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# Research on Mud Feature and Membrane Pollution of Membrane Bioreactor Container

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Membrane bioreactor is used for wastewater containing phenol treatment, and it also discusses the mixed aerobic granular dosing influence sludge characteristic of membrane bioreactor container. The results showed that the mixed aerobic granular sludge in the membrane bioreactor can effectively improve the sludge properties. It also improves the treatment effect. sedimentation performance is improved by using flocculent sludge to gradually increase additive amount of aerobic granular sludge, which was 100%. And the hydrophobic is better by SVI from 135.85 to 29.36 mL/g, Zeta potential from 20.302 rise to 4.325 mV. It leads the COD, NH3-N degradation in the waste water is improved. The Removal Rate of COD, NH3-N, NO3-N from 87.3%, 83.2% and 87.3% rise to 99.2%, 94.9% and 99.2%. At the same time, it also compares the various changes trend and changes of the membrane surface in different condition, it shows that different inhibitory effects membrane pollution, and membrane pollution membrane is reduced and flux recovery rate is rise in sludge with dosing condition.

## 1. Introduction

Phenol wastewater is a kind of organic concentration industrial wastewater which is difficult to deal with. At present, it is popular that the activated sludge is applied in wastewater to remove phenol. This method is effective to phenol, but ineffective to organic pollutants, in macromolecular polycyclic aromatic, and heterocyclic compounds and ammonia nitrogen. And many coking wastewater treatment companies are not stable. Sometimes most of the excrement is under standards which is polluted environment (Yu et.al, 2009). (Tamburini et.al, 2016) Some scholars successful use membrane bioreactor to degradation of phenol wastewater and optimization of A2/O and A/O technical system. On then other aspect, this method always blocked the membrane bioreactor, high cost, and it is ineffective to used in COD and ammonia nitrogen (Song and Zang, 2009) (Li et.al, 2002) (Yang et.al, 2006). All in all, compared with other treatment method, biochemical treatment is still the most economic and effective method. And the key point is that microbial populations, structure and performance. Recently, Aerobic granular sludge, with various population, high reactivity, rapid sedimentation speed, easy separation, plays a more important role, and it become more popular in the future (Wang et.al, 2009) (Zhong et.al, 2006) (Abdullah et.al, 2011) (Xiangjuan et.al, 2016) (Wang et.al, 2007) (Zhu et.al, 2006).Up to now, it is rare reported about the method treat wastewater which combined the aerobic granular sludge and membrane bioreactor.

Using the aerobic granular sludge in membrane bioreactor treats wastewater with phenol is researched. It is the advantages that various popularity and strong ability to resist impact load, thus this method has a function of about effective degradation when it treats wastewater. Furthermore, it is discusses the influence about different aerobic granular sludge mixed in sludge membrane bioreactor. And it also influences the degradation of phenol, COD and NH3-N. On the other aspect, it analyzes the revelation in 3D regression which enhance the foundation of the wastewater, containing phenol, treatment effect.

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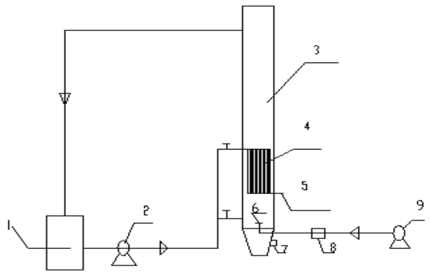
## 2. Experimental device and method

### 2.1 Experiment device

Figure 1 shows the submerged membrane bioreactor which is used in experiments, it is a cylindrical reactor, and it can contain 20L liquid. The unprocessed water flows from the bottom pipe entrance to membrane module which located in the center of the reactor. The membrane module is made of hollow fiber membrane, which material is polypropylene microfiltration membrane, and the aperture is 0.1 microns, membrane area is 0.2 $m^2$. The water flow outside water by Suction pump, at the bottom of the pipe is aeration, it can adjust the rate of air by the fluid.




1 - tank inlet 2 – tank inlet pump 3- membrane bioreactor membrane 4– membrane module 5- water outlet
6 - aerator joint 7 - mud hole 8- gas flow meter 9 - air pump

*Figure 1: Membrane bioreactor structure*

### 2.2 Experiment water

The water, simulated phenol with water, is used in experiment. Drugs and dosage quantity are shown in table 1.

