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Treating Heavy Oil Wastewater for Beneficial Use by Integrated Technology of Bio-Oxidation and RO

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Abstract
Heavy oil exploitation wastewater is characterized by its high concentration of emulsified oil, high salinity, high temperature and complex chemical components. This paper discuss a successful pilot-scale demonstration application of a unique technology integrating heat exchanger, gas floatation, biological contact oxygen, filtration, ultra-filtration, reverse osmosis at Chenzhuang oilfield. The scale of the process was about 360 m^3/d, and the performance of the treatment process, the effectiveness of the technology for removal of oil and for controlling RO membranes fouling, and the economic effect are also discussed. Operation results show that the biological contact oxidation--ultra filtration process can reduce the oil contents to less than 0.5 mg/L and TDS to less than 3. The conductivity of RO effluent is below 456 μS·cm^{-1}, the treated water can meet the required standard for steam-injected boiler, and it can also be used to prepare polymer solution for viscosity keeping.

Key words: Heavy oil wastewater; Biological contact oxygen; RO; Steam boiler; Polymer solution

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INTRODUCTION
The 373 block of Chenzhuang oilfield is heavy oil reservoir of Guantao formation, which is exploited by method of steam stimulation. Large amount of unwanted oil wastewater is produced during oil extraction, which has to be discharged or ineffectively re-injected (Pak & Mohammadi, 2008; Ma *et al*., 2012). Furthermore, plenty of fresh water is used to feed steam boiler. It is imperative to find out proper wastewater treating and recycling methods to make sure the regular production of oilfield with the advantages of high economic profits and low environmental pollution (Kharaka *et al*., 1998).

Reverse osmosis technology has been successfully applied in the desalination of sea water, industrial wastewater reuse and other fields because of its advantages of technical, operational maturity, energy consumption, investment and other aspects (Xu & Drewes, 2006; Gulde, 2003; Wu *et al*., 2012). However, various contaminants, including oil and grease (hydrocarbons), other organics, salts, silt, heavy metals and other suspended solids in produced water, which damage membranes seriously, limits its application. So, a unique treatment technology is designed in this paper to convert heavy oil wastewater into boiler feed water. The operation results on sites demonstrate the pretreatment of the biological contact oxidation--ultra filtration process can effectively remove the emulsified oil, SS, bacteria and other pollutants in the wastewater and prevent RO membranes fouling. The quality of RO effluent meets the standard of steam-injected boiler in oil fields. The treated water can also be used as alternative for fresh water to prepare polymer solution, and the viscosity of the polymer solution prepared with the treated water is higher than those prepared with running water.

1. EXPERIMENTAL

1.1 Heavy Oil Wastewater Characteristics
Characteristics of the heavy oil wastewater of Chenzhuang oilfield are given in Table 1.

Table 1
Water Quality Analysis of the Heavy Oil Wastewater

Index	Concentration range	Index	Concentration range
Ca^{2+}, mg/L	162.5~165.8	F^-, mg/L	2.1~9.8
Mg^{2+}, mg/L	117.0~123.8	Cl^-, mg/L	5644.4~6453.5
K^+, mg/L	82.2~85.6	SO_4^{2-}, mg/L	40.7~65.3
Na^+, mg/L	3478.2~3625.6	Ba^{2+}, mg/L	2.93~7.21
HCO_3^-, mg/L	823.6~850.8	COD, mg/L	332.0~458.0
Temperature, ℃	55.0~65.0	Oil and grease, mg/L	8.1~67.0
Total hardness, mg/L	893.7~930.3	SS, mg/L	10.0~57.0
Total dissolved solid, mg/L	10454.0~11354.0	Total iron, mg/L	0.1~0.2
Total alkalinity, mg/L	1350.0~1395.0	pH	7.70~8.02

1.2 Treatment Challenges

Membranes have been widely used to treat wastewater, but its performance depends on a number of factors, including water quality, feed temperature, pretreatment process, and the presence of contaminants which can foul the membranes (Qiao *et al*., 2008; Dou *et al*., 2011). Table 1 shows that the heavy oil wastewater contains a number of contaminants, including emulsified oil, suspended solids, hardness, and other dissolved solids, which can foul or scale the RO membranes seriously during the operation (Ang *et al*., 2006). So, effective pretreatment must be used to remove harmful contaminants and suspended solids from the water that can damage the membrane to ensure the long-term stable operation.

