

Effect of hydrophilic foamed copper on dynamic membrane formation in dynamic membrane bioreactor (DMBR)

C T Li¹, H J Liu^{1,2}, X Z Qian¹ and H H Yang¹

¹School of Space and Environment, Beihang University, 37 Xueyuan Road, Haidian District, Beijing 100191, China

E-mail: liuhj@buaa.edu.cn

Abstract. The effect of hydrophilic membrane material on the formation of dynamic membrane (DM) was investigated, by using a membrane module combined with a hydrophilic modified foam copper with 0-10 mm of thickness, 300 μm of pore size and an activated carbon sponge with 10 mm of thickness. The appropriate thickness of the hydrophilic membrane was selected to treat the refining wastewater. Hydrophilic modification and membrane formation experiments showed that water molecules were easier to spread on the surface of the foam copper, which could reduce the accumulation of sludge layer on the surface of the membrane module and increase the effluent's stability of the combined membrane module. Under experimental conditions, the proper thickness of the foam copper was 5 mm, the sludge layer thickness on the membrane surface was close to 0mm, and the effluent flux was stabled as 44 $\text{L}/(\text{m}^2\cdot\text{h})$, which was higher than that of the activated carbon sponge without using the hydrophilic foam copper, increased by 107%. Wastewater treatment results showed that the removal rate of COD in the DMBR system was 95.6%, and the removal rate of ammonia nitrogen was 98.5%.

1. Introduction

In the development of wastewater treatment technology, the use of membrane bioreactor (MBR) has become more and more extensive; however, membrane cost, high energy consumption and membrane fouling have become the main factors that limit the further promotion of MBR [1]. Thus, the dynamic membrane bioreactor (DMBR), with low energy consumption and low film cost [2], is paid more and more attention by researchers. Dynamic membrane bioreactor, with large pore size membrane substrate, is a new MBR process instead of conventional MBR, in which microporous membrane and ultrafiltration membrane are used [3]. DMBR's filtration process, intercepting the sludge and flocs, which formed the "dynamic film" for effective filtering process, is the biggest difference from traditional MBR [4]. While maintaining advantages of high filtration efficiency and small covering area, DMBR system significantly reduces the cost of the membrane, greatly improve the effluent flux [5].

Large-diameter membrane module was used as the substrate of Dynamic Membrane Bioreactor [6], microorganisms, suspended particulates and flocs of mixture in the reactor, is partially trapped in the grid, when passes through the membrane module [7], due to the suction pressure, moreover, partly attached to the mesh due to the adsorption of the material, after a series of complex processes, a dense layered structure formed [8]. Dense layer structure has a perfect filter performance for the suspended particulates in reactor [9], which could intercept most of particulate matter, like MLSS and dissolved



EPS, and maintain the stability of the effluent quality [10]. However, with the continuous operation of the experiment, the lamellar structure, accumulated on the surface of the membrane module, will collapse under the action of suction pressure, forming a thicker and more dense structure, thus, the effluent flux of the membrane reactor will gradually decrease [11]. Fan *et al* [12] reported that, the structure of dynamic membrane could mainly be divided into two parts, the mud cake layer and the gel layer. The structure of the cake layer, which contributes to the main filtration resistance, filters the large particle substances, the gel layer mainly adsorbed small molecules and dissolved substances. Zhang Jian *et al* [13] investigated the removal efficiency of COD, ammonia nitrogen, total nitrogen and other pollutants, the results showed that, dynamic membrane had some ability to remove pollutants, which may be related to the adsorption and filtration ability of the gel layer. Nowadays, industrial filter cloth, activated carbon sponge, nylon mesh, polyester filter cloth and silk screen are commonly used as membrane substrate [14], which is always hydrophobic materials, especially. You *et al* [15] reported that, using of hydrophobicity material, led to the accumulation of organic matter which was always negatively charged, and formed a relatively solid dense cake layer structure, because negatively charged substance could be easily adsorbed to hydrophobic membrane. The cake layer could not be removed by normal aeration scour, thus, the effluent flux and membrane lifecycle reduced, the degree of backwash affected and system operating costs increased [16]. To solve these problems, Xiong *et al* [17] used an elastic membrane material, this membrane could be retracted when sucked, and formed a thick and dense sludge layer, while it could protrude in the backwash process, conducive to the scour for sludge. Meng *et al* [18] reported that, hydrophobic solute, like EPS, produced by activated sludge could approach to the membrane surface, which was an entropy spontaneous process, because no hydrogen bonding between the hydrophobic membrane surface and H₂O, and the membrane filtration pressure (TMP) increased due to the surface adsorption and accumulation of hydrophobic solute.

