Application Prospect of Ceramic Membrane Coupling Process in Refinery Wastewater

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Abstract. Refinery wastewater has attracted wide attention because of its large amount and great environmental pollution. With the increasingly contradictory of water shortage, the deep processing of refinery wastewater has become a central issue of research. Membrane technology is widely used in advanced wastewater treatment processes, in addition, ceramic membranes are more competitive in the treatment of oily wastewater due to their unique advantages. This review summarizes the characteristics and treatment process of refinery wastewater, points out the current problems in the advanced treatment process, and describes the characteristics of the ceramic membrane and its application in refinery wastewater. Finally, the prospects and challenges faced by the wide application of ceramic membranes in refinery wastewater are forecasted.

1. Introduction
In recent years, the composition of the oil refining wastewater is becoming more and more complex and its biodegradability also gradually deteriorates. After the traditional process, the concentration of pollutants in the wastewater is still high, and the direct discharge into the natural water will cause serious pollution to the environment. At the same time, China has put forward more stringent emission standards for refinery wastewater; on the other hand, the amount of wastewater is considerable, and the reuse of wastewater is an effective way to solve the problem of water use in the current refining industry. To a certain extent, reuse of wastewater alleviates the problems of water shortage and pollution, and raises the efficiency of the enterprise, which has very high social and economic values.

2. Advanced treatment technology of refinery wastewater
With the maturity of water treatment technology, the continuous improvement of equipment technique, the technology of refining wastewater depth treatment has been greatly developed. At present, the main methods used for wastewater treatment are physicochemical, chemical and biochemical methods. The physicochemical methods include precipitation filtration, membrane separation and adsorption, the chemical methods include flocculation precipitation, ion exchange, electrodialysis, chemical oxidation, and electrochemistry, and biological methods mainly include membrane bioreactor and bioactive carbon. Membrane separation technology [1], adsorption technology and advanced oxidation technology have been widely used because of many advantages, such as high efficiency and almost none secondary pollution [2].
2.1. Membrane technology
Membrane separation is one of the most commonly used processes for advanced treatment of refinery wastewater, according to the size of the aperture, the membrane can be divided into microfiltration membrane (MF), ultrafiltration membrane (UF), nanofiltration membrane (NF) and reverse osmosis membrane (RO). The pore diameter of the membrane decreases with the order of MF, UF, NF and RO, and the fluid dynamic resistance of the liquid channel is also increased by in turn [3]. In engineering applications, MF and UF are often used for RO preprocessing. Membrane can be divided into organic polymer membrane and inorganic membrane according to the material. Organic membrane materials include cellulose, polyamides, polyolefins, and so on. The inorganic membrane can be divided into ceramic membrane, glass membrane and metal membrane. Membrane technique is mainly used to demineralization, deoiling and suspended solids removal from refinery wastewater [4]. It has many advantages such as small footprint and good quality of effluent. But the membrane fouling is inevitable, especially protein, polysaccharide and humic acid, which are the main causes of membrane fouling. The influence of organic substances in wastewater on the design and operation of membrane processes must be further studied [5]. Membrane fouling rate can be effectively reduced through effective pretreatment technology, and the membrane surface characteristics and operating conditions also have great influence on it [6].

2.2. Advanced Oxidation Technology
Advanced oxidation is a wastewater treatment method for oxidative decomposition of organic matter, which produces highly reactive free radicals (·OH, ·O3-) by oxidant in the reaction of electroluminescence or catalyst [7]. The general characteristics of the advanced oxidation mechanism are that organic compounds and oxidation free radicals produce organic radicals, and organic radicals collide with oxygen molecules to generate peroxide radicals, these radicals further decompose or react with other radical reactions to produce a series of intermediate products or are most eventually mineralized into CO2 and H2O [8]. Advanced oxidation processes have many advantages, such as fast reaction rate, mild reaction conditions, high degree of organic degradation, and hardly any secondary pollution. The most commonly used oxidation methods are ozone oxidation [9], Fenton oxidation [10], ultrasonic oxidation, and catalytic oxidation. The application of advanced oxidation technology in the refinery wastewater treatment can cause oxidation of refractory organics to small molecule organics or complete mineralization and effectively improve the biological properties of the wastewater. Many studies have shown that the ·OH generated by a single advanced oxidation method is limited. The combination of multiple advanced oxidation processes will promote the production of free radicals and enhance the ability of pollutants degradation. In addition, the treatment effect of advanced oxidation is related to the physical and chemical properties of the solution, the concentration range of pollutants, the operating conditions of oxidation process, the dosage of oxidizer and so on [11].