*Table 1: Artificial simulation of coking wastewater*

| The main ingredient | Concentration (mg/L) | The main ingredient | Concentration (mg/L) |
|---|---|---|---|
| glucose | 2000 | $KH_2PO_4$ | 15 |
| Beef extract | 100 | $K_2HPO_4$ | 35 |
| peptone | 150 | $FeSO_4 \cdot 7H_2O$ | 20 |
| $MgSO_4 \cdot 7H_2O$ | 15 | $CaCl_2$ | 100 |
| phenols | 375 | $NH_4Cl$ | 200 |
| Trace elements | 1(mL/L) | | |

### 2.3 Experiment mud

Flocculent sludge produced by the Harbin Lilin Treatment Firm, the SVI is 121.29 ml/g, sedimentation velocity v is 12.3 m/h, Zeta potential is 20.265 mV.

Granular sludge also produced by the Harbin Lilin Treatment Firm, which grows in the container made in organic glass, its effective volume is 4.0 L, and conversion rate is 50%.

Aeration pump and gas is provided energy, gas flow meter control volume, and the temperature of external reactor vessel and intelligent instrument controlled electrode between 29-31$^{o}$C, velocity of surface air is 3.2 cm/s, air is $m^3$/h, pH between 7.5 and 8, the fill-in water time is 5 minutes, aeration is between 325 to 340 minutes, sediment is between 10 to 20 minutes, drainage is between 5 to10 minutes, the growing time is 30 days (Song and Liang, 2008), mature granular sludge SVI is 25.62 ml/g, sedimentation velocity *v* is 32.3 m/h, Zeta potential is 4.236 mV.

### 2.4 Experiment method

The oxygen - anaerobic - aerobic process operation is included in experimental conditions (Song and Zhang, 2009), the process of $A^2$/O is 4 hours, and the quantity of dissolved oxygen is between 0.2 to 0.5mg/L, anaerobic period is 3 hours, dissolved oxygen is lower than 0.2 mg/L, aerobic period of time is 16 hours, dissolved oxygen is more than 2 mg/L, running time 15 days.

Experimental temperature is usual room temperature, granular and flocculent sludge are produced by different proportion vaccination in the reactor, which proportion 0, 20%, 40%, 60%, 80%, 100% are used in experiment, and the initial sludge concentration is 4000 mg/L[3], no mud during the reaction. The water pH is between 6.5 and 7.5. Vacuum pump operates on intermission, which suction time is 10 min, and stop time is 5 min. After the end of each cycle, the membrane module should be removed and cleaned, and it soaks in 0.3% sodium hypochlorite cleaning which is helpful to recovery membrane flux.

### 2.5 Analyze project and test methods
Standard method is a common test method which is usually used in routine analysis project.

## 3. Different percentage of aerobic granule influences sludge properties

With the increase of proportion of aerobic granular in sludge, the number of granular sludge in reactor is gradually increased and the performance of sludge is changed on experiment.

### 3.1 Settling performance of sludge
We test different dosing ratio aerobic granular of sludge periodically and record SVI to research the settling performance of sludge, its change as shown in figure 2.
The figure 2 shows that sludge settling performance is poor when flocculent sludge in reactor, the running time is 15 days, the average SVI is 135.85 ml/g; and the amount of aerobic granular mixed in the sludge is 20％, the average SVI is 83.99 ml/g. Compared with the flocculent sludge, the sedimentation performance of the latter is better. The amount of aerobic granular sludge is 40%, 60% and 80%, the average SVI is 60.60 ml/g, 49.99 ml/g, 37.77 ml/g, Especially, the percentage is reach 100, high degree of graining, and the average SVI is 29.36 ml/g, sludge settling performance has improved significantly.

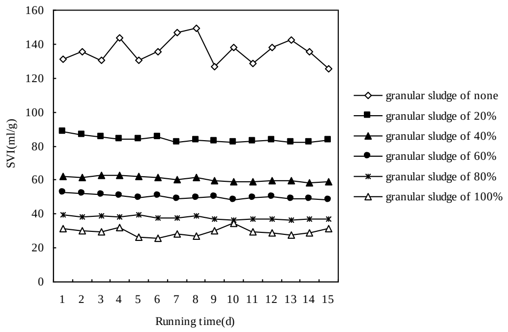



*Figure 2: Effect of aerobic granular sludge quantity on SVI*

With the increasing of dosing, the performance of aerobic granular sludge were improved obviously, the reason is the aerobic granular sludge sedimentation speed is fast. And when aerobic granular sludge additive, it carries the aerobic granular sludge, is increase gradually. It also accelerates the part of the flocculent sludge in the sink, thus the overall performance is improved.

