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To cite this article: Qi Han et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 392 022037

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Ceramic Membrane Coupling Process for Advanced Treatment of Electroplating Wastewater

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Abstract. Electroplating wastewater has attracted wide attention because of its large amount and complex components. It contains a variety of heavy metals and organics that are harmful to people’s healthy and the environment. With the continuous improvement of environmental protection requirements, the emission standards for electroplating pollutants have also been improved. Therefore, the advanced treatment of electroplating wastewater has become a hot spot in the current research. Membrane separation technology has been widely used in the advanced treatment of electroplating wastewater, especially ceramic membrane technology which is more competitive in practical application due to its unique advantages. In order to realize the advanced treatment of electroplating wastewater, the commonly used advanced treatment process and its existing problems were introduced firstly. Then the development of ceramic membrane technology in advanced treatment was discussed. And finally, a ceramic membrane coupling process for the advanced treatment of electroplating wastewater was proposed, which has good economic and social benefits.

1. Introduction
In recent years, the electroplating industry of our country has developed rapidly. Electroplating enterprises have been distributed in all walks of life (mainly in the electronics industry, machinery industry, light industry, aerospace and instrumentation industries) [1], and plating variety. On the one hand, the quality of electroplating wastewater becomes increasingly complex and the contaminant composition has not been easily controlled. With increasingly stringent environmental protection requirements, the conventional treatment process can no longer meet the requirements of environmental protection. Electroplating wastewater that does not meet the standard discharged directly into water body will cause serious pollution to the water environment. On the other hand, the discharge of electroplating wastewater is also increasing. Electroplating wastewater reuse is an inevitable trend for enterprise development. The reuse of electroplating wastewater can not only reduce the discharge of sewage, mitigate environmental pollution, and save water resources, but also have high social and economic value. Therefore, the advanced treatment of electroplating wastewater is imperative.

2. Advanced treatment technology of electroplating wastewater
At present, researches for electroplating wastewater treatment at home and abroad emphasize removal of heavy metal ions, and there are few researches for organic matter treatment technologies.
Conventional treatment technologies are mainly aimed at heavy metal pollutants, and the removal effect is good, but it is poor for treatment effect of organic pollutants, especially, persistent organic pollutants. Therefore, advanced treatment technology of electroplating wastewater mainly focuses on removal of persistent organic pollutants and achieves the reuse of wastewater. Right now, methods for advanced treatment of wastewater are mainly physicochemical, chemical oxidation and biochemical methods. The physicochemical methods include coagulation, adsorption, membrane separation, electrocoagulation [2], microelectrolysis [3]; chemical oxidation methods include advanced oxidation, chlorination [4]; biochemical methods are mainly biological aerated filter [5], membrane bioreactor [6], biological activated carbon [7], biofortification technology [8]. Coagulation, adsorption, membrane separation, and advanced oxidation processes are widely used because of their advantages such as high efficiency, no secondary pollution, simple equipment.

2.1. Coagulation process
As follow-up processing of electroplating wastewater biochemical treatment, coagulation can further remove organic matter and suspended matter in water. The mechanism that coagulation process removes organic matter is hydroxide flocs by hydrolysis of coagulant adsorb organic matter and remove it. Organic matter reacts with coagulant ion to produce insoluble complex. The flocs formed in the coagulation process have strong physical adsorption effect on macromolecular organic pollutants (molecular weight > 6000), and the removal effect is better [9]. Coagulation technology is mature and easy to operate. While coagulation alone is used as an advanced treatment process in actual wastewater treatment, the removal of organic matter is poor, can't meet the requirements of discharge or reuse. Therefore, more and more researchers have used coagulation in combination with other advanced treatments processes, which as a pretreatment or post-treatment process for adsorption, advanced oxidation, membrane separation and other technologies [10].

2.2. Adsorption process
Some refractory organics in electroplating wastewater are difficult to reach the discharge standard through secondary biochemical treatment, such as certain heterocyclic compounds, which can be removed by adsorption process. Adsorption process has a good removal effect on the refractory organics in electroplating wastewater, and it is convenient to operate. Refractory dissolved organics adsorbed to the surface of adsorbent by adsorption process to achieve the purpose of removal, which mainly relies on physical adsorption (molecular action), chemical adsorption (chemical bond interaction) or ion exchange adsorption (electrostatic attraction). Commonly used adsorbents are activated carbon, zeolites, volcanic rocks, resins, diatomite, etc., in which activated carbon is the most widely used in advanced treatment. Due to the large specific surface area and surface hydrophobic structure, activated carbon has outstanding adsorption capacity for most organic pollutants, especially non-polar and weakly polar organic pollutants with small molecular weight. At the same time, the surface contains a small amount of oxygen-containing functional groups, which has a certain removal effect for heavy metal ions [11]. In order to improve the adsorption performance of activated carbon and reduce the amount of activated carbon, the commonly used measures are optimize adsorption conditions, use modified activated carbon [12], and combine activated carbon with other advanced treatment processes [13].

2.3. Membrane separation technology
Membrane separation technology is a newly emerging high-efficiency technology to separation and purification that utilizes the pressure difference as the driving force to achieve separation by the pores of the membrane to intercept and pass different substances. According to the membrane pore size, it can be divided into: microfiltration (MF: 0.1-10 μm), ultrafiltration (UF: 2-100 nm), nanofiltration (NF: 0.1-2 nm), reverse osmosis (RO: <1 nm), etc. With the different membrane pore size, the separation mechanism and purification effect are different. RO technology is widely used in advanced treatment of electroplating wastewater. In Western developed countries, 80% of the electroplating
industry has achieved zero discharge of wastewater, which is basically achieved by membrane separation technology [14]. Membrane separation technology is a hotspot of research for advanced treatment technologies, which can effectively remove color, organic matter, some inorganic substances and microorganisms in water, and also can recover metals, the stability of effluent water quality, high separation efficiency, small floor space, and no secondary pollution.