1.3 Treatment Process

The pilot-scale project incorporating heat exchanger, gas floatation, biological contact oxygen, filtration, ultra-filtration, reverse osmosis (as shown in Figure 1). Heat exchanger can not only cool the high temperature heavy oil waste water ensuring the smoothly operation of the following units, but also increase the temperature of effluent of RO and save the fuel consumption of the boiler. Gas floatation is utilized to remove suspended oil droplets and suspended solids. Biological contact oxygen process use a bacteria community with capacity of heavy oil degradation to remove emulsified oil and other dissolved hydrocarbons. Ultra-filtration is used to remove small suspended solids and colloids, and decrease SDI. Then reverse osmosis desalination membranes are used for the removal of salts from the produced water.

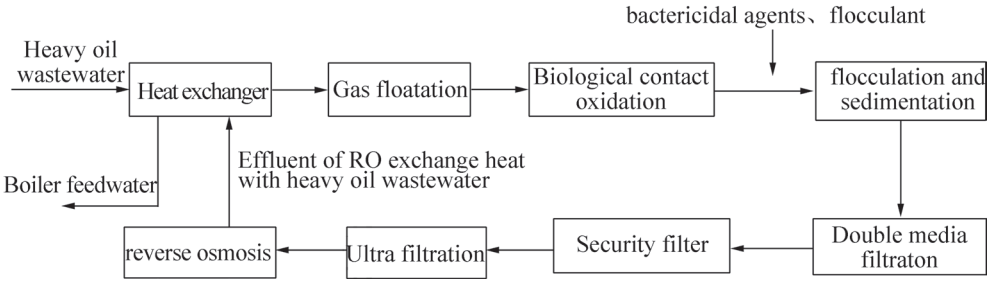

Figure 1
Process proposed for the treatment of the heavy oil wastewater

2. RESULTS AND DISCUSSION

2.1 Biological Contact Oxidation

Biological contact oxidation takes advantage of a bacteria community with capacity of heavy oil degradation, which was constructed by the techniques of limited cultivation, to remove oil in the produced water and degrade some of the organic contaminants. The bio-oxidation pond is a skid-mounted system consisting of 2 ponds installed in parallel, each sized 14.5m×2.4 m×3.1 m (in 4 stages). To allow for uniform water distribution and aeration, water distributors were installed at the bottom for each cell of the pond.

Data in Figures 2 and 3 show that the bio-contact oxidation can decrease the concentration of oil and COD to less than 1.5 mg/L and 120 mg/L respectively. This is due to the mechanism of aeration flotation, biological oxygen, interception and adsorption, food chain grade predator prey. Oil and other organic components are adsorbed to the bio-film surface, and then degraded by microbial oxidation. So, there is a concentration difference which allows the contaminants in wastewater be constantly adsorbed to the bio-film. Furthermore, the bacterial community structure is relatively stable after stable operation of the system. Protozoans swallow bacteria and bacteria use contaminants in wastewater as food for growth and reproduction. As a result, the oil and other organic contaminants that may cause membranes fouling are decreased gradually.

