Transactions on Environment, Energy and Earth Sciences
ISSN: 2960-1924, eISSN: 2960-2300 | Volume 1
MSREE 2023

Ceramic membrane - ozonation coupling process: research prospect of membrane fouling

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Abstract. Ceramic membrane - ozonation coupling is a promising wastewater treatment process, which combines the functions of membrane filtration rejection and advanced oxidation degradation. Abundant experimental studies have been carried out on this coupling system, but there is still a lack of comprehensive review. In this paper, the latest progress of this system is reviewed. Firstly, the configuration of the coupling system is briefly introduced. Then, the mechanism of the system is introduced. In particular, the structural characteristics of the CM are discussed. Finally, the formation type and prevention of membrane fouling are discussed and emphasized.

Keywords: CM; ozone; coupling; membrane fouling; hydroxyl radical

1. Introduction

As a kind of traditional water treatment separation material, organic polymer membrane has a series of disadvantages, such as narrow water quality range, easy deformation, unstable membrane pore size and so on. By contrast, ceramic membranes(CMs) have great advantages as inorganic membrane materials. In terms of chemical properties, it has good thermal stability, acid and alkali resistance[1], organic solvent resistance, oxidation resistance, reverse flushing, and strong anti-microbial ability; in terms of physical properties, it has excellent mechanical strength, narrow pore size distribution, high separation efficiency, and high permeability[2]. It improves the treatment efficiency, has better structural integrity, smoother surface, weaker adhesion to the stain, longer life, lower operation and maintenance costs, and lower susceptibility to membrane fouling. However, even so, once CMs membrane fouling occurs, it is not easy to alleviate and will cause serious losses.

Nowadays, the CM-ozone catalytic oxidation coupling process has been widely used in the treatment of industrial wastewater, domestic sewage and drinking water. Ozone has strong oxidizability and can mineralize and degrade pollutant molecules in water through direct oxidation and indirect oxidation (generation of·OH). CMs have high pore structure and high surface area, and their abundant micropores and nanopores are conducive to the separation of solid and liquid, and provide an ideal coating substrate[3], which provides a suitable support for heterogeneous catalytic oxidation. Compared with the traditional powder heterogeneous catalytic system, which has difficulties in particle aggregation and catalyst recovery, the coupling system can efficiently catalyze ozone in CM, and avoid the separation and recovery process, which has great potential.

At present, there are many studies on the mechanism and prevention and control of CMs membrane fouling, but there is a lack of systematic summary. Therefore, this paper reviews the configuration, degradation mechanism, engineering application examples, membrane fouling and prevention and control of CM-ozone coupling system, and focuses on the research progress of membrane fouling prevention and control in detail.

2. Overview of the Coupling System

2.1 Composition of the System

The main components of the CMs-ozone coupling system are : ozone generator, oxidation tower (including CM filter bed), tail gas destroyer and backwashing device, as shown in Fig.1 (post-ozone device is not shown). According to the location and working mode of the ozone aeration device, the system can be classified as : pre-ozone system (ozone dissolution is carried out in the feed tank), in-situ ozone system (ozone dissolution oxidation and membrane filtration are realized in the ozone oxidation tower at the same time), tube mixing system (ozone and water are combined in three/Y-type static mixers), membrane contact system (the CM itself is designed as a medium for spraying ozone) and post-ozone system (where ozone plays a role in regenerating the fouled membranes and realizing the recovery of permeable flux). Among them, the tube mixing mode is considered to be the transition from pre-ozone to in-situ ozone. According to the flow mode of water supply, the system can be divided into dead-end filtration and cross-flow filtration system. Dead-end filtration, also known as terminal filtration, is a process in which the raw water is placed upstream of the membrane, the solvent and the solute with a size smaller than the membrane pore penetrate the membrane, and the solute with a size larger than the membrane pore is intercepted by the membrane. The driving force is the pressure difference between the two sides of the membrane. Cross-flow filtration, also known as cross-flow filtration, is a process in which raw water flows parallel to the membrane surface under the impetus of a circulating pump. Different from dead-end filtering,the water flow produces two components of tangential shear force and normal pressure on the membrane surface, and the normal pressure makes the small molecule filtrate filtered out from the membrane pores.

