Estimation of Pore Size Distribution of Amorphous Silica-Based Membrane by the Activation Energies of Gas Permeation
Full-Scale Processing by Anaerobic Baffle Reactor, Sequencing Batch Reactor, and Sand Filter for Treating High-Salinity Wastewater from Offshore Oil Rigs

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Abstract: High-salinity wastewater discharged from offshore oil rigs (WORS) is harmful to marine environments. Therefore, WORS should be properly treated before discharge. In this study, a full-scale anaerobic baffle reactor (ABR) + sequencing batch reactor (SBR) + sand filter (SF) process was used for the first time to treat WORS at an inshore treatment terminal. After seeding with residual sludge from a municipal wastewater treatment facility, the start-up of the ABR and SBR was accomplished in one month. During a steady running period, the ABR + SBR process showed stable performance in treating WORS. The results of microbial diversity indicated that Rhizobiales, Thermotogales, and Actinomycetales were the most abundant genera in the ABR sample, while Acidobacteria DRC31, Lactobacillales, and Bacillales prevailed in the SBR sample. The results showed that ABR + SBR is a reliable process for WORS treatment, with the treated WORS meeting the National Sewage Comprehensive Emission Standards (GB8978-1996).

Keywords: aerobic treatment; anaerobic treatment; offshore oil rigs; oil wastewater; walnut shell

1. Introduction

Potential oil and gas resources exist in the South China Sea [1]. Considering the economic benefits, numerous offshore oil rigs for drilling oil and gas are presently in operation. Offshore oil rigs are efficient structures supporting offshore drilling, which is an important means of partly satisfying the increasing oil consumption in China. However, exploration and production generates considerable high-salinity wastewater discharged from offshore oil rigs (WORS) [2,3]. The South China Sea is an environmentally sensitive area, and the preservation of the ecosystem is necessary for the marine environment. In addition, thousands of people live in this area. Therefore, environmental protection is extremely important, and the appropriate treatment of WORS must be adopted in these oil rigs. In China, the legally qualified companies conducting offshore oil exploration and production are national oil corporations, among which the China National Offshore Oil Corporation (CNOOC) is one of the biggest. In order to protect the environment, the CNOOC constructed an inshore treatment terminal for oil and wastewater treatment. As a first step, physical treatment methods including electrolysis are applied. Among them, ultrafiltration (UF) was suggested as a treatment to remove
oil from WORS [4]. Although physical treatment methods provide good removal rates, high running costs and complicated operation hamper sustainable development, especially during periods of low oil prices. Therefore, environmentally friendly methods including biological methods that can treat wastewater at low cost are under consideration. However, biological treatment methods are limited by high salinity, biohazards, and oil. Biological processes have been successfully used to treat oil-containing wastewater [5,6]. Zhao et al. (2006) [7] investigated the use of B350M-group microorganisms to pre-treat oilfield wastewater and achieved the mean degradation efficiencies of 78% for the total organic carbon (TOC) and 94% for oil. Fakhru’l-Razi et al. (2009) [8] suggested that the biological pretreatment of oily wastewater could be both cost-effective and environmentally friendly. With biofiltration alone, the TOC, chemical oxygen demand (COD), Ultraviolet (UV) absorbance at 254 nm (UV254), ammonium, and turbidity removal rates can reach 46%, 46%, 23%, 50%, and 61%, respectively [5]. Pérez et al. (2016) [6] also achieved a COD removal rate exceeding 95% with an electrocoagulation (EC)-aerobic biofilter treatment of oil refinery wastewater. It is assumed that normal microorganisms in biological treatment plants cannot tolerate high-salinity conditions [9]. Therefore, salt marsh sediments or cultured strains are typically considered for the treatment of high-salinity wastewater [10]. However, they are not recommended for full-scale treatment plants because of their low operability and long start-up periods. Instead, sludge from municipal treatment plants is adopted as the seed sludge for full-scale biological treatments. However, such treatments have rarely been reported for WORS. To the best of our knowledge, this is the first report on full-scale biological treatment of WORS.

In this study, a full-scale biological treatment process including an anaerobic baffle reactor (ABR), sequencing batch reactor (SBR), and sand filter (SF) was evaluated in treating WORS. The start-up and running operations were studied. An economic analysis of the running cost was conducted, and microbial diversity analysis was performed to characterize the microbial population shift after ABR and SBR treatment.