### 3.2 Changing of sludge hydrophobic performance
The Zeta potential in the reactor can be investigated by Experiments. And different additive quantity of aerobic granular sludge has different Zeta potential, it shows in figure 3.
The figure 3 shows that full of flocculent sludge in the reactor, average of Zeta potential is 20.302 mV, the reactor sludge hydrophobic performance is poorer. When the additive amount of aerobic granular sludge was 20%, average of Zeta potential is 16.545 mV; and dosing quantity of aerobic granular sludge was 40%, 60% and 80%, the average of Zeta potential is 11.275 mV 9.260 mV, and 6.844 mV; and it up to 100%, that is full of the aerobic granular sludge reactor, the average of Zeta potential is 4.325 mV.

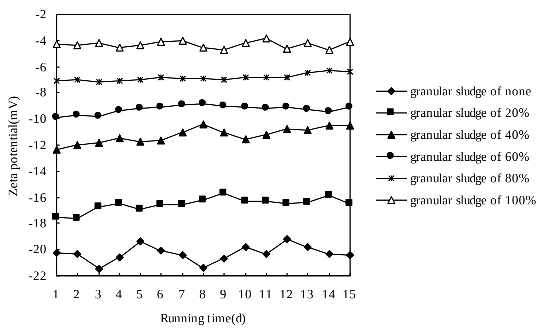



*Figure 3: Effect of aerobic granular sludge quantity on Zeta potential*

The composition of the sludge in the reactor is changed by different quantity of aerobic granular sludge in the membrane. The aerobic granular sludge is liable to hydrophobic which lead to Zeta potential is reduced in the reactor. According to the theory of surface hydrophobicity, with the increase amount of aerobic granular sludge, the reactor sludge hydrophobic is enhanced. It promotes the condensation of flocculent sludge, and the forms the granular sludge (Tamburini et al, 2016).

### 3.3 Changes of sludge degradation

Usually, we check the concentration of phenol, COD, $NH_3$-N and $NO_3$-N in the water, the changes show in figure 4.

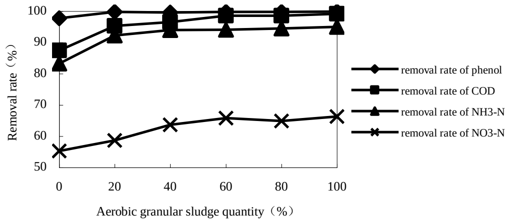



*Figure 4: Effect of aerobic granular sludge quantity on degradation ability*

Figure 4 shows different proportions of aerobic granular sludge have different removal rate of pollutants. And the removal rate will be increased with the increasing granular sludge. It will be stability when adding 60% of granular sludge.

If the reactor is full of the flocculent sludge, the average removal rate of phenol is 96.3%.The removal rate of phenol will be increased slightly with adding different ratio of aerobic granular sludge. Finally, it will be steady around 99.0%. As everybody knows, the phenol on the sludge may be poison which will influence the microbial growth. In opposite, the aerobic granular sludge is granular structure which has the ability of resistance to poison load.

After adding the granular sludge, COD removal rate increased from 87.3% to 99.2%, and the $NH_3$-N removal rate increased from 83.2% to 94.9%, $NO_3$-N removal rate increased from 55.3% to 66.3%, they are changed in a relatively large change range. It is close relative to the sludge concentration in reactor. There are multiple biomasses in the reactor. It is helpful to degradation in waste water which contains phenol; At the same time, the aerobic granular sludge is high density, and the diameter is also bigger. There is anoxic dissolved oxygen gradient in the transfer direction. It has functions of nitrification and de-nitrification, it is helpful to remove the $NH_3$-N and $NO_3$-N (Sun et.al, 2006).

## 4. Influence of membrane fouling

### 4.1 Change of membrane flux

In order to observe the influence of membrane granular sludge, which may be polluted the circumstance, we test the membrane flux in the reactor (Xing and Zhang, 2009). Finally, the membrane is cleaned at the end of the cycle, the membrane flux rises to 90%, and with the increment of recovery rate, which is the membrane flux rate, it is increased by the quantity of granular sludge dosing. According to the experiment, when the Granular sludge concentration is 100%, the membrane flux recovery rate can reach 94.1%.