In this study, a hydrophilic foamed copper material was attached to the activated carbon sponge. A composite membrane module was made up to investigate the mechanism of dynamic membrane formation, and the effects on effluent was also analyzed. The microorganism, suspended particles and flocs could be more evenly spread to the inner layer of activated carbon sponge, which was a hydrophobic material [19], due to the hydrophilic foam copper on the surface. This spatial structure could increase the stability of the effluent, reduce cake layer of the membrane surface, increase the flux of effluent, and improve treatment efficiency of DMBR system.

2. Materials and methods

In this study, a foam copper with 300 μm pore size was selected and modified by surface controlled oxidation method [20], attached to an activated carbon sponge with 10 mm thickness, as dynamic membrane module. After the domestication of the sludge, we started investigating the effects of membrane substrate in DMBR system.

2.1. Materials

The activated sludge was taken from Qinghe Sewage Treatment Plant, Beijing, China. Activated sludge, mixed with the refinery wastewater, was domesticated to adapt the quality of refinery wastewater. The MLSS concentration of domesticated activated sludge was 7.5 g/L, 5.5 g/L of MLVSS concentration. 10 mm thickness of activated carbon sponge was chosen, the hydrophilic copper foam components was 240×110 mm, 300 μm diameter, and its' thickness was 1 mm, 2 mm, 5 mm, 10 mm, respectively. Membrane substrate materials attached to both sides of ABS material, chosen for external support frame, sealed with glass glue. A set of MBR systems from Japan was used, and its' basic structure shown in figure 1.

Refinery wastewater was pumped to the reactor, by the peristaltic pump. Mud and water separation continued after organic matter degradation in the mixture. The suction power was provided by the suction pump, and oxygen was provided by a quartz sand microporous head underneath the membrane module.

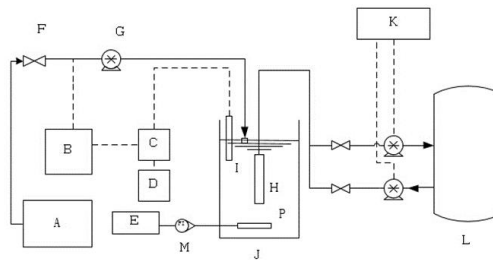


Figure 1. Experimental setup and experiment process.

A. waste water tank; B. transformer; C. level control controller; D. power supply; E. air compressor; F. valve; G. suction pump; H. DM module; I. level meter; J. reactor; K. PLC; P. aeration head; L. collection tank; M. flowmeter.

Pollutants in the refinery wastewater are shown in table 1.

Table 1. Water quality index of refinery wastewater.

	COD (mg/L)	NH ₃ -N (mg/L)	pH	NTU
parameter	633.23-812.67	32.9-33.4	11.2	77-863

2.2. Methods

2.2.1. Membrane hydrophilic modification. The surface properties of foamed copper were modified by "surface controlled oxidation", the foamed copper component was immersed in hydrochloric acid of 4.0 mol/L for 15 min, then washed with deionized water. 0.065 mol/L of potassium persulfate (K₂S₂O₈) and 2.5 mol/L of potassium hydroxide mixed aqueous solution were prepared. The washed foamed copper component was immersed in the above solution, heated at 60°C for 1 hour, then washed with deionized water, air dried, finally heated at 180°C for 2 hours to obtain a CuO film material.

The surface properties of the material were characterized by the German DataPhysics OCA20 contact angle tester, and the wettability of the material was analysed.

2.2.2. Membrane component selection. According to previous research [21], appropriate material mesh pore size of DMBR is between 100 μm to 500 μm. Thus, a pore size of 300 μm foam copper material was selected in our experiment, with thickness of 1 mm, 2 mm, 5 mm and 10 mm, respectively. Membrane components was made up by activated carbon sponge, which attached with hydrophilic foamed copper component. Under the same operating conditions, with a speed of 15 r/min, peristaltic pump pumped for 24 hours, measuring the thickness of cake layer and effluent flux.

2.2.3. Wastewater analysis. After the DM formed, wastewater was treated by the DMBR system. COD as well as ammonia nitrogen of influent, supernatant and effluent, were analyzed during the system running process. COD was measured by fast confined catalytic digestions, while ammonia nitrogen was measured by Nessler reagent spectrophotometry [22].