2. Materials and Methods

2.1. WORS

The composition of WORS including physico-chemical parameters is shown in Table 1. WORS is pretreated by natural settlement, coagulation, and walnut-shell filtration for oil separation. The pretreated WORS is grayish brown in color with an unpleasant smell attributed to dissolved sulfides (Table 1). Because of the changing production conditions of offshore oil rigs, the compositions of WORS show large fluctuations. The concentrations of salt and Cl\(^-\) are similar to those of sea water. Regarding the biochemical oxygen demand over a five-day test (BOD\(_5\)) concentration, it is possible to treat WORS using biological methods. However, anaerobic treatment is suggested to enhance the biodegradability of WORS.

Table 1. Composition of high-salinity wastewater discharged from offshore oil rigs (WORS) (including physico-chemical parameters).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>38–50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>'C</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>7.1–8.2</td>
</tr>
<tr>
<td>Salinity</td>
<td>g/L</td>
<td>27.4–31.8</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD)</td>
<td>mg/L</td>
<td>100–1479</td>
</tr>
<tr>
<td>Biochemical oxygen demand over a five-day (BOD(_5))</td>
<td>mg/L</td>
<td>36.1–650</td>
</tr>
<tr>
<td>Suspended solids (SS)</td>
<td>mg/L</td>
<td>140–610</td>
</tr>
<tr>
<td>Total nitrogen (TN)</td>
<td>mg/L</td>
<td>9–13</td>
</tr>
<tr>
<td>Total phosphorus (TP)</td>
<td>mg/L</td>
<td>7–12</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>mg/L</td>
<td>14,000–15,000</td>
</tr>
<tr>
<td>S(^2)-</td>
<td>mg/L</td>
<td>11.8–20.1</td>
</tr>
<tr>
<td>Oil</td>
<td>mg/L</td>
<td>11.5–15</td>
</tr>
</tbody>
</table>
2.2. Location and Treatment Process

The full-scale treatment plant is located at the CNOOC terminal in Weizhou Island, Beihai, China (Figure 1). Weizhou Island is almost round in shape with an east–west width of 6 km and a north–south length of approximately 6.5 km. The annual average temperature is 23 °C, and the average annual rainfall is 1297 mm with dry and wet seasons.

Figure 1. Location of high-salinity wastewater discharged from offshore oil rigs (WORS) treatment plant in China National Offshore Oil Corporation (CNOOC) terminal.

The full-scale treatment process was determined based on lab-scale and pilot-scale pre-experiments. ABR, SBR, and SF were adopted as the main units. The ABR unit comprises two tanks with the effective volume of 1500 m$^3$ and hydraulic retention time (HRT) of 36 h. The SBR unit comprises three tanks with an effective volume of 360 m$^3$. The operation cycle is set to 12 h, including 1 h filling, 8 h aeration, 2 h sinking, and 1 h discharge. During one operation cycle, 160 m$^3$ of ABR effluent can be treated by the SBR. In total, 3000 kg of digested sludge with a moisture content of 97% was collected from a municipal wastewater treatment plant. As shown in Figure 2, oil is first removed from WORS in an oil separation tank, and subsequently absorbed by a walnut-shell filter in a fixed-bed reactor. At first, the ABR is fully filled with freshwater. Then, WORS with a low oil concentration is gradually pumped into the ABR tanks, where anoxic or anaerobic environments are provided for organic degradation. The ABR effluent is then collected by a regulating tank, which provides the SBR influent. In the SBR tanks, the aerobic environment is controlled for further organic degradation and nutrient removal. Subsequently, the SBR effluent is filtered through the SF for further removal of suspended solids. Finally, the treated WORS meeting national standards is discharged into the deep sea.
Figure 2. WORS treatment processing flow chart (ABR: anaerobic baffle reactor; SBR: sequencing batch reactor; SF: sand filter).