With the continuous development of membrane separation technology, the combination process of several membrane separation technologies and the combination process of membrane separation technology and other technologies have gradually become the development trend of advanced treatment processes. At present, MF-RO combination process [15], UF-RO combination process [16], NF-RO combination process [17], and UF-NF combination process [18] have all been applied in the advanced treatment of electroplating wastewater and have been good effect. As the membrane is easily blocked by pollutants in the wastewater, membrane fouling issues affect the further development of the membrane separation technology. Only by controlling and reducing membrane fouling to prolong membrane life and reduce the cost, membrane separation technology can be more widely used in the advanced treatment of electroplating wastewater. The development of membrane materials with high stability, anti-pollution, long life, high-throughput and low-cost is the future direction of membrane separation technology.

2.4. Advanced oxidation process
Advanced oxidation Process (AOPs) is a highly efficient water treatment technique, that uses hydroxyl radicals (·OH) generated under certain conditions (electricity, light irradiation, catalysts, etc.) with strong oxidizing properties to oxidatively decompose refractory macromolecular organics into small molecular organics by the free radical reaction, and eventually converted to CO₂, H₂O and inorganic salts. AOPs is widely used in advanced treatment due to its fast reaction speed, thoroughness, non-selectivity, and no secondary pollution. AOPs, as an advanced treatment unit for electroplating wastewater, can oxidatively decompose refractory macromolecular organics into small molecular organics or completely mineralize the organics, and effectively improving the biodegradability of wastewater. AOPs includes ozone catalytic oxidation, fenton oxidation, photocatalytic oxidation, electrochemical oxidation, ultrasonic oxidation, supercritical water oxidation. In particular, ozone oxidation and fenton oxidation are more widely used in advanced treatment [19-20]. In the actual project, composition of wastewater is relatively complex, and single oxidation technology is difficult to meet the treatment requirements, therefore, combination of AOPs with other advanced treatment technologies has been widely researched [21-22].

3. Development of ceramic membrane technology in advanced treatment
With the wide application of membrane separation technology, in order to reduce membrane fouling and increase membrane permeation flux, researchers at home and abroad are committed to the development of anti-pollution and high-throughput membrane materials. Ceramic membranes stand out with their unique advantages. Ceramic membranes are a new kind of membrane separation material, which are a porous membrane made of inorganic materials such as Al₂O₃, ZrO₂, TiO₂ and SiO₂. The porosity is more than 30% and the pore size is 0.004-15 μm [23]. Ceramic membrane separation technology is mainly based on the "screening theory", that according to a certain range of membrane pore size, the material permeability of different molecular diameter is different, small molecules or liquid through the membrane and macromolecules or solids are trapped by membranes to achieve separation and purification purposes [24]. Ceramic membranes have many advantages such as high temperature resistance (1000 °C), high mechanical strength, good chemical stability, corrosion resistance, long service life (greater than 5 years) and large flux, that have been widely applied in industrial wastewater treatment such as oily wastewater, printing and dyeing wastewater.

In practical engineering, ceramic membrane technology is usually combined with processes such as coagulation, adsorption, and advanced oxidation to reduce the burden of ceramic membrane and prolong the work cycle. Chen Tianyi et al. [25] adopted powdered activated carbon as catalyst to
construct an ozone catalytic oxidation reactor with powder-activated carbon coupling ceramic membrane and researched its advanced treatment efficiency for coal gasification wastewater. The results showed that powdered activated carbon could effectively catalyze the oxidation of biochemical effluent from coal gasification wastewater by ozone within 30 min and the removal rate of COD reached 75% when powdered activated carbon was added at 2 g/L and ozone was added at 30 to 120 mg/L. The powdered activated carbon-ceramic membrane ozone catalytic oxidation reactor can continuously run at the flux of 50 L/(m²·h) and the effluent COD can be reduced to 50 mg/L. And the ozone in the reactor can effectively alleviate the membrane fouling, increase the critical flux from 35-40 L/(m²·h) to 50-60 L/(m²·h), reduce the transmembrane pressure difference by 35%-40%, and make the membrane component run steadily. However, the coupling process is still rare in the advanced treatment of electroplating wastewater and the mechanism of synergy and coupling between the processes is not yet clear, and further research is needed, which ceramic membrane technology combined with coagulation, advanced oxidation, adsorption and other processes.

4. Conclusion
Although ceramic membranes have unique advantages, there are still membrane fouling problem. In view of the complexity of electroplating wastewater, any single treatment technology may not reach the ideal effect. Therefore, it is necessary to develop an integrated process of ceramic membrane technology and other advanced treatment technologies, which gives full play to the advantage of various technologies to reduce running costs by alleviate membrane fouling and prolong the service life of ceramic membranes. The research of the integrated process for the advanced treatment and reuse of electroplating wastewater has good economic and social benefits.

Acknowledgement
This work was financially supported by the National Science Foundation of China (51678276), the key research and development program of Shandong Province (2016CYJS07A03-3, 2016GSF117012, 2018GSF117026) and the Shandong Provincial Natural Science Foundation (ZR2018BEE040).

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