3. Results and discussion

3.1. Surface properties of membrane

German DataPhysics OCA20 contact angle tester was used to measure the contact angle of membrane material. The contact angle could not be determined accurately. As the foam copper was a spatial mode structure, only its wettability could be roughly analyzed. Results of unmodified foam copper's

wettability were shown in figure 2.

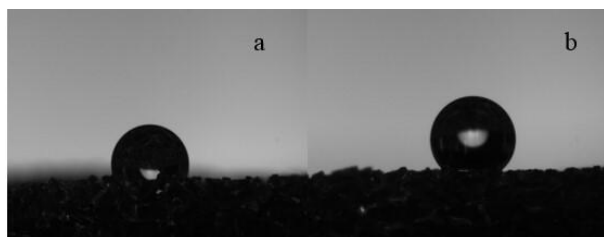


Figure 2. Results of unmodified foam copper's contact angle.

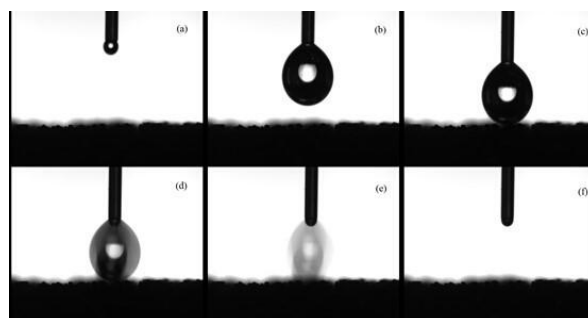


Figure 3. Results of modified foam copper's contact angle.

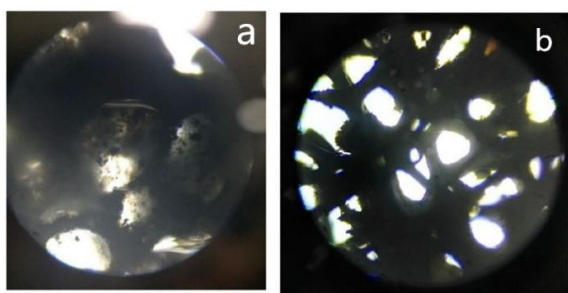


Figure 4. Pictures of flocs and microorganism on membrane module. (a), activated carbon sponge; (b), modified foam copper.

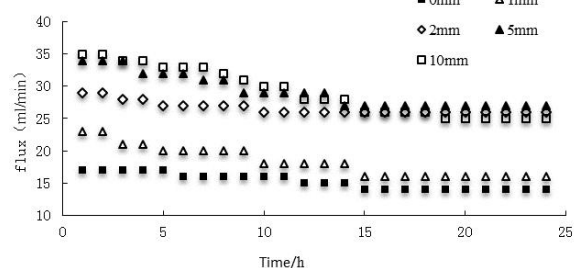


Figure 5. The effluent flux in membrane formation period.

Results of modified foam copper's wettability were shown in figure 3.

Pictures of flocs and microorganism, gathered on modified foam copper and activated carbon sponge after backwashing, were shown in figure 4.

It can be seen from figure 2, the macroscopic surface of the modified foam copper was not planar, and was composed of a porous structure, consisting of copper wires and gaps. The average contact angle of macroscopic surface was 123.5° , this material was in a hydrophobic state, thus, water molecules could not spread out on the surface of the foam copper.

As can be seen from figure 3, d and e, when a $5\ \mu\text{L}$ of droplet approached to the surface of the material, the droplet was sucked into the material. Figure 4 indicated that, flocs and microbial particles combined fast with hydrophobic material, while formed a loose structure in modified foamed copper. Compared with unmodified foam copper, hydrophilicity of modified foam copper improved obviously, water droplets could be completely spread out on the modified foam copper, and the solid particles in water could attach to the surface of the copper mesh or infiltrate to the internal of modified foam copper.

3.2. Membrane formation analysis

The modified foamed copper membranes, with the thickness of 1 mm, 2 mm, 5 mm and 10 mm, were attached to the activated carbon sponge, respectively. Under a condition of 1.5 L/min aeration, a peristaltic pump was used, with the speed of 15 r/min, to pump the mixture for 24 h, then measured thickness of cake layer and effluent flux. Flux changed as shown in figure 5.

Thickness of cake layer changed as shown in figure 6.