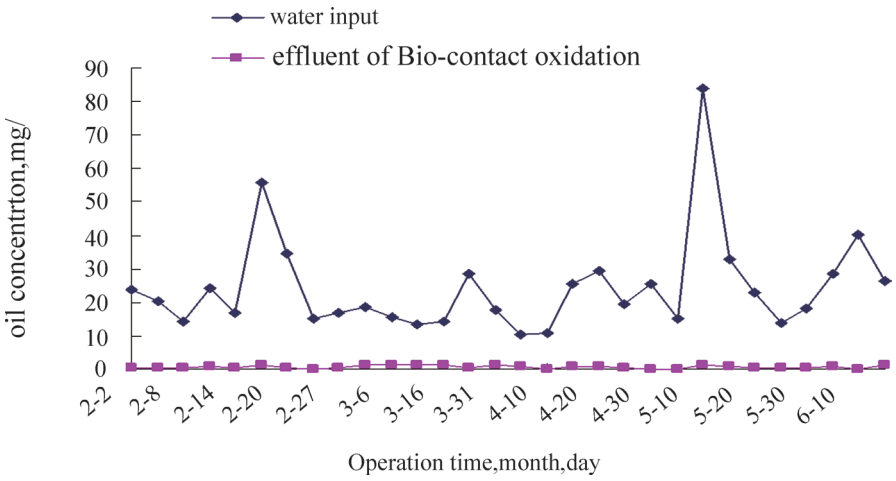

Figure 2
The Removal Effects of Oil by the Biological Contact Oxidation Process During Stable Operation

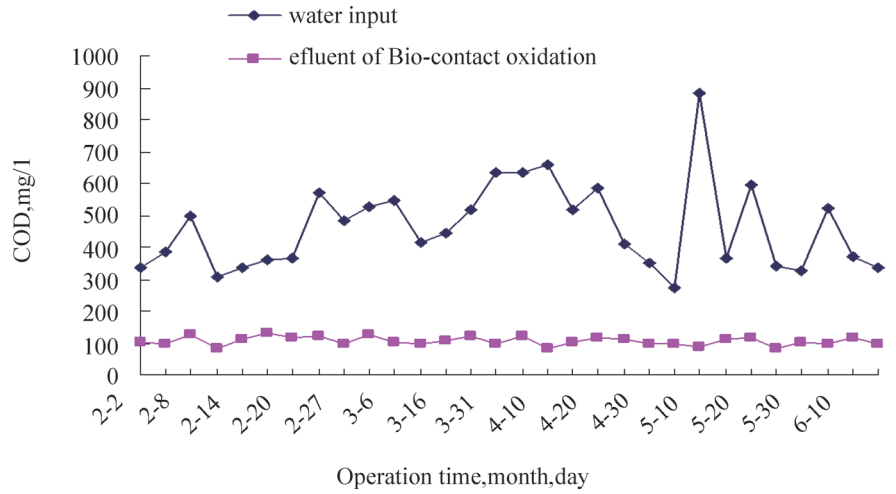

Figure 3
The Removal Effects of COD by the Biological Contact Oxidation Process During Stable Operation

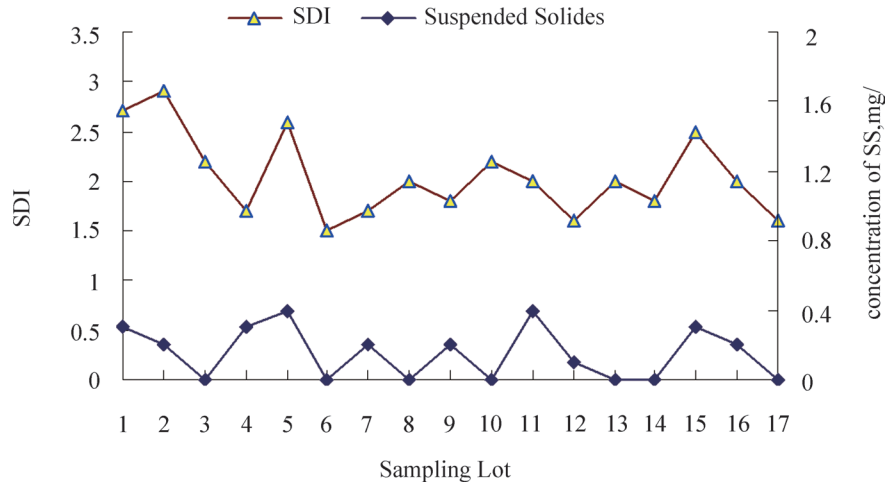

Figure 4
SDI and SS of Ultra Filtration Effluent

2.2 Ultra filtration

Ultra filtration is used as a ultimate pretreatment of reverse osmosis to remove bacteria, colloid, protein and other macromolecular materials. Inside and out hollow fiber ultra filtration modules are used with the molecular weight cut-off value of 100000 in the project.

