural organics, and the like [4-6]. These soils are easily adsorbed on the surface of the hydrophobic membrane by hydrophobic interaction between the soil and the membrane surface, resulting in a decrease in membrane flux and rejection.

Membrane fouling greatly reduces the service life of the membrane and increases the cost of use, which greatly affects the practical application of membrane separation technology.

3. Antifouling mechanism of biomimetic membrane

3.1. Construct a superhydrophobic antifouling surface

The lotus leaf grows in the sludge, but its leaves are almost always clean. It has a surface contact angle of up to 165° and a tilt of 2° [7]. Water droplets can roll on the surface and carry away dust. This self-cleaning phenomenon is called the “leaf effect”. Studies have shown that the superhydrophobic properties of the lotus leaf surface come from two reasons[8]: the waxy surface of the lotus leaf surface and the special structure of the surface. The surface of the lotus leaf has an orderly distribution of papillae with an average diameter of 5 to 9 μm, and a surface of 124 nm in diameter is distributed on the surface of each papilla. The contact angle of the surface of the lotus leaf is greater than 150° and can be considered as a superhydrophobic surface[9]. The super-hydrophobic surface is characterized by self-cleaning[10], anti-corrosion[11-12], anti-icing[13], oil-water separation[14] and anti-fog. The special structure of the lotus leaf surface and the low surface energy wax make the lotus leaf surface super-hydrophobic and self-cleaning. A surface having such a structure has a large contact angle and a small rolling angle. The larger the contact angle and the smaller the rolling angle, the stronger the hydrophobicity, oleophobicity and antifouling ability [15]. Inspired by the lotus leaf, researchers have new ideas for developing antiflouing biomimetic membranes.

Xu Jian[16] et al. modeled the structural characteristics of the surface of the lotus leaf, first prepared the micro-nano double structure of the polymer by molecular design, and then used the principle of self-aggregation, surface tension and phase separation of the polymer in the solvent evaporation process. A polymer surface similar to the surface texture of the lotus leaf was constructed by a one-step direct membrane formation method at room temperature. This surface has superhydrophobic and oleophobic properties. The water droplets can roll freely on the surface of the membrane, with a self-cleaning effect similar to that of the lotus leaf surface. Moreover, the super-hydrophobic and self-cleaning functions are maintained even after the outermost layer is destroyed.

Professor Ding Bin of Donghua University [17] constructed the imitation lotus leaf surface on the surface of conventional electrospun fiber membrane by combining electrospinning technology and electrostatic spray technology with hydrophilic modified polyacrylonitrile as raw material. Micro/nanostructured superwetting nanofiber surface. This surface exhibits superhydrophilicity and underwater superoleophobicity. By studying the physical structure of the surface of the membrane material and the influence of the wettability of the polymer on the underwater oleophobic properties of the membrane material, it was confirmed that the obtained membrane material exhibited a Cassie state wetting effect[18] on the oil droplets under water. The highly hydrophilic polymer body, the high porosity skin layer and the multi-stage roughness structure form a stable hydration layer on the surface of the membrane, which effectively reduces the contact area of the oil droplets with the membrane.
Thus, the resulting composite membrane material has excellent superhydrophilic and underwater superoleophobic properties, and exhibits excellent separation performance for highly emulsified oil-in-water emulsions. Moreover, the obtained separation membrane material exhibits good stability in the long-period separation process, and is expected to be applied to the field of large-scale oily wastewater purification, and has important guiding significance for designing and preparing high-efficiency low-energy oil/water emulsion separation membrane materials.

3.2. Construct a hydrophilic antifouling surface

A hydrophilic antifouling surface refers to a surface that is highly hydrophilic. It is generally constructed or modified from a hydrophilic polymer. The hydrophilic surface interacts with water molecules through hydrogen bonds or ionic bonds, and tightly combines a considerable amount of water molecules to form a hydration layer, which becomes a barrier for the adsorption of fouling on the surface, and acts as a fouling resisting, that is, antifouling effect[19]. Therefore, improving the hydrophilicity of the membrane is the main means to improve the membrane's ability to resist pollution[20].

Yang[21] et al. hydrophilically modified PVDF microfiltration membrane (MF) by in situ biomimetic silicidation. The deposition of Gallic acid (GA) /γ-aminopropyltriethoxysilane (APTES) hybrid coating on the PVDF MF achieves a transition from high hydrophobicity to high hydrophilicity of the PVDF. This was attributed to the synergistic effect with integration of the adhesive mussel-inspired biomimetic hybrid network and the in situ biomimetic silicification-induced hydrophilic hydrolyzed/condensed polysiloxane portion. It can be used in oil-in-water emulsion and protein wastewater treatment. The membrane prepared after the mixed coating deposition exhibited excellent hydrophilicity and water permeability. The water flux of the modified membrane was 54 times higher than that of the original membrane. The retention rate of modified ultrafiltration membrane to bovine serum albumin was as high as 96.6%, and the anti-pollution ability was increased by 70.8%. The deposited hydrophilic coating forms a stable hydration layer, which reduces the adsorption of contaminants, thereby significantly improving the antifouling performance. Moreover, the simple water rinsing treatment effectively restores the membrane filtration performance and ensures the reusability of the produced membrane.

