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Performance of Combined Process of Air Flotation- Sedimentation- Biological Contact Oxidation - Membrane Biological Reactor Treating Heavy Oil Wastewater

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Abstract

A study of the treatment of heavy oil wastewater was carried out using the combined process of dissolved air flotation-sedimentation- biological contact oxidation - ultra-filtration membrane. When hydraulic retention times (HRT) was 18h, removal rates of COD, oil and suspended substance (SS) approached at 73~75%, 98%~99% and 100%, respectively. The diversity of bacterias was increased after air flotation, the betaproteobacteria dominated after enriched bacterias of BW-1, BW-2, BW-3, WSW-4, 1-2-1 and 3-2-1 were added to contact oxidation tank. The combined process provided a suitable process in dealing with the complex heavy oil wastewater.

Key words: Heavy oil wastewater;Air flotation; Biological contact oxidation; Membrane biological reactor

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INTRODUCTION

Heavy oil wastewater has the characteristics of high temperature, high COD consisted of different classes of organic compounds such as chlorophenols (Moussavi, et al, 2014), polycyclic aromatic hydrocarbons and crude oil hydrocarbons, high salt concentration, high silica concentration and serious emulsification of oil and water. When treated with membrane, pretreatment processes usually are needed to reduce pollution and burden of membrane in order to decrease cleaning frequency even irreversible damage.

The conventional physical and chemical processes can only remove oil slick and less organics (Thangaraj, et al, 2007), cannot remove dissolved oil and emulsified oil, leading to severe pollution to subsequent processes.

In this study, dissolved air flotation-sedimentation-contact oxidation -ultrafilition membrane process was applied to purify the actual heavy oil wastewater from Shengli oilfield in China. Experiments were conducted to: (1) test the different performance of the system on four HRTs (Aguilar, et al, 2013) in terms of pH, COD, oil, SS which reflected the statuses of influents and effluents in five reaction tanks;(2)analyze BOD_5, TOC, TN, TP, ions; (3) identify the bacterial community of the water in each tank. The performance and analysis of testing datas optimized the HRT to increase treatment capacity, confirmed the best process procedure, ascertained the bacteria community for raw water treatment.

1. MATERIALS AND METHODS

1.1 Experimental Set-Up

The experimental set-up was established in an united stations in Shengli oilfield located in Dongying city. The reactors were divided into five compartments. Raw water from 2000m^3 buffer tank flowed into dissolved air flotation tank, 1.2m^3, which was used to cool,remove oil and COD. Then sedimentation tank, 1.9m^3, owned the effect of asphaltene and SS settlement. The contact oxidation tank, 1m^3, could remove most COD, nearly all dissolve oil and emulsified oil. In the end, the ultrafiltration equipment, 0.5m^3, completely removes SS and bacterias. Roots blower provided continuous aeration to aeration discs at the bottom of the air flotation tank and biological contact oxidation tank. Air flow was controlled by gas meters to 1.8m^3/h in dissolved air flotation,0.62m^3/h in the contact oxidation tank to satisfy the DO of 2~3mg/L which influenced the rate of degradation of the organics (Wells, 2009). The membrane was polytetrafluoroethylene hollow fiber with pore size of 0.1μm. The pressure of the membrane was about 0.2~0.5MPa in operation. The membrane equipment run 10min to produce purify water following with 1min to backwash and aerate.