2.3. Adsorption technology
Adsorption method is an adsorption and separation technology used in advanced treatment of refinery wastewater. The removal effect of refractory material in water is remarkable, the removal rate is stable and the operation is easy. When the wastewater passes through the adsorbent or the filter bed, the contaminants are adsorbed on the solid surface and thus separated from the water, and the adsorption takes place on the solid-liquid interface. At present, activated carbon, zeolite, volcanic rock and bentonite are commonly used as adsorbent in sewage treatment, and activated carbon is the most widely used in deep treatment [12]. The adsorption of pollutants by activated carbon exists in two forms, namely physical adsorption and chemical adsorption. Physisorption is due to its porous surface properties, van der Waals forces, and hydrogen bonding interactions. The adsorption process is affected by the molecular size of the adsorbate and the pore size of the adsorbent. Chemisorption is the chemical reaction of the adsorbate with the surface group of the adsorbent. Studies have shown that activated carbon has a good adsorption effect on most pollutants. The adsorption effect is not only related to the nature of adsorbents and adsorbates, the nature of the adsorption medium and the adsorption reaction
conditions also affect it, just like the temperature, pH, polarity and ionic strength of the adsorption medium. In order to improve the adsorption performance of activated carbon, the commonly used measures are optimizing adsorption conditions, modifying activated carbon [13], and using activated carbon combined with other processes [14].

3. Application of Ceramic Membrane in Wastewater Treatment

Although membrane technology is more advantageous than conventional treatment technology, the problem of membrane fouling caused by the advanced treatment of petrochemical wastewater has always been the focus of attention. One of the reasons is that when the oily wastewater passes through the membrane, the oil droplets are trapped and accumulate on the membrane surface, gradually forming a concentrated polarization layer, which leads to a decrease in the permeation flux. Another major cause is that the complex pollutant characteristics of petrochemical wastewater [15]. In recent years, in order to reduce membrane fouling and increase membrane permeation flux, domestic and foreign scientific research workers have conducted a lot of research, researched and obtained many effective methods, including modification of the membrane surface [16], the use of pulsed flow and turbulence promoters for filtration [17,18], use of membranes instead of fixed membranes and ultrasonic cleaning and other technical means, these technologies have achieved good pollutant removal effect [19], and effectively reduced the fouling formation on the membrane surface and slowed down the concentration polarization. However, whether it is a single membrane filtration or a membrane bioreactor, the ceramic membrane is more resistant to contamination than organic membranes in petrochemical wastewater treatment.

3.1. Ceramic Membrane Properties

The ceramic membrane is a type of inorganic membrane made of metal oxides (Al2O3, TiO2, ZrO2) and other materials, different oxide materials have different chemical and thermal stability according to the operating conditions. Each oxide has different surface charge in the solution, so different materials can be selected according to the need [20,21]. The ceramic membrane is composed of porous and asymmetric structure, which consists of porous support layer, middle layer and thin membrane with different density. The aperture range of ceramic membrane pore size covers from microfiltration to nanofiltration. According to the morphology of ceramic membrane, it can be divided into flat membrane, tubular membrane and multi-channel membrane [22].

Ceramic membrane has the advantages that polymerized organic membrane can't compare with: (a) good chemical stability, acid resistance, alkali resistance and organic solvent resistance; (b) high mechanical strength; (c) strong resistance to microorganism, no action with microorganism; (d) high temperature resistance; (e) narrow pore size distribution and high separation efficiency. In addition, there are abundant hydroxyl groups on the surface of the ceramic membrane and the inner wall of the pore size, which has strong polarity and hydrophilicity. The interface energy of the water and the membrane is smaller than the interface energy of the oil and the membrane, and the oil droplets are not easily adsorbed on the membrane surface, thus the ceramic membrane exhibits hydrophilicity and oleophobicity, and is resistant to oil and other hydrophobic organic pollutants.