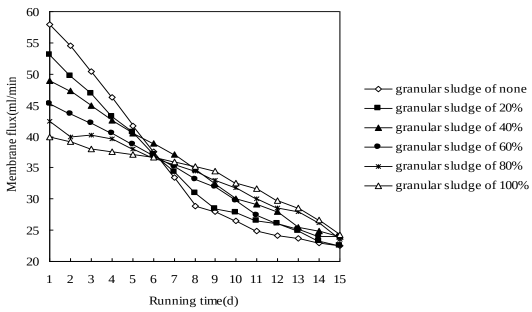
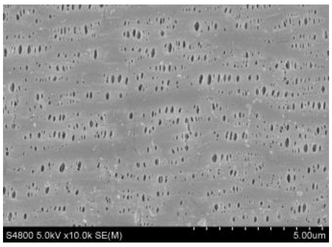



*Figure 5: Effect of granular sludge dosing quantity on membrane flux removal*

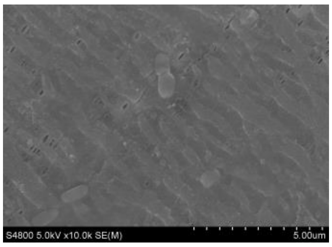
Figure 5 shows that if no granular sludge, the membrane flux may be decreased from 58mL/min to 21.3mL/min. At the beginning, gel layer is formed quickly, at the end of the reaction, the flux reduced rate is 63.3％.The flux reduced rate may be decreased after adding granular sludge. If it is full of granular sludge, it may decrease to 42.8%. At the beginning of the reaction, the space in the gel layer is large, which lead the transfer resistance is small, flux decreased slowly. Latter, there is the transfer press, it increases the gel layer density, and resists transfer thing, at the same time. The flux decline rate is increased and releases the membrane pollution.

**4.2 Analysis of membrane superficial**

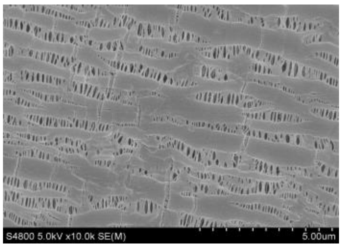
In order to observe the membrane pollution, we test it in three situations, which are new film on surface, no granular sludge, and adding granular sludge. At the end of the cycle, we also use scanning electron microscopy and observe the membrane, it shows on figure 6.




(a) The new Membrane inside surface




(b) Membrane inside surface after of processing waste water no granular sludge




(c) Membrane inside surface after of processing waste water 100% granular sludge

*Figure 6: The different stages of the membrane photos scanning electron microscope*

Figure 6 shows that “a” is the new film surface, and it can clearly see that the pore structure in the inner membrane. If no granular sludge in waste water, it only can observe few film holes. Inner surface has been covered with the microbial membrane, and formed the sludge layer. The flocculent sludge particle is small which will be blocked by the membrane channel or hole in the inner wall of the membrane. Without granular sludge, it may be decreased. We can observe the many holes by adding different quantity granular sludge. If the granular sludge is bigger than the membrane diameter, little granular sludge sit the surface of the membrane or block the hole. The surface of the membrane forms the layer which made of sludge. Compared the flocculent sludge, the granular sludge is bigger and ellipsoidal. The contacted surface becomes larger because of the different adding of granular sludge.

It is important that the granular sludge is bigger than the membrane diameter, it may block the membrane channel or sludge adsorption. In additional, if the space rate in granular sludge gel layer is higher than in flocculent sludge gel layer, the resistance may be small in transfer processing. The polluted sludge be reduced, the decline rate also be reduced. Thus, with the incensement of granular sludge, the membrane pollution will be decreased.

## 5. Conclusion

The physical and chemical properties of sludge in reactor can be changed by more aerobic granular sludge. With the increasing amount of aerobic granular sludge, the sludge’s SVI fell from 135.85 mL/g to 9.36 mL/g, Zeta potential increased from -20.302 mV to -4.325 mV hydrophobic performance is improved, and the sludge concentration increased significantly.

Membrane bioreactor additive can also improve the degrade performance of the sludge, and the effect on phenol removal is less relativity, it more relative to COD, $NH_3$-N, $NO_3$-N, COD removal rate increased from 87.3% to 87.3%, $NH_3$-N removal rate increased from 83.2% to 94.9%, $NO_3$-N increased from 55.3% to 66.3%.

After filling in granular sludge, the attenuation of membrane flux membrane bioreactor is reduced gradually, the rate of granular sludge concentration is 100%, the pass rate decreases from to 63.3% to 42.8%. With the increase of granular sludge, Outer protective layer of membrane density becomes stronger, which can reduce the jam rate and degree of the hole, and increases the membrane flux. Finally, the pollution of membrane is deduced.

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