Zhao[22] et al. dopamine as a biomimetic cation mineralization inducer constructed a novel TiO$_2$-based antifouling hybrid membrane dopamine/TiO$_2$ hybrid nanoparticles (DA/TiO$_2$ HNPs) in PVDF. The prepared hybrid membrane exhibits uniform nanoparticle dispersion, higher surface hydrophilicity, high surface energy, underwater superoleophobicity and higher mechanical strength. The surface of the membrane is hydrophilic, and it is easy to form a hydration layer on the surface of the membrane, which plays an important role in oil adhesion and scaling. The hydration layer on the surface of the membrane is responsible for preventing direct contact and interaction of the oil with the membrane and promoting super-oleophobicity under water[23]. This ensures that the PVDF/DA/TiO$_2$ hybrid membrane has good antifouling ability and self-cleaning ability in the oil-water separation process. Moreover, the hybrid membrane has a high deoiling rate of 99.5% or more. After the membrane was washed with deionized water, the flux of the membrane showed varying degrees of flux recovery. The hybrid membrane has reusability and durability. Therefore, the prepared antifouling PVDF/DA/TiO$_2$ hybrid membrane has a good application prospect in industrial oil water treatment.

Professor Xu Zhikang from Zhejiang University and others[24] have developed a block copolymer separation membrane for biomimetic mineralization. By combining the structural characteristics and performance advantages of organic polymer and inorganic nanomaterials, this study successfully endowed the composite separation membrane with strong mechanical strength, high chemical stability, strong hydrophilic, anti-pollution and catalytic properties, and realized the high-performance and multi-functional design of block copolymer separation membrane materials. The block copolymer separation membrane has the advantages of uniform pore size and adjustable, and has a unique application prospect in the field of high-precision special separation such as virus removal and drug
separation. It is recognized as the development direction of the next generation of high performance separation membranes.

3.3. Construct a reactive self-cleaning surface
As an important biocatalyst, enzyme has the characteristics of high catalytic efficiency, strong specificity, mild reaction conditions and no pollution. It is widely used in pharmaceutical, environmental protection, food, brewing and other fields. The enzyme is immobilized on the surface of the membrane, and the catalytic properties of the enzyme and the excellent separation performance of the membrane are organically combined to achieve in-situ degradation of contaminants and improve the antifouling performance of the membrane.

Chen[25]et al. applied carbon nanotubes and laccases to the surface of the membrane by means of mixed filtration to prepare a biomimetic dynamic membrane for advanced treatment of printing and dyeing wastewater. The biomimetic dynamic membrane has excellent dye removal rate, antifouling ability and stable flux. Contaminants are removed by the synergistic effects of adsorption, enzymatic degradation, and membrane separation of carbon nanotubes. Laccases can degrade contaminants in situ and reduce the saturation of contaminants. In long-term tests, biomimetic dynamic membranes have higher resistance to contamination and removal. The addition of carbon nanotubes improves the hydrophilicity of the membrane and further enhances the antifouling ability. Backflushing also removes the inactive biomimetic layer and recreates new biomimetic dynamic membranes. Therefore, biomimetic dynamic membranes are reusable and sustainable. It has a good application prospect in water treatment.

4. Conclusions and future outlook
Antifouling biomimetic membranes generally have higher water flux and separation capabilities. In wastewater treatment, especially oil-containing wastewater, antifouling biomimetic membranes have broad application prospects. At present, the research on antifouling biomimetic membranes are not mature enough to achieve large-scale application.

Future research on biomimetic membranes can focus on these aspects: finding a more rational model to study its mechanism; researching new anti-contaminant materials such as bacteriostatic and increasing hydrophilicity, reducing the adsorption and deposition of contaminants, and increasing the surface negative charge Innovative and optimized synthesis technology to achieve large-area preparation; broaden the application field of biomimetic membrane and so on. The combination of membrane material science and life sciences is of great significance for promoting the development of membrane materials science.

Acknowledgement
This work was financially supported by The National Science Foundation of China (51408260), The Key Research and Development Program of Shandong Province (2016GSF117006) and The Open Project of State Key Laboratory of Green Building in Western China(LSKF201807).