3.2. The Application of Ceramic Membrane in the Treatment of Refinery Wastewater

At present, the industrialization and commercialization of ceramic membrane products at home and abroad have reached a high level. The application of ceramic membrane in water treatment has penetrated into many fields, such as seawater desalination pretreatment, water treatment, domestic sewage and industrial wastewater treatment, and has achieved good application effect in the oil wastewater treatment.

Madaeni used ceramic MF membrane (γ-Al2O3, 200nm) to treat the coking wastewater from the petrochemical plant [23]. When the influent concentration of COD in the ceramic membrane is 2210mg/L, the transmembrane pressure difference is 15bar and the temperature is 70 Celsius, the coke removal rate is as high as 100%, and the removal rate of COD is 72%. The experimental results of Abadi showed that the removal rate of ceramic MF membrane (α-Al2O3, 200nm) for petroleum, total
suspended solids and turbidity is 85%, 100% and 98.6%, respectively, and the discharge quality meets local emission standards [24].

In actual wastewater treatment, ceramic membrane is usually combined with other processes such as advanced oxidation, coagulation and adsorption to further improve effluent quality and reduce membrane fouling rate [25].

Fan’s studies showed that the degradation rate of endocrine disruptors [26], personal drugs and nursing products by O3 oxidation and ceramic membrane (60nm) filtration was more than 98%, and the continuous operation of 120h transmembrane pressure increased slowly (<2kPa); the removal rate of direct filtration is only about 50%, and the transmembrane pressure difference increases faster in the same time (>11kPa). Yong used coagulation-ceramic membrane process to treat the landscape lake water [27]. When the amount of polysilicon-iron-zinc coagulant is 25 mg/L and the operating pressure of the ceramic membrane is 0.09 MPa, the removal rates of COD, TP, and TN were 84.02%, 75.31%, and 58.22%, respectively. The study found that after coagulation pretreatment, the ceramic membrane flux can be significantly increased. In the same operating cycle, the combined process and the ceramic membrane were run alone, the flux increased by 28.15%.

However, the application of ceramic membranes combined with coagulation, advanced oxidation, and adsorption processes in advanced treatment of refinery wastewater is still relatively rare. In particular, the synergy and coupling mechanism between the processes is not yet clear, and the effect of the chemical properties of refinery wastewater on the treatment efficiency of the advanced treatment process remains to be explored.

4. Concluding remarks
The ceramic membrane has unique advantages in the advanced treatment of the refinery wastewater, but the membrane pollution problem is inevitable. The mechanism and characteristics of the pollution of the ceramic wastewater by the refinery wastewater still need to be further studied. Coupling ceramic membranes with other processes can exert synergies between processes, and the analysis of the synergy between processes will help promote the use of ceramic membranes in refinery wastewaters.

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References
[1] Abbasi M, Mirfendereski M, Nikbakht M, Golshenas M and Mohammadi T 2010 Performance study of mullite and mullite-alumina ceramic MF membranes for oily wastewaters treatment Desalination 259 pp 169-78.
[2] Zhu X, Tu W, Wee K H ang Bai R 2014 Effective and low fouling oil/water separation by a novel hollow fiber membrane with both hydrophilic and oleophobic surface properties J. Membr. Sci. 466 pp 36-44.
[3] Munirasu S, Haji M A and Banat F 2016 Use of membrane technology for oil field and refinery produced water treatment—A review Process Saf. Environ 100 pp 183-202.
[4] Elmaleh S, Ghaffor N 1996 Cross-flow ultrafiltration of hydrocarbon and biological solid mixed suspensions J. Membr. Sci. 118 pp 111-20.
[5] Howe K J, Clark M M 2002 Fouling of microfiltration and ultrafiltration membranes by natural waters Environ Sci Technol. 36 pp 3571-76.
[6] Childress A E, Elimelech M 1996 Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes J. Membr. Sci. 119 pp 253-68.
[7] Cai W 2016 Application of catalytic ozonation in the treatment of organic wastewater Technology Innovation and Application p 146.
[8] Zhang W B 2003 Treatment of Organic Pollutants in Water by Homogeneous and Heterogeneous
Advanced Oxidation Techniques. GUCAS.