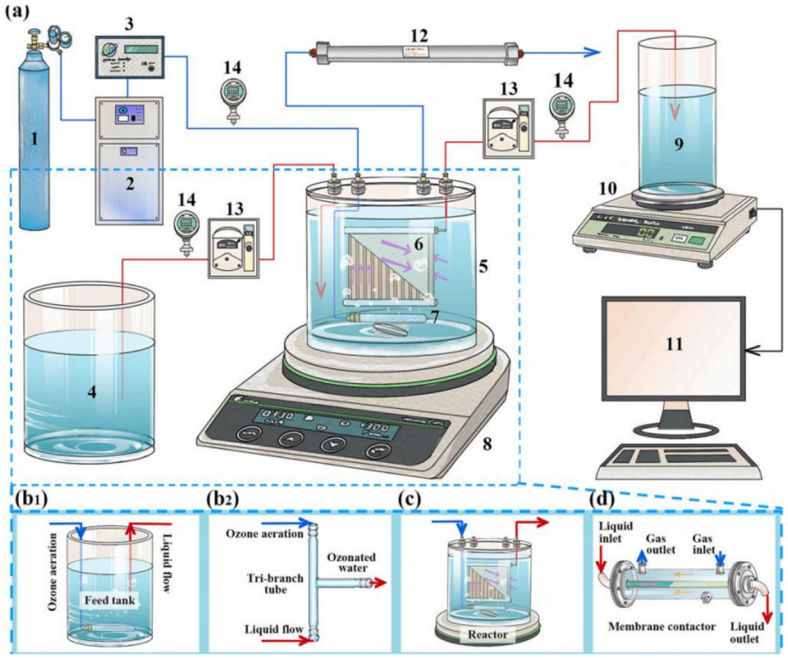

Fig.1 Coupling system diagram (from[3]) (a) working devices. (b) different ozone aeration modes. (b_1) pre-ozone, located in 4.(b_2) pipe mixing, located between 4 and 5.(c) in-situ ozone.(d) membrane contactor, replacing reactor 5. Symbols: 1 Oxygen cylinder 2 Ozone generator 3 Ozone analyzer 4 Feed tank 5 Ozone oxidation tower reactor 6 CM 7 Aerator 8 Magnetic stirrer 9 Discharge tank 10 Electronic balance 11 Analytical equipment 12 Exhaust gas destroyer 13 Pumps 14 Flow meters