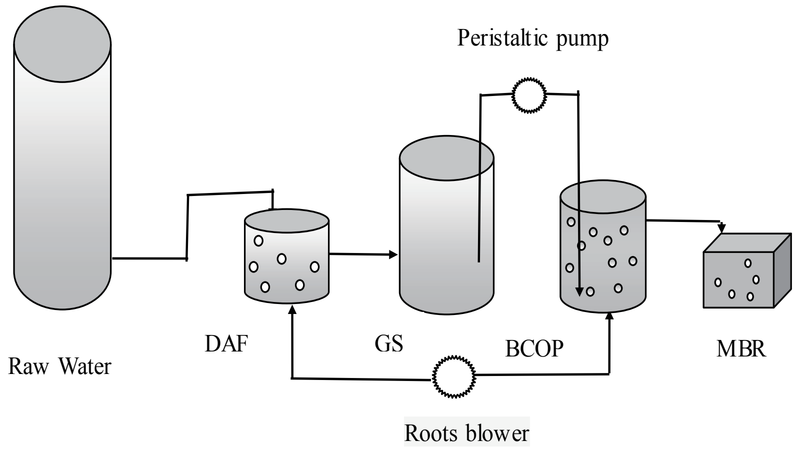


Figure 1
Schematic diagram of experimental set-up

1.2 Wastewater Characteristics

Table 1 presents the characteristics of wastewater. The COD of the raw water varied in the range from 258mg/L to 376mg/L; BOD was 125~175mg/L, then biodegradability（BOD/COD） of the wastewater was more than 0.3, indicating feasibility of biochemical treatment. So, the necessary pretreatment of most heavy oil wastewater with low biodegradability and high toxicity was not needed for this wastewater. Total nitrogen (TN) and total phosphorus (TP) concentration were 23mg/L and 1.7mg/L, meeting the needs of bacteria growth instead of adding extra nutrients.

Table 1
Characteristics of Heavy Oil Wastewater of the United Station

Parameter	Concentration	Parameter	Concentration
pH	6.72~6.92	Mg^{2+} (mg/L)	94~127
SS(mg/L)	50~96	Ca^{2+} (mg/L)	298~357
T(℃)	48~60	Sr^{2+} (mg/L)	55~68
Oil(mg/L)	24~58	Cl^- (mg/L)	8475~9022
COD(mg/L)	258~376	S^{2-} (mg/L)	7.8~12.9
BOD_5(mg/L)	125~175	SO_4^{2-} (mg/L)	66~92
TN(mg/L)	18~25	CO_3^{2-} (mg/L)	0
TP (mg/L)	0.9~2.2	HCO_3^- (mg/L)	525~614
Na^+ (mg/L)	5462~5587	TDS(mg/L)	14890~16223
K^+ (mg/L)	11~15		

1.3 Start-Up and Operation

The first stage, air flocation tank, sedimentation tank and biochemical tank were filled with raw water and then activated sludge derived from other heavy oil sewage treatment plant was added to biochemical tank. Bacterial community included four bacterial strains characterized by standard methods of bacterial identification from sewage:BW-1,BW-2 which belong to Bacillus cereus, BW-3, WSW-4 which were Bacillus stratosphericus. The other, from the strain library of Shengli oilfield, two efficient hydrocarbon degrading bacteriastrains:1-2-1 which was identified as Brevibacillus borstelensis and 3-2-1 which was tested as Brevibacillus were screened. The enriched bacterias were added into contact oxidation tank. After 48 hours' aeration, raw water was domesticated in continuous cultivation with 24h HRT.

The second stage, domestication had been completed, biofilm formation was observed after six days. After a period of stable operation, the residence time was reduced to 18h, 12h, 8h with continuous influx.

1.4 Sampling and Analytical Methods

Water samples taken from outlets of the reaction tanks were detected. Besides, sample point was located in biochemical tank from the outlet side position at 15cm where water quality was stable and representative. Raw water and membrane effluent were directly sampled. All samples were sealed in plastic bottles and timely determined to prevent water deterioration. Measurements of the particle size of samples should add nitrilotriacetic acid stabilizer to prevent particle size change.