The backwash wastewater from SF, supernatant of sludge thickening, and wastewater generated from the sludge dewatering equipment are returned to the ABR tank for further treatment. Residual sludge is collected and treated in the sludge thickening tank. The concentrated residual sludge is further dewatered using a plate and frame filter press, forming a residual sludge pie, which is shipped for landfilling.

\[ \text{COD}_{Cr}, \text{SV30}, \text{suspended solids (SS)}, \text{BOD}_{5}, \text{oil}: \] Filtered \( \text{COD}_{Cr} \) (1 \( \mu \)m) was measured by the closed reflux colorimetric method [11]. SS and volatile suspended solids (VSS) in effluent and sludge samples were measured in accordance with Standard Methods [12]. Oil was measured by infrared spectrophotometry (ET1200, EURO-TECH, Croydon, UK). Total nitrogen (TN) was determined by the persulfate method [13] using the UV spectrophotometric screening method for quantification of TN as \( \text{NO}_3^- - \text{N} \) (the oxidization product of the persulfate digestion). The pH was measured by using a pH meter (9010, Jenco, San Diego, CA, USA), and dissolved oxygen (DO) was measured by using a DO meter (6010, Jenco, San Diego, CA, USA).

2.3. DNA Extraction and 454 High-Throughput Sequencing

Samples were collected during the start-up and steady running period. DNA was extracted using the E.Z.N.A. Soil DNA Kit (OMEGA Biotec. D5625-01, Norcross, GA, USA) according to the manufacturer’s instructions. Partial 16S rRNA gene amplicons were generated using TransGen AP221-02 (TransStart Fastpfu DNA Polymerase) and ABI GeneAmp® 9700. Duplicate polymerase chain reaction (PCR) products were pooled and purified using the AXYGEN gel extraction kit (Axygen, New York, NY, USA). Sequencing was performed using the 454 GS FLX+ instrument (Roche, Branford, FL, USA), and sequencing method manual XLR70 kit.

Raw 454-pyrosequencing data were analyzed using Mothur v.1.40.0 (https://www.mothur.org/wiki/Main_Page). Operational Taxonomic Units (OTU) with 97% confidence was used for the construction of OUT Rank-Abundance curve. Heatmaps were constructed to reflect the relative abundance of phylotypes at different taxonomical levels as described by [14].
3. Results and Discussion

3.1. Start-Up Period

3.1.1. ABR

The ABR effluent was recycled to the inlet port to dilute the high-salinity WORS. The ABR treatment performance during the start-up period is shown in Figure 3. On days 6–9, no samples were collected due to the effect of typhon. Therefore, there is a gap between days 6–9. Due to the diluting effect of the filled freshwater, during the first 5 days, removal rates approaching 65% are achieved in the ABR. Subsequently, the removal rates decrease to below 10%. An average removal rate of 15% is achieved during the start-up period, after which a removal rate of 40% is achieved. Usually, 3 months are required for anaerobic sludge cultivation. In this case, the cultivation period was only 30 days; presumably, the performance can be improved by providing more time. An average removal rate of 30% can be achieved by ABR after 3 months of cultivation. During the start-up period, the ABR influent is 120–370 mg/L, which is lower than the designed influent concentration (Table 1). As the concentration of the ABR effluent is lower than the designed concentration of the SBR influent, the ABR effluent is directly discharged into the SBR tanks without further treatment.

![Figure 3. ABR treatment performance during start-up period.](image)

3.1.2. SBR

The start-up of SBR was accomplished in 30 days because of the lack of experience in the full-scale treatment of WORS (Figure 4). Similar to Figure 3, there is also a gap between days 6–9. SBR tanks No. 1 and 3 were filled with 10,000 kg of seed sludge and 80 m$^3$ of freshwater. Subsequently, air was introduced for 24 h without any feed. As the seed sludge was used for treating low salinity municipal wastewater, the salinity was gradually increased for sludge cultivation. On days 0–6, WORS with a dilution of 1:4 with freshwater and a volume of 16 m$^3$ was fed into No. 1 and No. 3. On days 7–14, the dilution rate and treating capacity were changed to 1:2 and 40 m$^3$/day, respectively. On days 15–22, the dilution rate and treating capacity were further changed to 1:1 and 80 m$^3$/day, respectively. On days 23–29, WORS without dilution was treated with a designed treating capacity of 160 m$^3$/day. On days 1–10, no effluent was discharged from No. 1 and No. 3. From day 11 onward, effluent was discharged according to the influent volume. To balance the organic carbon and nutrients, urine and KH$_2$PO$_4$ were added into the influent.
As shown in Figure 4, the average effluent COD concentration from the three SBR tanks was 67.6 mg/L with COD removal rates of 65%. The SBR effluent could meet the discharge standards. During the start-up period, yellow-black sludge foam reaching 10 cm in thickness was found. Numerous filamentous bacteria were observed by microscopy and attributed to the low sludge loading rate. Therefore, excess sludge was discharged in order to maintain low mixed liquid–solid sludge, and nutrients such as urine and phosphate fertilizers were added to balance the substrate ratio. Through this process, sludge expansion could be eliminated. During the first few days, the SBR effluent contained significant SS, and the effluent was passed through the SF to remove the SS. Backwash was frequently applied to prevent SF blockage. When cultivation in SBR was accomplished, small amounts of SS remained in the SBR effluent. Therefore, subsequent application of SF was not employed.