References
[1] Wang H, Liu Y F, Peng D M, Wang F D and Lu M X 2013 The development of membrane separation technology and its application prospect Applied Chemical Industry. 42(3) 532-4
[2] Ling S J, Qin Z, Huang W W, Cao S F, Kaplan D L and Buehler M J 2017 Design and function of biomimetic multilayer water purification membranes Science Advance. 3(4) 1-11
[3] Liu Z Z, Xu S G and Li S D 1997 Membrane fouling and cleaning in UF and MF Technology of Water Treatment. 23(4) 187-93
[4] Tummons E N, Tarabara V V, Chew J W and Fane A G 2016 Behavior of oil droplets at the membrane surface during crossflow microfiltration of oil–water emulsions J. Membr. Sci. 500 211–24
[5] Alsohaimi I H, Kumar M, Algamdi M S, Khan M A, Nolan K and Lawler J 2017 Antifouling
hybrid ultrafiltration membranes with high selectivity fabricated from polysulfone and sulfonic acid functionalized TiO$_2$ nanotubes Chem. Eng. J. 316 573–83

[6] Xu Z, Ye S, Zhang G, Li W, Gao C, Shen C and Meng Q 2016 Antimicrobial polysulfoneblended ultrafiltration membranes prepared with Ag/Cu$_2$O hybrid nanowires J. Membr. Sci. 509 83–93

[7] Su C H and Chen Q M 2008 Research progresses of the surface similar to lotus leaves Chemistry Bulletin. 1 24-31

[8] Feng L and Jiang L 2002 Adv. Mater. 14 857-1860

[9] Lee H J and Michielsen S 2006 Llotos-effect: Superhydrophobicity Journal of the Textile Institute. 97(5) 455-62

[10] Zhang X Y, Zhou L, Liu K S and Jiang Lei 2013 Bioinspired multifunctional foam with self-cleaning and oil/water separation Adv. Funct Mater. 23(22) 2881-86

[11] Zhang F Z, Zhao L L, Chen H Y, Xu S L, Evans D G and Du X 2008 Corrosion resistance of superhydrophobic layered double hydroxide films on aluminum Angew. Chem. Int. Ed. 47(13) 2466 -69

[12] Haase M F, Grigoriev D O, Mohwald H and Shchukin D G 2012 Development of nanoparticle stabilized polymer nanocontainers with high content of the encapsulated active agent and their application in water-borne anticorrosive coatings Adv. Mater. 24 2429-35

[13] Guo P, Zheng Y M, Wen M X, Song C, Lin Y C and Jiang L 2012 Icophobic/antiicing properties of micro/nanostructured surfaces Adv. Mater. 24(19) 2642-48

[14] Wen L P, Tian Y and Jiang L 2015 Bioinspired super-wettability from fundamental research to practical applications Angew. Chem. Int. Ed. 54(11) 3387-99

[15] Zhang M L 2005 Crude nano structure—lotus leaf Journal of Yunnan University 27(5) 462-4

[16] Xie Q, Xu J, Feng L, Jiang L, Tang W, Luo X and Han C C 2004 Facile creation of a super—amphiphobic coating surface with bionic microstructure Adv. Mater. 16 302–5

[17] Ge J L, Zong D D, Jin Q, Yu J Y and Ding B 2018 Biomimetic and superwettable nanofibrous skins for highly efficient separation of oil-in-water emulsions Adv. Funct. Mater. 1705051-60

[18] Cassie A B D and Baxter S 1944 Wettability of porous surfaces Transactions of the Faraday Society. 40 546-51

[19] Zhao X, Su Y, Liu Y, Zhang R and Jiang Z 2015 Multiple antifouling capacities of hybrid membranes derived from multifunctional titania nanoparticles J. Membr. Sci. 495 226–34

[20] Rana D and Matsuura T 2010 Surface modifications for antifouling membranes Chem. Rev. 110 2448–71

[21] Yang X B, Sun H G, Pal A, Bai Y P and Shao L 2018 Biomimetic silicification on membrane surface for highly efficient treatments of both oil-in-water emulsion and protein wastewater ACS Appl. Mater. Interfaces. 10 29982–91

[22] Zhao X T, Jia N, Cheng L J, Liu L F and Gao C J 2018 Dopamine-induced biomimetic mineralization for in situ developing antifouling hybrid membrane Journal of Membrane Science. 560 47-57

[23] Shi H, He Y, Pan Y, Di H, Zeng G, Zhang L and Zhang C 2016 A modified mussel-inspired method to fabricate TiO$_2$ decorated superhydrophilic PVDF membrane for oil/water separation J. Membr. Sci. 506 60–70

[24] Zhou H J, Yang G W, Zhang Y Y, Xu Z K and Wu G P 2018 Bioinspired block copolymer for mineralized nanoporous membrane American Chemical Society. 12 11471-80

[25] Chen W S, Mo J H, Du X, Zhang Z E and Zhang W X 2019 Biomimetic dynamic membrane for aquatic dye removal Water Research. 151 243-51