The determinations of water samples-pH, T, COD, TSS, SS, total hardness, HCO_3^-, TN, TP followed a standard methodology. DO were measured by the kit for quick determination of dissolved oxygen. And pH was measured by a pHS-3C pH meter. TSS was detected with gravimetric method. The oil contents in five effluent were measured by carry 50 ultraviolet spectrophotometer. BOD was measured by ETT99724A type microcomputer BOD measuring instrument. UV-vis spectrophotometer (Unico4802 UV/VIS) was used to measure the concentration of NO_3-N at 220 nm in the standard methods. Biofilm,microbial species and morphology were observed by BX 50 Nicon microscope; Na^+, K^+, nitrite, nitrate, sulfate, Mg^{2+}, Ca^{2+}, Sr^{2+}, Cl^- used ICS900 ion chromatography of Thermo Fisher Scientific. Bacterias were determined by stepwise dilution method. Particle sizes were determined by Mastersizer3000 particle size analyzer. COD were measured by WMX type COD microwave digestion apparatus with 20min digestion time to the digestion liquid consisted of 5mL effluent,5mL potassium dichromate solution,5mL sulfuric acid-silver sulfate solution.

2. RESULTS AND DISCUSSION

2.1 COD Removal

COD and its removal efficiency of every HRT were shown in Fig.2. Dissolved gas flotation has been proved its effect on floating suspended solids,oil and grease(COD) (Wang, et al, 2010). Bacterias in sedimentation tank also have effect on removal of COD, but because of no aeration and poor stirring uniformity, the removal rate was low. After biochemical effects of contact oxidation tank, COD was further reduced. The COD removal efficiency decreased from 79.0% to 61.6%, as HRT shorten from 24H to 8H. Suitable HRT for continuous degration of solubilized organic matters was 12H to 8H.

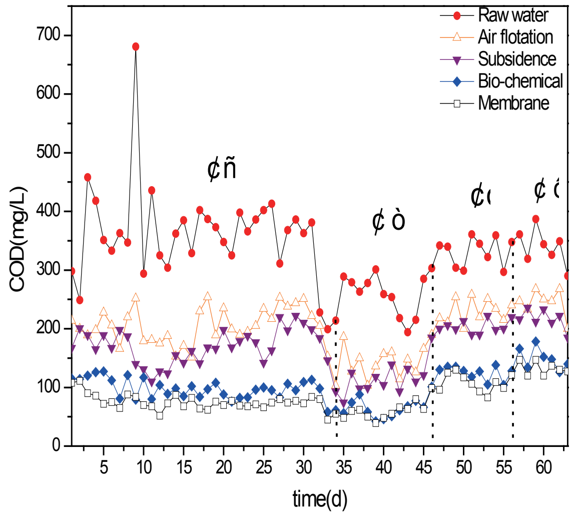


Figure 2
COD and its removal efficiency oat different residence time (Ⅰ:24h,Ⅱ:18h， Ⅲ:12h,Ⅳ:8h）

2.2 SS REMOVAL

Fig. 3 is the drift of suspended substances in every reaction tank. Air flotation,sedimentation can remove part of suspended solids. The bottom of the sedimentation tank was found a large number of inorganic substances. Biochemical system could adsorb a great deal of SS, reducing most of the rest of suspended substances. When the water flowed fast on 8h HRT, biofilm fallen off and the absorption ability subsided, leading to the SS increase. The SS were removed mainly by ultrafiltration, the effluent of system was below 1mg/L.

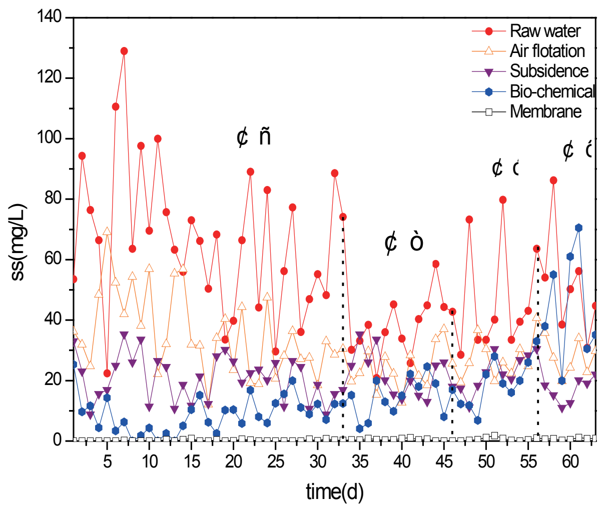


Figure 3
SS and its removal efficiency at different residence time (Ⅰ:24h,Ⅱ:18h， Ⅲ:12h,Ⅳ:8h）