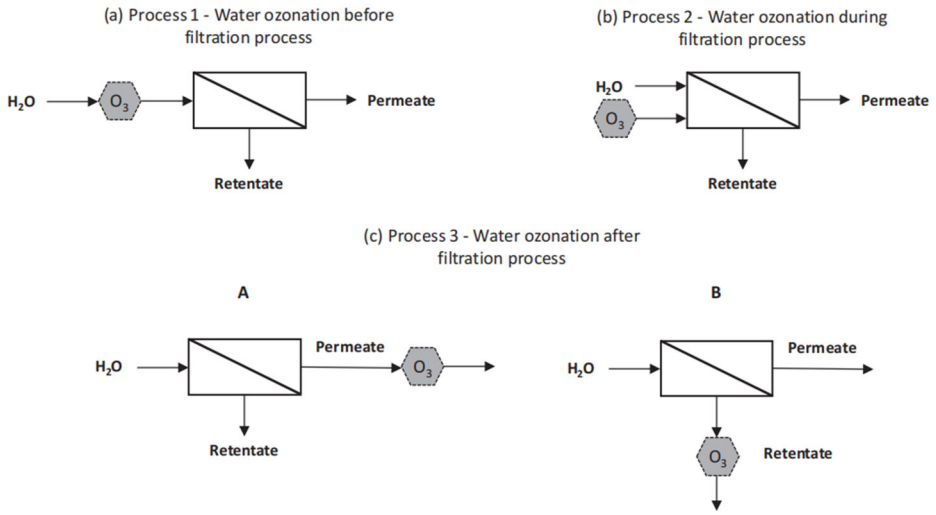

Fig.2 Process flow diagram (from[2]) a. Pre-ozone b. In-situ ozone c. Post-ozone

2.2 Working Mechanism

2.2.1 Ozone oxidation

Ozone in water reacts with organic pollutants through direct oxidation and indirect oxidation. Direct oxidation is a selective reaction of molecular ozone to organic compounds, including electrophilic substitution reaction, cycloaddition reaction and nucleophilic reaction. After ozone is injected into the coupling system, the direct oxidation will first occur, and the functional groups such as the double bond in the double bond organic matter, the amide group and the hydroxyl group in the phenolic substance will be degraded to form the degradation intermediate product. In contrast, indirect reactions, also known as free radical reactions, are non-selective reactions caused by high reactive oxygen species (ROS) produced by the decomposition of ozone in water. This mechanism generally occurs after direct oxidation, involving a series of ROS, mainly with highly oxidizing·OH. Indirect oxidation will further mineralize the intermediate products and eventually completely degrade to form inorganic substances, such as CO_2 and water. In this process, active sites, including oxygen vacancies, Lewis acid / basic sites, defect sites, etc., are considered to promote the conversion of ozone molecules to ROS. Hui ZHAO et al.[4] studied the performance of $NiFe_2O_4$-H catalytic ozonation of phenol wastewater, and found that the Lewis acid sites on the surface of the catalyst are both the adsorption center of ozone and the catalytic reaction center.When the reaction time was 21 min, the ozone consumption rate in the catalytic system was 97.6 %, while that in the ozone system alone was only 56.3 %.

2.2.2 Adsorption and repulsion of membrane

The retention mechanisms of pollutants by CMs include adsorption, pore size exclusion (also known as size screening or filtration) and electrostatic exclusion. The rejection of pore size is the main separation mechanism of CMs: the separation layer pore size of CMs is generally 2-200 nm, and its filtration accuracy covers microfiltration (MF) and ultrafiltration (UF). After proper modification, it can reach nanofiltration (NF). When the diameter of organic molecules is large and exceeds the pore size of the membrane, it will be retained on the influent side. Small molecules with a diameter smaller than the pore size (such as ammonia nitrogen, humic acid, etc. [5]) cannot be removed by pore size interception. At this time, ozone oxidation plays a leading role in degradation. However, recent studies have shown that[3], the pore size exclusion effect may also have a significant interception effect on small molecules: researchers used NF membranes modified by two-dimensional nanomaterials to intercept some small molecules (including soluble silica and humic acid, etc.), and the rejection rate can reach about 60% [6]. Nevertheless, the potential of the of NF CMs-ozone coupling system in such applications[6] has not yet been explored.

In terms of electrostatic repulsion, the surface of CMs (especially metal oxide coatings or surfaces loaded with metal catalytic molecules) may have positive/negative charges, which will generate repulsion for pollutants and molecules with the same charge. Electrostatic repulsion can improve the inhibition efficiency of the membrane and reduce the membrane fouling caused by the deposition of organic matter on the membrane[7].

In terms of adsorption, the adsorption of the membrane is a prerequisite for the removal of pollutants, and the adsorption of pollutants on the membrane is the premise of screening and degradation. Based on the Bruno-Emmett-Taylor (BET) method, the porosity of the membrane was characterized by N_2 adsorption/desorption. The results showed that the original CMs had a high specific surface area and its mesoporous structure had a large adsorption capacity.

2.2.3 Coupling enhancement between membrane and ozone

In the in-situ ozonation reactor, CM filtration and ozone membrane contactor, the membrane is in direct contact with ozone, and the rejection/adsorption of the membrane has a significant synergistic effect with the ozone reaction. Compared with ozone treatment alone, the use of the membrane improves the removal of organic molecules. The existence of the membrane will enhance the effect of ozonation from two aspects : enhanced aeration and enhanced degradation. The mechanism is the 'confinement effect' of membrane pores: when ozone acts alone, the solubility is low, its own mass transfer is limited, and the mass transfer rate with the raw water is slow [8], and the utilization rate of·OH is low. Under static conditions, ozone is only in contact with the surface of CMs.Although the membrane surface can also promote ozone decomposition, the mass transfer of ozone is limited due to the large reaction system of the reactor, so the static decomposition effect of ozone is poor, even close to the decomposition rate of ozone in pure water [9]. The diameter of the membrane pore channel of CMs is 0.1 ~ 100μm [10], the size and shape of the membrane pore are easy to control, and the membrane pore structure can also be manufactured according to the requirements, which will become an important microreactor that is difficult to accurately prepare and narrow the channel by conventional methods [11]. In addition, billions of membrane pores can be obtained per square centimeter of membrane, and the large specific surface area will enhance the processing capacity of the microreactor. Even though the contact time between ozone water and membrane pores may be only milliseconds, its catalytic effect is still very obvious.