[9] Schumacher J 2006 Ozonation and Advanced Oxidation of Wastewater: Effect of ODose, pH, DOM and HO-Scavengers on Ozone Decomposition and HOGeneration Ozone-Sci Eng 28 pp 247-59.

[10] Li Z, Zhou S G, Yuan Y, Liu M and Wang Y 2010 A novel bioelectro-Fenton system for coupling anodic COD removal with cathodic dye degradation Chem. Eng. J. 163 pp 160-3.

[11] Miklos D B, Remy C, Jekel M, Linden K G, Drewes J E and Hübner U 2018 Evaluation of advanced oxidation processes for water and wastewater treatment – A critical review Water Res. 139 pp 118-31

[12] Boehler M, Zwickenpflug B, Hollender J, Ternes T, Joss A and Siegrist H 2012 Removal of micropollutants in municipal wastewater treatment plants by powder-activated carbon Water Sci. Technol 66 p 2115.

[13] Liu Z, Li L, Tang L, Shi R, Gu Q, Liang X and Yao X 2013 Investigation of adsorption performance on 1,2-dichloroethane by heat and acid modified activated carbon J. Environ. Chem. Eng. 1 pp 131-6.

[14] Valdès H, Zaror C A 2006 Heterogeneous and homogeneous catalytic ozonation of benzothiazole promoted by activated carbon: kinetic approach, Chemosphere 65 pp 1131-36.

[15] Ji Y 2015 Membrane technologies for water treatment and reuse in the gas and petrochemical industries Advances in Membrane Technologies for Water Treatment pp 519-36.

[16] Ulbricht M 2006 Advanced functional polymer membranes Polymer 47 pp 2217-62.

[17] Howell J A, Field R W and Wu D 1993 Yeast cell microfiltration: Flux enhancement in baffled and pulsatile flow systems J. Membr. Sci. 80 pp 59-71.

[18] Wakeman R J, Williams C J 2002 Additional techniques to improve microfiltration Sep. Purif. Technol. 26 pp 3-18.

[19] Chai X, Kobayashi T and Fujii N 1998 Ultrasound effect on cross-flow filtration of polyacrylonitrile ultrafiltration membranes J. Membr. Sci. 148 pp 129-35.

[20] Lee M, Wu Z and Li K 2015 Advances in Membrane Technologies for Water Treatment, Woodhead Publishing Oxford pp 43-82.

[21] Hof S, Ogier J, Vries D, Beerendonk E F and Cornelissen E R 2011 Cornelissen Comparison of ceramic and polymeric membrane permeability and fouling using surface water Sep. Purif. Technol. pp 365-74.

[22] Xu N P, Xing W H and Zhao Y J 2003 Inorganic membrane separation technology and application Beijing Chemical and Chemical Press pp 105-10.

[23] Madaeni S S, Monfared H A, Vatanpour V, Shamsabadi A A, Salehi E, and Daraei P 2012 Coke removal from petrochemical oily wastewater using γ-Al2O3 based ceramic microfiltration membrane Desalination 293 pp 87-93.

[24] Abadi S R H, Sebzari M R, Hemati M, Rekabdar F and Mohammadi T 2011 Ceramic membrane performance in microfiltration of oily wastewater Desalination 265 pp 222-8.

[25] Li Y L, Deng Z Y, Liu H and Dong Y C 2017 Advances in research of inorganic ceramic membrane separation coupled advanced oxidation technology in water treatment Membrane Science and Technology 37 pp 134-141.

[26] Fan X J, Tao Y, Wang L Y, Zhang X H, Ying L, Wang Z and HiroshiNoguchi 2014 Performance of an integrated process combining ozonation with ceramic membrane ultra-filtration for advanced treatment of drinking water Desalination 335 pp 47-54.

[27] Mao Y J, Wang L P, Ji Y F, Song C L and Du E D 2013 Study on eutrophication of eutrophic water by coagulation-ceramic membrane combination process Journal of Changzhou University 25 pp 20-22.