IOP Conf. Series: Materials Science and Engineering **392** (2018) 042031 doi:10.1088/1757-899X/392/4/042031

A Review Of Hydrogen-Based Membrane Biofilm Reactor To Remove Oxidized Pollutants From Water

Yuhang Yuan[1,2,3], **Hua Lin**[1,2], **Zhiyi Lin**[1,2], **Yian Wang**[1,2]

[1] Guangxi Key Laboratory of Environmental Pollution Control Theory and Technology, Guilin University of Technology, Guilin, China

[2] Collaborative Innovation Center for Water Pollution Control and Water Safety in Karst Area, Guilin University of Technology

[3] Guilin, China, Email: 619869200@qq.com

Abstract: This paper introduces the mechanism of action for the Hydrogen-based membrane biofilm reactor and the current status at home and abroad. Hydrogen-based Membrane Biofilm Reactor can remove a variety of oxidizing contaminants from water bodies (such as inorganic anions: nitrates, sulfates, bromates, perchlorates, etc.; Chlorinated compounds: 2,4 Dichlorophenol, p-Chloronitro-benzene, Benzene, Trichloroethane, Trichloroethylene, Chloroform, etc.; heavy metal ions: dichromate, arsenate, selenite, etc.; antibiotics: chlortetracycline, tetracycline, etc.), and degrade them into low-toxic or non-toxic substances. Finally, the problems existing in the reactor are summarized and the prospects for future development are forecast.

1. Introduction:

In recent years, with the continuous development of human production and life, the problem of water pollution has become increasingly serious. At present, oxidizing pollutants in water are concerned because of their potential health risks. These contaminant include inorganic anions (nitrate, sulfate, bromate, perchlorate, etc.), halogenated organic compounds (2,4 dichlorophenol, p-chloronitrobenzene, trichloro-ethane, trichloroethylene, chloroform, etc.), Heavy metal ions (dichromate, arsenate, selenate, etc.) and antibiotics (chlortetracycline, tetracycline, etc.)[1-4]. These substances have high solubility and stability in the water environment. It is difficult for traditional biological treatment techniques to control their content below the standard limit [5]. Long-term exposure to this water environment will increase the risk of cancer and drug the resistance to the accumulation of antibiotic resistance genes in human cells.

Traditional sources of drinking water, especially groundwater sources, have low levels of organic matter and dissolved oxygen, which makes it difficult to remove the oxidizing contaminants in water by ordinary biological treatment methods. Hydrogen-based membrane biofilm reactor (MBfR) is a new type of water treatment technology. It uses hydrogen as an electron donor to remove oxidizing contaminants under low-carbon and low-oxygen conditions. It combines the microporous membrane aeration with the biofilm method. The microporous membrane serves as both a channel for transporting hydrogen and a carrier for the attachment of microorganisms. The product after reaction is trapped or released by the membrane. With the development of hydrogen production technology in recent years, the reduction in the cost of hydrogen production has provided broad prospects for the use of hydrogen-based biofilm reactors[6].

2. Hydrogen-Based Membrane Biofilm Reactor（MBfR）

2.1Reactor Introduction

The main body of MBfR is composed of a Plexiglas cylinder, a magnetic stirring device, inlet and outlet water, and air supply lines. The influent water is pumped from the bottom into the Plexiglas reactor by the peristaltic pump and discharged from the top of the reactor. The Plexiglass barrel contains two hollow fiber gas transfer membranes. The H_2 passes through the micro-holes in the hollow fiber transfer membrane to achieve bubble-free exposure. The way of gas is to provide electron donors for the reduction reaction of microorganisms from inside the membrane to outside the membrane. The hydrophobicity of the hollow fiber gas transfer membrane reduces the occurrence of membrane fouling, and at the same time, the smaller diameter of the membrane caused the larger the specific surface area. It can be used well as a carrier for microbial attachment. The magnetic stirring and stirring device is placed at the bottom of the reactor, and the water quality is uniformly mixed by magnetic stirring. The following (Fig Ⅰ) is a schematic diagram of the principle of a hydrogen-based biofilm reactor. [7]