Li 's group[9] studied the ability of alumina CM doped with manganese oxide to decompose ozone. It was found that doped manganese oxide CM can strongly promote ozone decomposition, and its ozone decomposition ability can be increased by about 17%. Further study on the ozone decay rate in ozone water(0.8 L) - CM (60 cm^2) system showed that the doping of manganese oxide CM resulted in a significant decrease in ozone concentration in the system during cyclic filtration. DING et al.[12] constructed a new type of two-dimensional iron oxide composite manganese dioxide (Fe_3O_4-MnO_2) hollow fiber CM to achieve efficient degradation of tetracycline hydrochloride wastewater under the assistance of ozone. The removal rate is as high as 86.9%, which is much higher than that of single ozone process. It can be seen that the confinement effect of membrane pores promotes the mass transfer of ozone to a large extent, and improves the contact probability and decomposition efficiency of ozone and membrane pore surface.

2.3 Structure and Properties of CMs

As the center of the coupling system, the physical and chemical properties of CMs, such as pore size, porosity, specific surface area and hydrophilicity, will have a key impact on the working efficiency of the system. Therefore, the appropriate material selection is the guarantee of good performance. The commonly used materials for CMs include ceramic oxides such as Al_2O_3, TiO_2, ZrO_2, SiO_2, and non-oxides such as SiC and Si_3N_4[13]. CMs can be divided into three layers according to their characteristics and functions : the outermost layer is the support layer, with high porosity and large average pore size, which determines the mechanical strength and chemical stability of the membrane ; in the middle of the transition layer, the ceramic powder of the separation layer is prevented from

infiltrating into the support layer to help the better combination of the two. The innermost layer is the separation layer, and the inner surface of the transition layer is sintered to form a dense thin layer, which controls the separation accuracy of the filtration range of the membrane.According to the filtration method, the shape of CMs can be divided into flat plate, disk or tube. The former two correspond to cross-flow, and the latter corresponds to dead-end flow. The supporting function of the support layer is usually realized by Al_2O_3 or TiO_2 with high mechanical strength and stable chemical properties. The corresponding thickness is usually a few mm, and the pore size is 900-2000 nm[14]. The interlayer and separation layer are usually realized by TiO_2, ZrO_2 or $KTiOPO_4$, with a thickness of 10-100 μm and 1-10 μm respectively, and a pore size of 500-600 nm [14] and 2-200 nm respectively.

a. b. c.

Fig.3 a. Sectional structure of CMs b. Tube CMs c. Flat CMs

In the traditional reaction process, the lifetime of ·OH in water is very short (< 10μs), which is difficult to be effectively utilized. However, in the confined space, the utilization rate of · OH was significantly improved. Zhang et al. [15] found that there was a significant inverse correlation between the concentration of ·OH and the distance from itself to the surface. Under confined conditions, the · OH exposure per unit area increased by up to 23 times, and the half-reaction cycle was shortened to 14s, much smaller than at least 3h under non-confined conditions[16]. It can be seen that the confined space can shorten the diffusion distance of · OH, ensure that · OH can contact with pollutants within its half-life, and improve the utilization rate of · OH. On the other hand, it can also enrich pollutant molecules and free radicals in local areas[15] and increase the reaction rate. Improving the microporosity of CMs can construct confined space, which requires the use of nanomaterials. Nanomaterials such as nano-TiO2, nano-MnO_2, Ag and carbon nanotubes are widely used in the modification of CMs. On the one hand, the loading of nanoparticles can improve the confinement ability, on the other hand, it can change the pore size distribution of the CM and improve the membrane interception accuracy. Byun et al.[17] prepared a modified catalytic membrane by loading MnO_2 nanoparticles on the surface of CMs of UF, and compared it with the surface water treated by ozone-membrane coupling before modification (the separation layer material is TiO_2). It was found that the degradation rate of SDS THMs of the nano-modified membrane was 39%, which was significantly better than 23% of the unmodified membrane, and the number of coating layers had a certain effect on the catalytic performance, and the effect was the best when 20 layers of nano-coating.

3. Membrane Fouling in the Coupling System

3.1 Fouling Types and Formation Mechanism

Membrane fouling is divided into reversible and irreversible fouling according to the degree. The former is light and can be eliminated by means of membrane cleaning, while the latter is heavy and cannot be alleviated or eliminated by hydraulic means. The proportion of irreversible pollution in CMs pollution is small, and the recovery of its initial flux is relatively easy. According to the pollution pathway, CMs pollution can be divided into membrane pore blockage, pore adsorption and cake layer blockage(Fig.4). The membrane pore blockage is assumed that the pollutant particles are blocked in