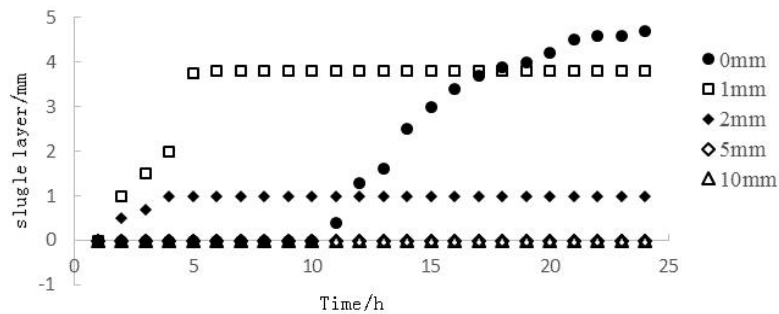


Figure 6. The thickness of sludge layer in membrane formation period.

It can be seen from figures 5 and 6, in a certain range, the flux of the dynamic membrane increased with thicker modified foamed copper. Flux of the membrane module, with a large thickness of the modified foamed copper, tended to be stable, and gradually approached. This might be because, at the beginning of the operation cycle, the sludge particles in the mixture could not accumulate on the surface of the foamed copper when passed through the thicker foam copper, which was evenly dispersed, partially redropped into the reactor. Part of the sludge flocs evenly tiled in the activated carbon sponge spatial structure. Flux of the membrane module increased, because it formed a sludge layer with thin and loose structure. While a thin modified foamed copper used, the sludge particles quickly gathered in the activated carbon sponge spatial structure, and then compressed, forming a thick and dense cake layer, making the membrane flux reduced. It can be seen from figures 4 and 5, appropriate thickness of the modified foamed copper was 5 mm, with which the stability flux was 29 mL/min, no cake layer remained on the surface, and the running cost was less than that of 10mm modified foamed copper mouldle.

From the changes of foam copper material's wettability, we can see that, there was a difference in a degree of spreading of water molecules on foam copper material's surface, due to the difference of wettability. Research showed that the sludge layer and the gel layer in the DMBR system, both have the filtering effect [12]. Most of the sludge particles were filtered out by the sludge layer's mechanical filtration, and the small molecules were adsorbed by the gel layer. Water molecules were more difficult to spread inside the hydrophobic material, and air bubbles formed often in the hydrophobic copper mesh or activated carbon sponge pore, forming an unstable factors, which could affect the stability of effluent quality. While water molecules could easily spread out in the hydrophilic material, so that the sludge particles could spread out into the activated carbon sponge spatial structure, forming a stable, dense sludge layer and gel layer, to keep a more stable effluent quality. While sludge could not be firmly bonded to the surface of the copper substrate, due to the spread of water molecules, and the sludge on the surface could naturally fall off through the water erosion, reducing the sludge resistance, increasing the flow of effluent.

3.3. Analysis of effluent quality

A 5 mm thick foamed copper membrane module was selected, and attached to the activated carbon sponge, making a composite membrane module. The membrane module was connected to the MBR system, COD and ammonia nitrogen were measured.

3.3.1. COD analysis. After completion of the sludge domestication, the dynamic membrane module was placed into the reactor, and the COD concentration of the refining wastewater was 743 mg/L on average. During the operation cycle of the DMBR system, effluent and the reactor supernatant COD concentration were measured every two days. The 60-day experimental data were analyzed and the results are shown in figure 7.

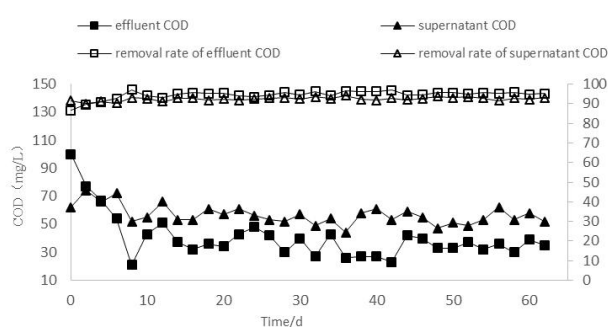


Figure 7. COD changes with time.