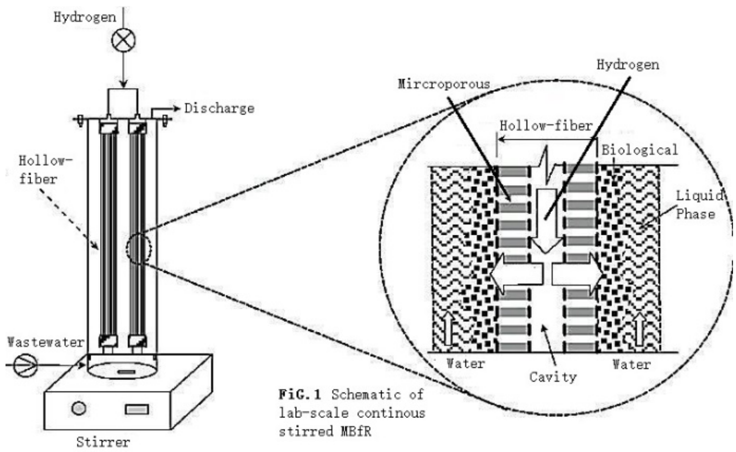

FIG.1 Schematic of lab-scale continous stirred MBfR

2.2 Mechanism of action

Taking nitrate as an example, nitrate-reducing bacteria in autotrophic reducing bacteria use nitrate nitrogen and nitrite nitrogen as electron acceptors for respiration. Hydrogen acts as an electron donor, then reducing nitric acid to nitrogen, and obtaining energy from it. As a result, It achieves the purpose of reducing TN in water.

Hydrogen autotrophic microbial reduction can proceed smoothly, relying on the following four conditions: 1. Contaminants are dissimilated electron acceptors that can provide energy for microbial growth; 2. Reduction reactions are usually endothermic (ΔGo<0) ; 3. The concentration of pollutants can ensure the continued growth of microorganisms; 4. Provide a carbon source for microbial assimilation[8-10].

MBfR has conducted more extensive research in the United States and Japan[11]. Nerenberg et al. [4]have performed Gibbs free energy measurements on oxidizing substances that can be reduced by hydrogen as an electron donor. Some results are shown in Table 1.

Table 1. Microbial Reduction of Oxidized Contaminants with Hydrogen as Electron Donor.

Substance	Reaction formula	ΔG°（KJ/e^-）
Bromate	$BrO_3^- + 3H_2 \rightarrow Br^- + 3H_2O$	-136
Perchlorate	$CIO_4^- + 4H_2 \rightarrow CI^- + 4H_2O$	-118
Nitrate	$NO_3^- + 2.5H_2 + 0.5H^+ \rightarrow 0.5N_2 + 3H_2O$	-112
Selenate	$BrO_3^- + 3H_2 \rightarrow Br^- + 3H_2O$	-71

Arsenate	$H_2AsO_4^- + H_2 + H^+ \rightarrow H_2S + HS^- + 8H_2O$	-45
Sulfate	$2SO_4^{2-} + 8H_2 + 3H^+ \rightarrow H_2S + HS^- + 8H_2O$	-19
Dichromate	$CrO_4^{2-} + 1.5H_2 + 2H^+ \rightarrow Cr(OH) + H_2O$	-9

As can be seen from the figure, the use of hydrogen as an electron donor to remove oxidizing contaminants can be carried out spontaneously.

3. Application of MBfR in water treatment

3.1 inorganic anions

In recent years, inorganic salt ions in water have received widespread attention because of their potential hazards. For example, BrO3, a by-product of disinfection caused by ozone disinfection, has a potential risk of carcinogenic and mutagenesis. Perchlorate is mainly derived from the pyrotechnic manufacturing industry. It can inhibit the absorption of iodine by the human thyroid gland, and affecting the thyroid's physiological function[12, 13].

Nerenberg et al[14] showed that there are dissimilated-reducing bacteria in the MBfR cultured with nitrate and bromate. It was used to reduce the bromate to bromide. When the influent concentration was 1500 μg/l, its content was reduced to 10 μg/l in 50 minutes. The study also showed that nitrate and nitrite partially inhibit the bromate reaction and nitrite inhibition is stronger. Up to 50 mg/l bromate had no inhibitory effect on denitrification. Nerenberg et al[4] used MBfR to remove perchlorate from groundwater. They found that when perchlorate and nitrate concentrations were 5.6 and 60 mg/L, the perchlorate concentration could be reduced to 4 μg/l or less, and the removal rate was close to 100%. Xia Siqing et al[15, 16] studied the influencing factors of the use of MBfR to remove nitrates from water. Increasing the H_2 pressure or reducing the nitrate load in short-term experiments favors the removal of nitrogen from nitrates; when the nitrate concentration is low, the degradation rate increases with the increase of concentration; when the nitrate concentration is less than 100 mg/L, the total nitrogen removal rate reaches 95% in 24 hours; when the nitrate concentration is greater than 120 mg/L, denitrification is inhibited and reduced efficiency.