each membrane pore, so that the water cannot flow out; pore adsorption assumes that there is an attraction between the pollutant particles and the pore wall of the membrane (such as electrostatic adsorption, π-π interaction, van der Waals force and hydrogen bond, etc. [18]), and the particles are deposited on the pore wall, so that the decrease of membrane flux is proportional to the decrease of membrane pore volume; filter cake layer fouling refers to the gradual deposition and accumulation of pollutants on the membrane surface during membrane filtration, forming filter cakes and causing clogging. Concentration polarization is the main reason for the formation of filter cake layer : the concentration of pollutants in the membrane side area is higher than that in the liquid phase, so the concentration polarization layer is generated from the membrane side to the liquid side, which inhibits the movement of pollutant molecules against the concentration gradient to the membrane side. From the point of view of the difficulty of removing pollution, filter cake blockage (generally reversible by physical cleaning) < membrane pore blockage (more impervious and partially reversible by chemical cleaning) < pore adsorption (basically irreversible) [19]. From the perspective of pore size, the main cause of MF membrane fouling is pore adsorption, because the pore size of the membrane is large, which is conducive to the adhesion of small molecular pollutants ; however, the pore size of UF and NF membranes is relatively small, and the fouling molecules are difficult to enter the membrane pores directly. The fouling is more in the form of membrane pore blockage and cake layer fouling [20].

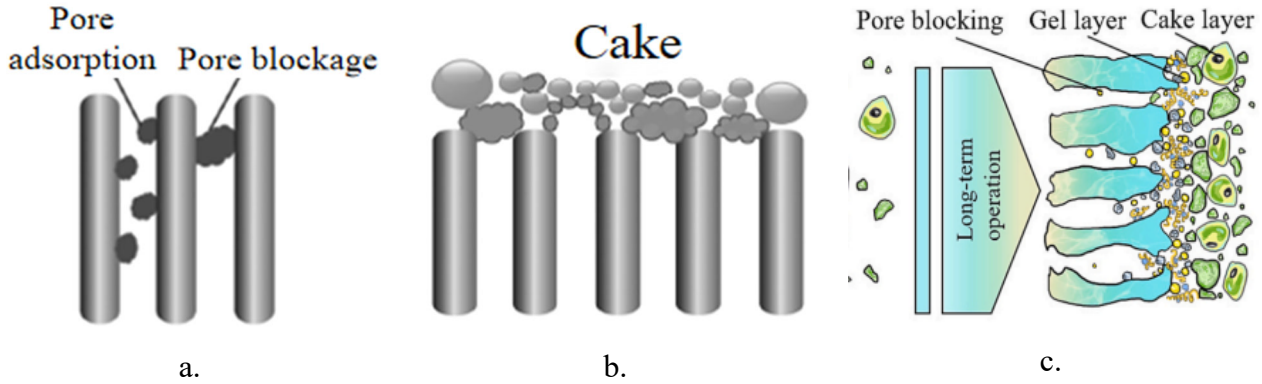

Fig.4 a. Pore blockage/adsorption b. Cake blockage c. Mechanisms and fouling positions

CMs pollution follows which of the above pollution models depends on the type of pollutants, and each pollutant has a specific membrane fouling mechanism. Taking CMs pollution in water supply and drainage engineering as an example, the main contribution is the natural organic matter (NOM) in water, including protein, humus and polysaccharide[21]. The main pollution mode of protein was membrane pore adsorption, and the binding with membrane pore wall was electrostatic force and hydration. It is worth noting that compared with the single protein system, the aggregation of multiple protein molecules often aggravates membrane fouling. For example, Yining WANG et al.mixed a variety of proteins and found that when the filtrate pH was in the middle of the isoelectric point of the two proteins, the two proteins attracted and agglomerated each other due to carrying heterogeneous charges, which aggravated the deposition in the membrane pores. Humus is mainly found in natural surface water and urban sewage. Its molecular structure has a large number of hydroxyl groups that are easy to dissociate H +, so it is often negatively charged in a neutral environment. The main pollution modes are cake layer pollution and membrane pore blockage. L. DE ANGELIS et al.studied the effect of humic acid (HA) in water on the separation performance of iron oxide CM. It was found that the aggregation of HA on the surface of CM caused the blockage of membrane pores. In addition, the negative charge of humus also changed the hydrophilicity and hydrophobicity of the membrane, which seriously affected the membrane flux. Polysaccharides are mainly derived from the secretions and debris of natural aquatic organisms and the production and domestic wastewater of modern society [22], and the representative substance is sodium alginate. Dong CHEN et al. [23] studied the fouling behavior of CMs(Al_2O_3) of MF and UF by sodium alginate,

and found that sodium alginate significantly aggravated the fouling of CMs in neutral water environment. Polysaccharides are usually negatively charged under natural water pH conditions .After analysis, the surface of the selected CM is positively charged in neutral water environment, and electrostatic attraction occurs with negatively charged sodium alginate, causing serious membrane fouling.