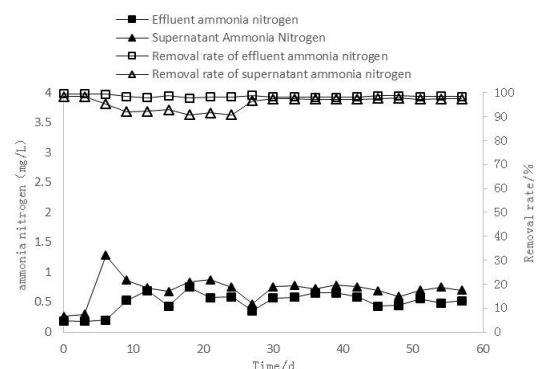


Figure 8. Ammonia nitrogen changes with time.

It can be seen from figure 7 that, the average effluent COD concentration was 34.10 mg/L, the average removal rate was 95.56%. The COD concentration of the supernatant was 56.50 mg/L, and the average removal rate was 92.25%. The dynamic membrane contributed little to the COD removal rate of raw water. The experimental results showed that, the contribution of membrane to COD removal was only 3.5%. In the early stage of the membrane system operation cycle, the COD of effluent dropped sharply, and 10 days later of operation, the COD of effluent became stable. According to the mechanism analysis of dynamic membrane formation, the dynamic membrane was formed by large particle size particles, proteins, polysaccharides and other EPS or SMP, originally, became a cake layer. The surface of the cake layer was gradually deformed, under the action of suction pressure, the pore size became smaller, the effluent quality getting better, and transmembrane pressure difference on the membrane module became larger. When the pressure on activated carbon sponge exceeded a certain degree, the activated carbon sponge would be deformed, part of the original filter layer would be destroyed, and a small part of the small particles leaked out into the effluent, led to the slightly addition of COD value. As the new particles continued to fill into the spatial structure, filter layer inside activated carbon sponge became normal, and then formed a complete dynamic membrane. This process continued to cycle and eventually achieved dynamic balance.

3.3.2. Ammonia nitrogen analysis. Ammonia nitrogen removal rate changes with time in figure 8.

It can be seen from figure 8 that, the average removal rate of ammonia nitrogen in the membrane module was 98.50%, the average removal rate of $\text{NH}_3\text{-N}$ in supernatant was 97.84%, with a larger thickness of the membrane module, some of the ammonia nitrogen, which could not be removed inside the reactor, was partially absorbed and removed in the sludge layer, thus, the ammonia nitrogen removal rate of effluent was higher than that in supernatant. The removal efficiency of $\text{NH}_3\text{-N}$ by sponge substrate dynamic membrane bioreactor was better than that of polyester nonwoven fabric. Under the same operating conditions, the aerobic and anaerobic regions formed by the sponge membrane substrate, which strengthen the combination of aerobic and anaerobic, achieving a better nitrification effect.

3.4. Discussion

Recently, the researchers of DMBR field mainly focused on the critical flow, the choice of different membrane materials, wastewater treatment effect and the improvement of the DMBR control system. However, there were few scholars focused on the surface performance of the membrane material, the spatial structure of membrane materials, to reduce the membrane fouling problems and enhance the system reliability. Therefore, this research used a hydrophilic state, spatial structure copper foam, as the DMBR membrane module, and investigated its characteristic. Experimental results showed that, the sludge on the surface of the membrane module was obviously reduced, membrane formation time sharply reduced, the flow was increased, and the removal rate of COD was significantly promoted,

which fully meet the technological requirements of wastewater treatment. These indicate that, The DMBR system has a good ability for sewage treatment, which could degrade the conventional pollutants such as COD. Meanwhile, this study first used hydrophilic copper foam material as the membrane module, the results indicated that it could effectively reduce membrane fouling, this was because hydrophilic groups on the surface of the membrane module and water molecules combines, forming a stable layer of water film, thus, substances such as sludge cannot combine with membrane components surface. Under the action of water flow, sludge was rinsed clean, thus, the effluent flow of the system was also increased, and the production efficiency of the system improved.

In the backwash process, sludge structure in the hydrophobic material was dense and fast, and big flushing pressure was needed to meet the backwashing requirements, meanwhile, more pressure could damage material's spatial structure, reduce the service life of the membrane. While membrane structure in hydrophilic material was relatively loose, which could be washed under a low flow rate, thus, more energy could be saved. In this case, the choice of the membrane material could tend to be a hydrophilic material of self-cleaning ability, low energy consumption, and long service life.

4. Conclusion

In the research field of dynamic membrane bioreactor, the use of hydrophilic material deserved more attention, because it can not only improve DMBR's defects, but also be a foundation for DMBR mechanism research. For example, the connection between structure characters and the formation of filter layer on the surface, and the relationship between surface structure character and the stability of spatial structure of filter layer, are worthy researching. In a nutshell, the ultimate aim of DMBR research is to improve the filtering stability of the membrane module, eventually to promote the DMBR process.