2.3 Oil Removal

Fig.4.is the removal efficiency of oil effluents. Oil content incresaed as the HRT decreased in every tank. The reason for this phenomenon can be interpreted with the effect of aeration flotation which can remove most of the light oil and heavy oil. And lighter agglomerates formed by a large number of light oil and gas bubbles can be easily floated and skimmed from the top surface of DAF, and settlement tank can greatly reduce heavy oil because there was some heavy oil at the bottom. On the other hand, hydrocarbon degradation bacterias reduced dissolved oil and emulsified oil in water. The multi section treatment of oil was carried out by means of three stage process:air floatation,sedimentation and biochemical effect, reducing the pollution to membrane.

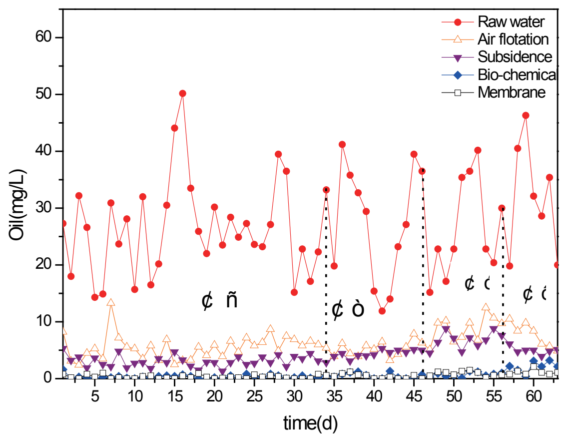


Figure 4
Oil and removal efficiency at different residence time (Ⅰ:24h,Ⅱ:18h，Ⅲ:12h,Ⅳ:8h）

2.4 Removal of BOD,TN, and TP

Bacterias played a key role in biochemical treatment of sewage. In this experiment, the temperature of raw water is 48-52℃, which belongs to high temperature for bacterias. When the temperature was decreased, degradation ability of bacterias for COD was enhanced. Contact oxidation tank was joined in enriched bacterias. Bacterias utilized BOD, nitrogen source and phosphorus source, resulting in changes of BOD,TN and TP, suggesting the degree and effect to sewage. Table 2 showed the treatment efficiency .The residence time had less influence on the removal rate of BOD. The effluent BOD was extremely low which can effectively prevent the growth of the subsequent SRB and inhibited pipes and equipment corrosion. As concerned as total organic carbon（TOC）which can be linked with COD, the romoval of TOC in DAF run up to 30.2%, then settling removal rate can be neglected, as well as the biochemical removal rate of TOC was 31.72%. Besides, the removal efficiency of membrane filtration can also be neglected. The removal of the total nitrogen was very low in the first three process for DAF and settlement effluents did not detect nitrate and nitrite. Nitrobacterias played the main role in contact oxidation tank when nitrogen was at an appropriate level (Rajagopal, 2013). TP was removed mostly by contact oxidation tank under the condition of aeration and microbial action.

Table 2
The Tendency of BOD,TN,TP in Five Tanks

Position	HRT(h)	Raw water	DAF	Sedimentation	Biochemical	Membrane
BOD/(mg/L)	18	75	45	40	14	4
BOD/(mg/L）	12	80	56	50	18	8
TOC/(mg/l)	18	133.7	93.36	93.78	64.03	61.07
TN/(mg/L)	18	27.76	27.95	27.29	24.05	22.42
TP/(mg/L)	18	0.54	0.34	0.36	0.25	0.01

2.5 Bacterial Communities

The DNA sample was received and the sequence of Paired-end by Illumina platform filters low-quality reads. The overlap relationship between reads splices these reads into Tags and 97% similarity under the clustering is used to classify species of OTU. All the samples received add up to 415121 Tags. The abundance of OTU was primarily explained by the species richness of the sample. The diversity of Alpha (Alpha diversity) was analysis of species diversity of single sample, including the observed species index,Chao index,ACE index, reflecting species richness of the sample community. And the Shannon index and Simpson index influenced by the species richness in a community sample and species evenness reflected species diversity.