3.2 Prevention and Control Methods

3.2.1 Selection of coupling modes

(1) Aeration mode

The coupling of ozone aeration and CMs not only greatly improves the degradation efficiency, but also significantly inhibits membrane fouling[24]. There are two mechanisms : First, the high oxidation of ozone can inhibit the growth of microorganisms in water and alleviate the biological pollution of the membrane. Second, ozone will change the structure and properties of organic pollutants, and will easily cause membrane pollution. The macromolecular organic matter is oxidized and degraded into small molecular substances, thereby alleviating the organic pollution of the CM. However, pre-ozonation is more suitable for reducing reversible fouling (cake layer blockage and membrane pore blockage in some cases), and in-situ ozone can reduce irreversible fouling (membrane pore blockage and pore wall adsorption)[25]. When the pre-ozonation mode is selected, the structure of the high molecular weight organic matter in the feed solution will be decomposed and broken into low molecular weight fragments that can penetrate into the membrane. CHENG X 's group[26] studied the CMs pollution caused by NOMs under pre-ozonation. It was found that pre-ozonation could reduce the total membrane fouling index caused by HA, SA and SRW by about 39%, 78% and 42%, respectively. The molecular weight distribution of humic acid and sodium alginate gradually shifted to the low molecular range, and the molecular weight cut-off decreased from 60 kDa to 10 kDa and below. However, the fragments are difficult to be completely mineralized, and it is easier to enter the membrane pores, which aggravates irreversible pollution and the difficulty of subsequent membrane cleaning. In terms of cost, the cost of equipment in the form of ectopic coupling is higher[38].

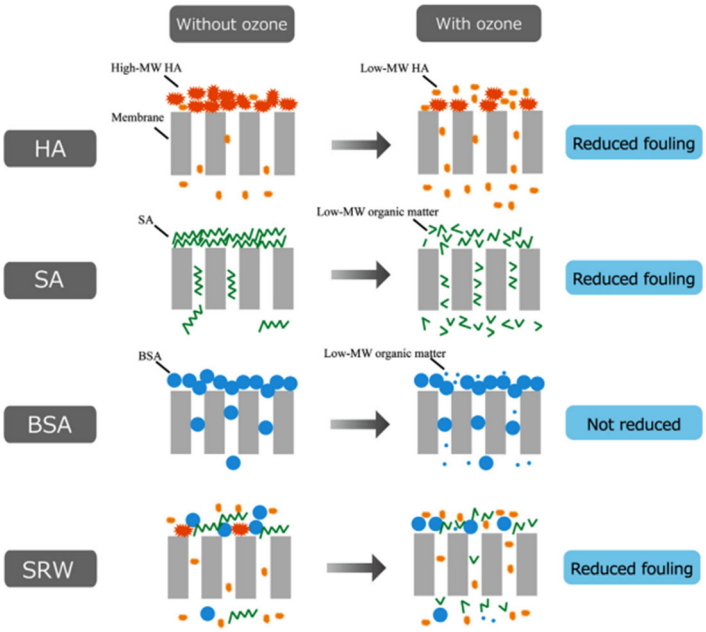

Fig.5 (from [33]) Schematic diagram of the influence of pre-ozone on CMs(UF) fouling by HA,SA,BSA and SRW

Due to the membrane pore confinement effect, in-situ ozonation has more opportunities to produce ROS represented by·OH, which accelerates the decomposition of pollutants attached to the membrane

pores or deposited on the membrane surface. Zhenghua Zhang et al.[39] used salicylic acid (SA) as a molecular probe to verify that the in-situ ozone model can catalyze the formation of·OH:·OH will oxidize SA to 2,3-dihydroxybenzoic acid (SA-3). The CSA-3 / CSA ratio of pre-ozone and in-situ ozone was measured within 60 min, and the latter was 0.39, which was significantly higher than the former 0.29. In-situ ozone can also effectively reduce the transmembrane pressure difference. For example, Wei et al. [19] exposed 1 mg/L ozone to the flat CMs(UF) membrane module for in-situ treatment of algae wastewater. When running for 35 min, the transmembrane pressure difference only increased by 8.6 kPa, which was significantly lower than the 35.9 kPa without in-situ action, which alleviated the fouling of the membrane. In addition, the aeration shear force of in-situ ozone can also destroy the adhesion between fouling and membrane channels, thereby reducing fouling blockage of membrane pores[28]. From a cost perspective, in-situ action can effectively reduce equipment costs[38].