3.2 Heavy metal ions

In recent years, heavy metal pollution incidents have occurred in an endless stream. Most pollution incidents are caused by illegal activities of enterprises. For example, Minamata disease caused by cadmium pollution in Japan, and pollution incidents of chromium residue in the end of 2009 in Hunan, China. Heavy metals are generally difficult to be used by the human body. A large number of heavy metals are enriched in the human body by the food chain. In the human body, it can have a strong interactions with proteins and enzymes in the human body to make them inactive,and it may also cause chronic poisoning due to the accumulation of certain organs in the human body. Most of the traditional water treatment technology use physical and chemical methods to remove contaminants by precipitation, but they are likely to cause secondary pollution. At present, the biological treatment method has a good development prospect in the treatment of heavy metal pollution.

Chung et al[17] and Pan[18]studied the removal of arsenate from water by MBfR. They found that 1. Nitrate reducing bacteria can reduce As(V) to As(III), As(III) can precipitate with sulfides. 2 .The increase of nitrate concentration also inhibit the reduction of As, while the change of influent As(V) concentration will have a greater impact on reactor reduction As(V) and SO_4^{2-}, when the concentration of As(V) in water changes from 0.25mg/l to 2 mg/l, the reduction rate decreased from 77.6% to 69.3%.At the same time, it also caused that the reduction rate of SO_4^{2-} was significantly reduced. The supply of S^{2-} was insufficient, and the system appeared As(III) Accumulation, thus affecting the total arsenic removal effect of the system. 3. When the partial pressure of hydrogen is lower than 0.06 MPa, increasing the partial pressure of hydrogen can increase the reduction flux of As(V). But above this value, there is no obvious promotion effect. Chung et al[17]. demonstrated that Cr(V) reduced to Cr(III) rapidly under normal MBfR denitrification conditions and environmental inoculum, and it was the best when PH value was close to 7. The research has also shown that increasing the hydrogen pressure can increase the rate and extent of Cr(V) reduction to Cr(III). The final Cr(III) can be precipitated by the small up-regulation of pH to form $Cr(OH)_3$ precipitates which are removed by filtration. Chung et al[9]. and Wang Chenhui et al[19]. investigated the use of MBfR to remove selenate from water. It was found that the partial pressure of hydrogen had a significant effect on the removal of selenate from water, and the reduction of nitrate concentration favored the reduction of selenium. At a concentration of $NO_3^- - N$ of about 10 mg/L and an inlet concentration of about 25 mg/L of SO_4^{2-}, the partial pressure of hydrogen is set to 0.04 MPa in the reactor and the inlet Se(VI) is In the range of 0.25 to 2 mg/L, the total Se removal rate can reach 80% or more. Zhou et al[20]. found that MBfR can reduce Pd(II) to Pd(0), which provides a theoretical basis for the recovery of this important catalyst in the future.

3.3 Chloroorganics

In recent years, the chlorine content in drinking water has increased significantly. For example, 2,4-dichlorophenol (DCP), p-chloronitrobenzene (p-CNB), trichloroethane (TCA), trichloromethane (CF), trichloroethylene (TCE), etc., and toxic substances N-Nitrosodimethylamine (NDMA). The reason is that most of the drinking water is disinfected with liquid chlorine. These "triple" substances pose a great threat to human health.

Xia et al[21]. used MBfR to remove 2-CP in water when the bioreactor was adjusted to a stable state, the removal rate of 2-CP could reach 99%, and the autotrophic bacteria in MBfR have a high removal efficiency of 2-CP. Li et al[7]. studied the influencing factors of degradation of p-CNB by MBfR and found that the optimal pH for the degradation of pollutants by hydrogen-based autotrophic microorganisms was 6.7 to 8.2, among which nitro reduction, reductive dechlorination, denitrification and sulfate reduction. The best PH is 7.7, 8.2, 7.2, 7.2 respectively. The optimal pH for p-CNB removal was 7.7-8.2. Chung et al[22]. studied the use of MBfR to remove NDMA and found that the H_2 partial pressure has a great influence on the removal of NDMA, and the removal rate can reach more than 96% under suitable conditions. Chung et al[23]. demonstrated that the TCE in water removed from MBfR is feasible. TCE-dechlorinated bacteria are present in the reactor and the enrichment of TCE-dechlorinating bacteria can be achieved by continuous influent water. Chung et al[24]studied the effect of hydrogen partial pressure and sulfate concentration on MBfR removal of TCE and CF in water. The results showed that MBfR dechlorination reaction was rapid and the removal rate gradually increased with time. Increasing the partial pressure of hydrogen can accelerate the dechlorination reaction rate, but sulfate can inhibit the dechlorination reaction.