Figure 5 detected the speices of bacterias in sedimentation tank,biochemical tank and membrane effluent at phylum level on 18 HRT. The microbial community structure was decided by the operation condition (Yadav, et al, 2014). The bacterias changed significantly after the contact oxidation. Proteobacterias, including many pathogenic bacteria, such as the types of

Escherichia coli, Salmonella, Vibrio, Helicobacter pylori and so on, occupy larger proportion in three kinds of water. Most of the bacterias were facultative or obligate anaerobic heterotrophic for the removal of COD. The relative abundance of proteobacteria which played an important role accounted more than 70%. Most bacterias were gram negative bacteria and camp facultative or obligate anaerobic heterotrophic life.

The sedimentation tank contained abundant bacterial species. It had been found that microaeration condition led to a more diverse bacterial community for treating brown water and food waste. In the sedimentation tank, alpha Proteobacteria dominated. Besides, it also contains a small amount of other proteobacterias. Clostridium in the sedimentation tank was anaerobic and microaerophilic and exists widely in the corrupt soil,human and animal intestinal. Not only thermotogae which occupies small percentage of bacterias adapted to different salt concentration and temperature but also could utilized carbohydrates. From the quantity and the level of phylum, the settlement tank included acidobacteria,actinobacteria, bacteroidetes, chloroflexi which had the ability to degrade macromolecular organics, proteobacteria, planctomycetes, OP11, OD1, nitrospirae, firmicutes ,SBR1093 which was the most dangerous bacteria to corrode the pipes and equipments, acidobacteria, verrucomicrobia, chlamydia, syntrophic bacteria, Chloroflexi, Firmicutes, acidobacteria, Chlamydia which is widespread in nature and infectious occupy a large proportion. Experiments showed that the firmicutes which screened out four enriched bacterias could produce extracellular enzymes such as cellulase, lipase and protease hydrolysis to utilize chemicals which were difficult to deal with. The Proteobacteria ang Firmicutes were the most abundant and effective bacterias in wastewater treatment. Further more, the Firmicutes could treat the deleterious and refractory wastewater. The representative species of chlorobi which contains cyanobacteria, volvox and the sulfide bacteria can restore the inorganic sulfur and electron donor as energy. The concentration of sulfuric acid transformed by 12.89mg/L sulfur ions in raw water in contact oxidation effluent was increasing to 62~65mg/L from 35mg/L by green sulfur bacteria after aeration in DAF tank. The actinobacteria which could degrade carbohydrates into monosaccharides, and furtherly fermente into lactic acid acetic acid, formic acid or pyruvic acid, bacteroidetes which can hydrolyze the protein into aminoacids and organic acid, or lipids into small molecule are the most abundant facultative bacterias in wastewater treatment. Planctomycetes which was important bacteria could use nitrite under hypoxia oxidation to transform ammonium ion (NH_4^+) to generate nitrogen to obtain energynitrite, achieving the removal of TN by mean of nitrification and denitrification.