(2) Filtration mode

Compared with dead-end filtration, cross-flow filtration greatly reduces the susceptibility to membrane fouling by the shear stress generated by cross-flow on the membrane surface. Although the energy cost of the latter is higher than that of the former, it significantly saves the cost of membrane operation and maintenance, which is conducive to the sustainable operation of CMs. In the dead-end filtration process, the movement direction of the solvent and solute is perpendicular to the membrane surface. As the filtration volume increases, the accumulation of membrane fouling causes the membrane separation performance to decrease, and periodic cleaning is required to restore the membrane flux. In the cross-flow filtration process, the movement direction of the retained solute is tangent to the membrane surface, and the tangential hydraulic shear force can alleviate the deposition of pollutants on the membrane surface, thereby reducing the thickness of the filter cake layer and reducing the fouling resistance of the filter cake layer [22]. Lukka et al.[27] studied the effects of dead-end and cross-flow flow conditions on the membrane resistance of CM in the separation and recovery of whey protein from industrial whey by convolutional neural network. The results showed that the flow's Reynolds number(R_e) is 3.49×10^5 when the cake layer fouling resistance(R_f) is $7.26 \times 10^{12} m^{-1}$ in the dead-end mode, and the R_e increases to 6.3×10^4 corresponding to the same R_f($7.26 \times 10^{12} m^{-1}$) in the cross-flow mode. The R_e required for cross-flow is lower when the same fouling resistance is generated, which fully indicates that even with a lower R_e, cross-flow conditions can have a same level of anti-fouling performance.

Table 1 (from[27]) Experiment data comparison of the two different filtration modes

(DE=Dead end; CF=Cross flow)

Exp.No	Test/train	TMP(kPa)	R_e	pH	Rejection coefficient	R_f($\times 10^{12} m^{-1}$)	R_{cp}($\times 10^{12} m^{-1}$)
DE 9	Train	400	3.49×10^5	4	0.80	7.26	25.89
CF 3	Train	250	6.30×10^4	4	0.83	7.26	14.23

Other process conditions during the operation of ozone-CMs, such as ozone dose, feed temperature and transmembrane pressure (TMP), also affect membrane fouling. The increase of ozone dose can reduce membrane fouling, enhance the degree of aeration, shear turbulence intensity and increase the yield of ROS, although there is a threshold dose. The increase of sewage feeding temperature can reduce the viscosity of the feed liquid, which is conducive to the turbulent diffusion of pollution molecules and reduce the concentration polarization. The increase of TMP is unfavorable to the

membrane, which will accelerate the concentration polarization and the formation of the filter cake layer, threatening the long-term stable operation of the membrane module.

3.2.2 Membrane modification

(1) Hydrophilicity / hydrophobicity

The influence mechanism of hydrophilicity and hydrophobicity on membrane fouling is generally related to charge attraction/ repulsion. For example, S.J.LEE et al. studied the fouling characteristics of humic acid (HA) on the surface of CMs, and found that HA can be adsorbed on the surface of hydrophilic CMs, resulting in a decrease in the hydrophilicity of the whole membrane after adsorption. When the pH was 7, both the surface of the iron oxide CM and HA were negatively charged and thus repelled. The accumulation of HA formed a hydrophobic interface between the filtrate and the CM. S. FAKHFAKH et al. studied the effect of bovine serum albumin on membrane fouling, and found that the protein had strong hydrophobicity at the isoelectric point (pHzpc = 4.7). Therefore, when the pH of the filtrate was close to 4.7, the membrane fouling was significantly aggravated. Improving hydrophilicity can make the membrane have better surface chemical conditions to repel electronegative organics, and the coupling with ozone makes the membrane less susceptible to fouling. The adjustment of hydrophilicity and hydrophobicity is generally based on the adjustment of electrical properties. For example, Fei WANG et al. loaded the surface of α-Al_2O_3 CM by sol-gel method. The formed SiO_2 layer significantly alleviated the membrane fouling caused by humic acid through electrostatic repulsion, and the flux loss rate decreased from 66% to 26% after modification. However, although the inhibition of membrane fouling is attributed to hydrophilicity, the enhancement effect of hydrophobicity on ozone mass transfer efficiency and oxidation effect is higher than that of hydrophilicity. Ma et al.[30] compared the equilibrium liquid phase ozone mass concentration of hydrophilic and hydrophobic modified CMs. Under the same operating conditions, the latter can reach 4.3 mg / L, while the former is only 3.8 mg / L. In terms of ozone volumetric mass transfer coefficient, the latter is 0.3469 min^{-1}, while the former is only 0.2396 min^{-1}. The influence of hydrophilic and hydrophobic modification on membrane fouling should be further studied.