3.4 Antibiotics Organics

At present, antibiotic pollution of water has become a global problem. For example, long-term drinking of water containing antibiotics can cause intestinal diseases, allergic reactions, and even affect the human immune system[25]. Antibiotics commonly found in water include tetracycline (TC) and chlortetracycline (CTC), and so on.

Taskan et al[26] successfully completed simultaneous denitrification and biodegradation of TC using MBfR. With the increase of hydrogen pressure, the removal rate of TC could reach more than 85%. By controlling nitrate and TC loads, H2 pressure ,HRT, TC and nitrate, MBfR can be efficiently degraded TC and nitrate in the reactor. Aydin et al[27]performed the simultaneous removal of chlortetracycline and nitrate in water using MBfR. Their research shown that the removal rates of chlortetracycline and nitrate are 96% and 99% at a hydrogen pressure of 2 psi and an HRT of 5 hours. . And they identified the dominant bacteria that degrade CTC.

4. Major problems

As a new type of water treatment technology, MBfR has some problems on the practical application:

(1) Reduction of hydrogen transfer efficiency due to bacterial growth on the outer surface of the hollow fiber membrane and some crystal particles trapped by the biofilm during treatment of water contaminants.

IOP Conf. Series: Materials Science and Engineering **392** (2018) 042031 doi:10.1088/1757-899X/392/4/042031

(2) The falling off of the biofilm will inevitably lead to an increase in total suspended solids in the effluent, and it is necessary to add a filtration device.

(3) The higher hardness in the actual water will cause calcification on the surface of the reactor and affect the operation of the reactor.

(4) Various ancillary facilities such as magnetic stirring devices during the experimental phase are still to be considered in practical applications.

(5) The choice of membrane plays a crucial role in the treatment effect. The characteristic of the biofilms and the efficiency of hydrogen transfer from the abovementioned various removal reactions are important factors for the removal of effective pollutants from the hydrogen-based MBfR.

5. Outlook

MBfR have the advantages of low cost, high processing efficiency, no secondary pollution, etc., which are in line with the future trend of environmental protection and safety of water treatment.

It also provides new ideas for the treatment of human beings drinking high-quality water in the future. In the future, research hotspots for hydrogen-based membrane reactors will focus on improving the hydrogen-conducting efficiency by changing the membrane materials ,the reactor structure and optimizing the structure. The purpose is to better adapt to various changes in the actual water treatment and lay the foundation for future practical applications.

Acknowledgements

Yuhang Yuan and Hua Lin contributed equally to this work, and Hua Lin is corresponding author (linhua5894@163.com). This work was supported by National Natural Science Foundation of China (No. 51408146), Guangxi Natural Science Foundation (No. 2016GXNSFBA380207 and No. 2016GXNSFAA380204).

References:

[1] Richardson, S D 2003 Disinfection by-products and other emerging contaminants in drinking water *European Journal of Cancer* **39**(18): 666-84.

[2] WenQi Peng and XiangWei Zhang 2005 *Quality and method of modern water environment* Chemical Industry Press.

[3] Tran N H, M Reinhard, and Gin K Y 2018 Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions-a review *Water Res*. **133**: 182-207.

[4] Rittmann B E and Nerenberg R 2004 Hydrogen-based, hollow-fiber membrane biofilm reactor for reduction of perchlorate and other oxidized contaminants *Water Science and Technology* **49**: 223-30.

[5] SiMin Sun and JangFeng Cheng 2005 Membrane bioreactor for drinking water treatment *GuiZhou Chemical industral* **30**: 22-25.

[6] Lin, C Y, Thi M N, Chen-Y Chu, Hoang-J Leu and Chyi-H Lay 2018 Fermentative biohydrogen production and its byproducts: A mini review of current technology developments *Renewable and Sustainable Energy Reviews* **82**: 4215-20.

[7] HaiXiang Li, Hua Lin, ShaoHong You, XiaoYin Xu and SiQing Xia 2015 Analysis of factors Affecting the removal of p-Chloronitrobenzene by hydrogen-based membrane biofilm reactor. *Research of Environmental Sciences* **28**: 304-09.