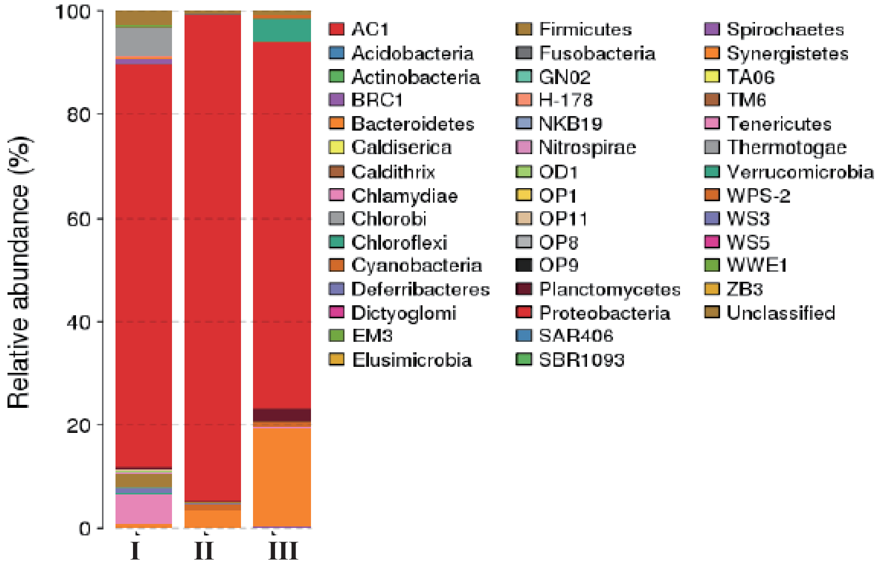
Contact oxidation tank was added enriched bacterias to promote the removal rate. The percentage of proteobacterias in contact oxidation tank was increased than sedimentation tank effluent. Under the condition of adding the same proportion of four bacterias, gammaproteobacteria became dominant bacteria. Alphaproteobacteria showed a lightly decrease, and betaproteobacterias got a small growth. Caldithrix, planctomycetes, firmicutes, acidobacteria, syntrophic bacterias decreased because of competitive disadvantage. In addition, actinobacteria, bacteroidetes, chloroflexi, GN02, Firmicutes, BRC1, OP11, OD1, verrucomicrobia, chlamydia, epsilonproteobacteria, thermotogae were completely lost the advantage for living environment of aeration. SBR1093 disappeared bacause this bacteria could only survive in the presence of low molecular oxygen. Due to the light and proper nutrition, Cyanophyta emerged until shading to the contact oxidation tank. The process efficiency was greatly increased, so that the core bacteria of contact oxidation was convinced as gamma bacteria, bearing the main function of COD degradation. Moreover, the brevibacillus and brevibacillus borstelensis of firmicutes beared the removal functiona of small amount of dissolved oil. HP(Bacillus cereus) and HT(Brevibacillus brevis) could degrate the saturated hydrocarbons with high carbon chain. It found the genera Pseudomonas, Flavobacterium, Comamonas, Cytophaga, Sphingomonas, Acidovorax and Bacillus form the community in actived sludge when the contaminants in influent were mainly composed of alkanes, aromatic and polycyclic ydrocar-bons..

The number of proteobacteria in membrane effluent decreased owing to low COD from contanct oxidtion tank. But facultative anaerobic Chloroflexi with the green pigment increased significantly, including bacteriochlorins as the reaction center and the antenna as molecular bacteriochlorins. Chloroflexi was suitable to grow with no shading treatment relatively low DO in membrane tank. Bacteroidetes, nitrospirae were emerged again, and Firmicutes also increased greatly that it also worked in the membrane tank. In terms of proteobacterias, alphaproteobacteria ratio increased slightly, betaproteobacteria and gammaproteobacteria decreased.The number of Flavobacterium also increased. Many other bacteria such as optitutae, phycisphaerae and verrucomicrobiae in the outlet breeded at the pipe.