The operation parameters are as follows: run by cross-flow filtration; equipped with automatic backwashing system and chemical cleaning system; the maximum inlet pressure 0.5 MPa; backwashing pressure ≤ 0.20 MPa; backwash flow 220-300 L·h; backwashing frequency 20-60 min.

Sludge density index (SDI) and concentration of suspended solids of ultra filtration effluent are shown in Figure 4. The SDI and SS are below 3.0 and 0.3 mg/L respectively, and it would meet the quality requirement of the influent of following reverse osmosis unit.

2.3 Reverse Osmosis

16 reverse osmosis membrane elements (BW30-365) of American DOW are selected and arranged in two-segment. Conductivity of influent and effluent were 17500~19840 μS·cm^{-1} and 362~456 μS·cm^{-1}, respectively. The detailed result of water quality analysis of influent and effluent was showed in Table 2. The water quality meets the standard of steam-injected boiler in oil fields.

The treated water can also be used as alternative for fresh water to prepare polymer mother liquor. The viscosity of the polymer mother liquor prepared with the treated heavy oil waste water remained at 3000~3350 mPa·s, which is higher than that prepared with the running water of 2400~2500mPa·s. Dilute the polymer mother liquor to the concentration of 1500 mg/L with wastewater and examine the long-term stability of polymer solutions under 70 ℃. Results (Figure 5) show that the viscosity of polymer solution prepared with the treated heavy oil waste water can keep stable for a long time, which is beneficial to enhance oil recovery.

Table 2
Water Quality Analysis

Parameter	Influent mg/L	Effluent mg/L
Sodium	3454.5	101.2
Potassium	78.3	12.4
Calcium	155.3	8.9
Magnesium	105.6	0
Fluorin	5.9	0
Chlorine	5458.7	107.3
Sulfate	80.2	14.5
Bicarbonate	8.35.8	76.2
Total hardness	260.9	8.9
Oil content	12.6	0.2
Mineralized degree	10168.4	320.5
Total iron	0.5	0
Suspended solid	26.3	0.1

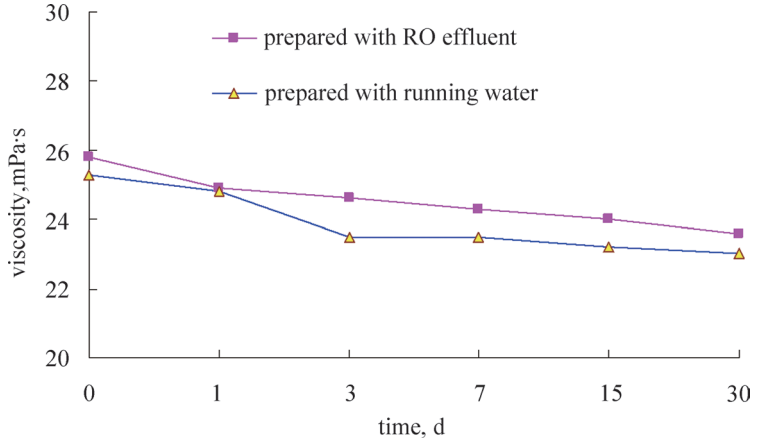

Figure 5
Long-Term Stability of the Polymer Solution

2.4 Economic Effect Analysis

The operating costs of the process is 4.255 yuan/m^3 including energy cost 2.805 yuan/m^3 and chemical agents 1.45 yuan/m^3. The total operation cost is 9.60 yuan/m^3 taking the depreciation, labor and maintenance costs into account. However, reuse of 1t waste water can save 17.3 yuan, including freshwater cost 4.8 yuan/m^3, invalid reject cost 8yuan/m^3 and boiler fuel costs 4.5 yuan/m^3. So, this technique, which can not only save fresh water resources, but also prevent the discharge of wastewater, has many environmental benefits and social benefits.

CONCLUSION

The hybrid biological contact oxidation-ultra filtration-reverse osmosis system is robust in treating heavy oil waste water. Biological technology with special advantages in removing dissolved oil, emulsified oil and other organic pollutants can controls RO fouling. The quality of RO effluent meets the standards of steam-injected boiler in oil fields. The treated water can also be used to prepare polymer solution. The technology has remarkable economic and social benefits, and contributes largely to the sustainable development of Oilfield.

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