[8] XiaSheng Gu, HongYing Hu and XiangHua Wen 2006 *Microbiology in the Water Treatment[M] China Architecture.*

[9] Jinwook C and Nerenberg R 2006 Bioreduction of selenate using a hydrogen-based membrane biofilm reactor *Environmental science & technology* **5**(40).

[10] Rittmann B E and M P L *Environmental biotechnology: principles and applications[M]* 2012. Tata McGraw-Hill Education.

[11] ZhongDe Tang, XiaoYuan Yao and ShiFan Wei 2009 A review of Hydrogen-based Membrane

IOP Conf. Series: Materials Science and Engineering **392** (2018) 042031 doi:10.1088/1757-899X/392/4/042031

Biofilm Reactor to remove oxidized pollutants from drinking water *Industry Water* **40**: 05-10.
[12] Alain B,Claude C and Christophe R 2012 Risk assessment of chemicals in drinking water: Perchlorate and bromate *Environ Risque Sante* **11**: 316-21.
[13] Cao J S, Elliott D and Weixian Z 2005 Perchlorate Reduction by Nanoscale Iron Particles *Journal of Nanoparticle Research* **7**(4-5): 499-506.
[14] Downing L S and Nerenberg R. 2007 Kinetics of microbial bromate reduction in a hydrogen-oxidizing, denitrifying biofilm reactor *Biotechnol Bioeng* **98**(3): 543-50.
[15] SiQing Xia, FoHua Zhong and YanHao Zhang 2008 Study on the Influencing Factors of Removal of Nitrate in Water by Hydrogenotrophic Denitrification *China Water and Wastewater* **24**(21): 5-8.
[16] SiQing Xia, FoHua Zhong and YanHao. Zhang, H. Li, and X. Yang 2010 Bio-reduction of nitrate from groundwater using a hydrogen-based membrane biofilm reactor *Journal of Environmental Sciences* **22**(2): 257-62.
[17] Chung J, Li X and Rittmann B E 2006 Bio-reduction of arsenate using a hydrogen-based membrane biofilm reactor *Water Reserch* **40**(8): 1634-42.
[18] SiYu Pan，SiQing Xia，ChenHui Wang and Shuang Shen 2015 Bio-reduction of arsenate using a hydrogen-based membrane biofilm reactor *Acta Scientiae Circumstantiae* **35**(12): 3781-88.
[19] ChenHui Wang, XiaoYin Yu and SiqingXia 2014. Bio-reduction of selenate using a hydrogen-based membrane biofilm reactor *China Enviroment Science* **34**(6): 1442-1447.
[20] Zhou C, Ontiveros-Valencia A, Wang Z, Maldonado J, Zhao H P, Krajmalnik-Brown R and Rittmann B E 2016 Palladium Recovery in a H2-Based Membrane Biofilm Reactor: Formation of Pd(0) Nanoparticles through Enzymatic and Autocatalytic Reductions *Environ Sci Technol* **50**(5): 2546-55.
[21] S Xia, Z Zhang, F Zhong and J Zhang 2011 High efficiency removal of 2-chlorophenol from drinking water by a hydrogen-based polyvinyl chloride membrane biofilm reactor *Hazard Mater*, **186**(2-3): 1367-73.
[22] Chung, J, C-H Ahn, Z Chen and Rittmann B E 2008 Bio-reduction of N-nitrosodimethylamine (NDMA) using a hydrogen-based membrane biofilm reactor *Chemosphere* **70**(3): 516-520.
[23] Chung J, krajmalnik-Brown R and Rittmann B E. 2008 Bioreduction of Trichloroethene Using a Hydrogen-Based Membrane Biofilm Reactor *Enviromental Science& Technology* **42**(2): 477-483.
[24] Chung J and Rittmann B E 2007 Bio-reductive dechlorination of 1,1,1-trichloroethane and chloroform using a hydrogen-based membrane biofilm reactor *Biotechnol Bioeng* **97**(1): 52-60.
[25] Qiao M, Ying G G, Singer A C and Zhu Y G 2018 Review of antibiotic resistance in China and its environment *Environ Int* **110**: 160-172.
[26] Taskan B, Hanay O, Taskan E, Erdem M and Hasar H 2016 Hydrogen-based membrane biofilm reactor for tetracycline removal: biodegradation, transformation products, and microbial community. *Environ Sci Pollut Res Int* **23**(21): 21703-21711.
[27] Aydin E, Sahin M, Taskan E, Hasar H and Erdem M 2016 Chlortetracycline removal by using hydrogen based membrane biofilm reactor *Hazard Mater* **320**: 88-95.