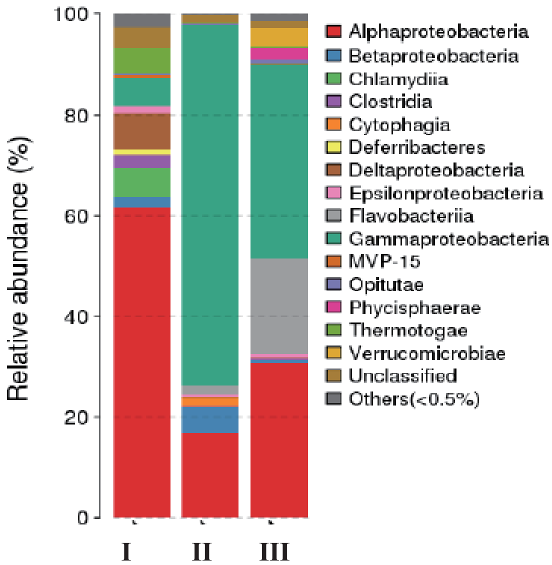
Based on the data, bacterial diversity of raw water increased greatly after aeration. Adding enriched bacteria to contact oxidation cut down the bacterial diversity but betaproteobacteria dominant in contact oxidation, bearing the main responsibility of the removal of COD, More importantly, hydrocarbon degradation bacteria-brevibacillus and brevibacillus borstelensis of firmicutes remove the dissolved oil and emulsified oil in wastewater. Biochemical effluent COD is low, so the numeber of proteobateria in membrane tank reduced. But hybrid bacteria breeds in the pipeline of membrane equipment.So the experiment can provide guidance for the proportion of Engineering bacteria.

Table 3
Characteristics of Community Diversity in Three Tanks

Sample	Tag	OTU	Chao	Ace	Shannon	Simpson
Sedimentation	117556	662	664.23529	668.87572	3.560449	0.099628
Contact oxidation	114784	387	425.95161	440.49204	1.866963	0.419044
Membrane	114540	439	480.60000	482.99804	3.527086	0.070342



(5-a)



(5-b)

Figure 5
Reative abundance of sedimentation,contact oxidation, membrane effluent at phylum and class level
(Ⅰ: effluent of sedimentation tank; Ⅱ:effluent of contact oxidation tank;Ⅲ:effluent of membrane)

CONCLUSIONS

DAF-sedimentation - contact oxidation - MBR process for heavy oil wastewater treatment achieved success. The results were presented as follows: removal rates of COD, oil and suspended substance (SS) approached at 73~75%, 98%~99% and 100% at HRT of 18h, respectively. The species of bacteria in sewage increased after aeration. Adding the enriched bacteria, beta Proteobacteria and bacillus become dominant in removal of COD and oil, respectively.

REFERENCES

Moussavi, G., Ghodrati, S., & Mohseni-Bandpei, A. (2014). The biodegradation and COD removal of 2-chlorophenol in a granular anoxic baffled reactor. *J. Biotechnol, 184*, 111–117.

Thangaraj, K., Kapley, A., & Purohit, H. J. (2007). Characterization of diverse Acinetobacter isolates for utilization of multiple aromatic compounds. *Bioresource Technology, 99*, 2488–2494.

Aguilar, M. A. R., Fdez-Güelfo, L. A., Alvarez-Gallego, C. J., & García, L. I. R. (2013). Effect of HRT on hydrogen production and organic matter solubilization in acidogenic anaerobic digestion of OFMSW. *Chem. Eng. J. 219*, 443-449.

Wells, G. F., Park, H. D., Yeung, C. H., Eggleston, B., Francis, C. A., & Criddle, C. S. (2009). Ammonia-oxidizing communities in a highly aerated full-scale activated sludge bioreactor: betaproteobacterial dynamics and low relative abundance of Crenarchaea. *Environ. Microbiol, 11*, 2310–2328.

Wang, L. K., Shammas, N. K., Selke, W. A., & Aulenbach, D. B. (2010). *Flotation technology*. Humana Press,c/oSpring erScience+BusinessMediahttp://dx.doi.org/10.1007/978-1-60327-133-2.

Rajagopal, R., Massé, D. I., & Singh, G. (2013). A critical review on inhibition of anaerobic digestion process by excess ammonia. *Bioresour. Technol, 143*, 632–641.

Yadav, T. C., Khardenavis, A. A., & Kapley, A. (2014). Shifts in microbial community in response to dissolved oxygen levels in activated sludge. *Bioresour. Technol, 165*, 257–264.