References

- [1] Kiso Y, Jung Y J, Ichinari T, Park M, Kitao T, Nishimura K and Min K S 2000 Wastewater treatment performance of a filtration bio-reactor equipped with a mesh as a filter material *Water Res.* **34**(17) 4143-50
- [2] Liang S, Qu L, Meng F, Han X and Zhang J 2013 Effect of sludge properties on the filtration characteristics of self-forming dynamic membranes (SFDMs) in aerobic bioreactors: Formation time, filtration resistance, and fouling propensity *J. Membrane Sci.* **436** 186-94
- [3] Zhang Y J 2012 Research progress of dynamic membrane bioreactor *J. Membrane Sci. Technol.* **2032**(2013) 2117-23
- [4] Chu H, Zhang Y, Zhou X, Zhao Y, Dong B and Zhang H 2014 Dynamic membrane bioreactor for wastewater treatment: Operation, critical flux, and dynamic membrane structure *J. Membrane Sci.* **450** 265-71
- [5] Yu K 2006 Development and prospects on dynamic membrane bioreactor (DMBR) *J. Water Purif. Technol.* **2025**(2002) 2014-8
- [6] Wu Y X 2004 Operating characteristics of self-forming dynamic membrane bioreactor at high flux *J. Chin. Water Wastewater* **2020**(2002) 2005-7
- [7] Ye M S, Zhang H M and Yang F L 2008 Experimental study on application of the boundary layer theory for estimating steady aeration intensity of precoated dynamic membrane bioreactors *Desalination Environ. Sci.* **230**(1-3) 100-12
- [8] Xiong J, Fu D F, Singh R P and Ducoste J J 2016 Structural characteristics and development of the cake layer in a dynamic membrane bioreactor *Sep. Purif. Technol.* **167** 88-96
- [9] Ersahin M E, Ozgun H, Tao Y and van Lier J B 2014 Applicability of dynamic membrane technology in anaerobic membrane bioreactors *Water Res.* **48** 420-9
- [10] Liu H, Yang C, Pu W and Zhang J 2009 Formation mechanism and structure of dynamic membrane in the dynamic membrane bioreactor *Chem. Eng. J.* **148**(2-3) 290-5
- [11] Hu Y, Wang X C, Tian W, Ngo H H and Chen R 2016 Towards stable operation of a dynamic membrane bioreactor (DMBR): Operational process, behavior and retention effect of

- dynamic membrane *J. Membrane Sci.* **498** 20-9
- [12] Fan B 2003 Filtration capability of the bio-dynamic membrane *J. Environ. Sci.* **2024(2001)** 2091-7
- [13] Zhang J 2007 Structure and function of dynamic membrane in the dynamic membrane bio-reactor *J. Environ. Sci.* **2028(2001)** 2147-51
- [14] Hong J M 2011 Study on performance of dynamic membrane bioreactor with different membrane materials *Chin. J. Environ. Eng.* **2005(2012)** 2311-4
- [15] You C Y 2005 Study on mechanism and control of gel layer forming on membrane surface *J. Jiangsu Environ. Sci. and Technol.* **18(14)** 11-3
- [16] Lu J D 2006 A bench-scale dynamic membrane bioreactor for purification of wastewater *Environ. Sci. Technol.* **2029(2005)** 2093-4
- [17] Xiong J D, Fu D F and Singh R P 2014 Self-adaptive dynamic membrane module with a high flux and stable operation for the municipal wastewater treatment *J. Membrane Sci.* **471** 308-18
- [18] Meng F G 2006 Effect of activated sludge properties on short-term membrane fouling in submerged membrane bioreactor based on statistical analysis *Chin. J. Environ. Eng.* **2027(2007)** 1348-52
- [19] Qu M N 2016 Research and development of functional superhydrophobic materials *Chem. Prog.* **2016(2012)** 1774-87
- [20] Qian B T 2006 Super-hydrophobic CuO nanoflowers by controlled surface oxidation on copper *J. Inorg. Mater.* **21(23)** 747-52
- [21] Li X B 2007 Development of research on the dynamic membrane separation technology *J. Membrane Sci. Technol.* **27(24)** 91-5
- [22] China National Environmental Monitoring Centre 2002 Water and wastewater monitoring and analysis methods *China Environmental Science Press* **2002** 2210-20 2276-81