(2) Roughness

Greater fouling potential was found in CMs with larger pore size and higher roughness. Therefore, smoother membrane surface can enhance antifouling by reducing the accumulation of particles in the valley structure. The modification of CM with more compact and flat nanocatalysts to obtain higher anti-fouling resistance has been a research hotspot in the past decade. Bo Zhu et al. used a tubular Al_2O_3 membrane coupled with ozone to remove the chromaticity and TOC in the secondary effluent, and used the sol-gel method to attach a fine nano-catalytic TiO2 layer to the surface of Al_2O_3. X-ray diffraction (XRD) and N_2 adsorption showed that 4 nm anatase existed on the membrane surface. Comparing the flux of the ' bare ' membrane (pore size about 0.58μm) with the modified membrane within 2 hours, the former is reduced to 45% of the initial value, and the latter is reduced to 60%. However, Dong et al.[31] pointed out that with the increase of membrane surface roughness, the adsorption of pollutants will also increase, but at the same time, the enhanced membrane surface disturbance effectively hinders the deposition of pollutants on the membrane surface, thereby reducing the mechanical interception of pollutants by membrane pores. Therefore, the influence and effect of changing roughness on membrane fouling also need to be further explored.

3.2.3 Membrane cleaning

(1) Traditional physical and chemical cleaning

Traditional cleaning methods include physical, chemical and physicochemical cleaning methods. Physical cleaning method is by means of water or gas flushing membrane. Ai[32] used tap water backwashing to clean CMs from coking wastewater treatment. Experiments showed that at room temperature, the membrane flux recovered by 60 % after the first cleaning. However, with the increase of cleaning times, the recovery rate will gradually decay. Kang[33] et al. found that steam cleaning was more effective than physical backwashing in cleaning CMs in synthetic organic wastewater.

However, there are still irreversible pollutants on the membrane surface after physical washing. Fan Dong [34] explored the chemical cleaning method of CM in the treatment of papermaking wastewater : 1.0 % HNO3 solution was used to clean the contaminated CM. Within a certain cleaning time, the flux recovery rate of the CM can reach 73.6 %. Some scholars at home and abroad also combine physical and chemical methods. WenLi et al.[35] investigated the physical and chemical combined cleaning scheme of CMs during the filtration of sugarcane juice. The results showed that the membrane flux recovery rate was as high as 96.6 % when the contaminated membrane was cleaned by the combined process of 'industrial purified water backwashing → 1% NaOH and 0.5% NaClO mixed solution cleaning → 0.5 % HNO3 cleaning'.

(2) Post-ozone cleaning

Compared with the traditional chemical cleaning, the post-ozone system has stronger cleaning ability. The research related to the backwashing of CMs by ozone aeration liquid showed that the membrane resistance was almost completely eliminated after backwashing. This may benefit from the enhanced confined oxidation process[3] and the accelerated membrane pore aeration rate. Post-ozonation provides new possibilities for the regeneration and recycling of membranes in the future, and is the fundamental means to maintain stable membrane permeation to prevent membrane fouling. Fujioka et al. [36] used pure water to regenerate the membrane once used. After 2.5 min of backwashing, the transmembrane pressure difference was still higher than the initial value of the membrane, and the flux recovery could not be achieved. The α-Al_2O_3 tubular membrane was regenerated by post-aeration with water containing 2mg/L ozone, and the flux recovered within 2.5 min. For the membrane with a transmembrane pressure of 143 kPa, the transmembrane pressure was restored to the initial value after 3 min of regeneration.

4. Conclusion and Prospect

In this paper, the configuration, mechanism and pollution prevention of CM-ozone system are reviewed, and the latest progress and engineering examples of coupling system in about ten years are integrated. Based on the existing technical characteristics, the following aspects should be further discussed in the future :

1) Cost reduction of the system. The expensive manufacturing cost of CMs limits the wide application of the system to a certain extent.

2) The stable optimization of aeration part. In the future, no / microbubble aeration [37], multi-point dosing and other means can be used to improve the aeration effect of ozone.

3) In-depth membrane modification. The influence of hydrophilicity/hydrophobicity, roughness and other properties on membrane fouling has not been fully explored, and further work is needed.

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