3.2. Steady Running Period

After the start-up period, the full-scale ABR–SBR system was operated for a steady running period. During this period, the daily treatment capacity was 500–1250 m³, the water temperature was 38–50 °C, the influent pH was 7.1–8.2, and the influent COD was 100–1479 mg/L (Table 1). The ABR effluent was monitored daily for one year, and an average COD removal rate of 35% was achieved from day 60 onward. The start-up period of ABR was accomplished in the first 2 months. BOD₅ was used to evaluate the effect of ABR pretreatment (Figure 5). As shown in Figure 5, the BOD₅ ratio is increased from 40% to 80% on average by ABR pretreatment, which helps SBR to further decrease the ABR effluent COD. Therefore, ABR pretreatment is very important in this process. The composition of the effluent from the ABR–SBR treatment is shown in Table 2. The effluent COD concentration is 30–60 mg/L with an average COD removal rate exceeding 80%. The effluent NH₄⁺–N concentration, oil concentration, and SS are below 5 mg/L, 1 mg/L, and 30 mg/L, respectively. During the steady running period, the ABR–SBR system showed stable removal rates of COD, oil, SS, and NH₄⁺–N, and the effluent quality met the National Sewage Comprehensive Emission Standards (GB8978-1996). As the SS in the effluent of the ABR–SBR system met the standards, subsequent SF was not applied. A short-cut pipe was used for discharging the SBR effluent directly into a clarified tank, where the treated water quality could be monitored before drainage.
Figure 5. Biochemical oxygen demand over a five-day test (BOD\textsubscript{5}) change during ABR pretreatment.

Table 2. Composition of treated WORS by ABR–SBR.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Effluent</th>
<th>Average Removal Rate</th>
<th>Standards \textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>30–35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>7.5–8.5</td>
<td>-</td>
<td>6–9</td>
</tr>
<tr>
<td>Salinity</td>
<td>g/L</td>
<td>27.4–31.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>COD</td>
<td>mg/L</td>
<td>&lt;60</td>
<td>80%</td>
<td>100</td>
</tr>
<tr>
<td>SS</td>
<td>mg/L</td>
<td>&lt;30</td>
<td>85%</td>
<td>70</td>
</tr>
<tr>
<td>NH\textsubscript{4}+–N</td>
<td>mg/L</td>
<td>&lt;5</td>
<td>55%</td>
<td>15</td>
</tr>
<tr>
<td>Cl\textsuperscript{-}</td>
<td>mg/L</td>
<td>14,000–15,000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S\textsuperscript{2}−</td>
<td>mg/L</td>
<td>&lt;1</td>
<td>93%</td>
<td>1</td>
</tr>
<tr>
<td>Oil</td>
<td>mg/L</td>
<td>&lt;1</td>
<td>92%</td>
<td>10</td>
</tr>
</tbody>
</table>

\textsuperscript{a} National Sewage Comprehensive Emission Standards of China (GB8978-1996).

3.3. Microbial Diversity

During the start-up and steady-running periods, sludge samples from the seed sludge, ABR, and SBR were collected, and DNA was sequenced and analyzed by 454 high-throughput sequencing. Then, the microbial communities in the samples were analyzed using this data. The detected sequences in the samples were clustered and grouped in terms of operational taxonomic units (OTUs). Taxonomic classification was performed at the genus level. In the seed sludge, Acidocella and Acidovorax were the dominant genera. During the steady-running period, Rhizobiales, Thermotogales (phylum Thermotogae), and Actinomycetales (phylum Actinobacteria) were the most abundant genera in the ABR sample, while Acidobacteria DRC31 from the phylum Chloroflexi, Lactobacillales, and Bacillales from the phylum Firmicutes prevailed in the SBR sample [15]. The seed sludge from the municipal wastewater treatment plant could survive in WORS, and its microbial diversity changed noticeably to adapt to the changing conditions following cultivation.

3.4. Running Cost

The treatment plant runs for 24 h using a three-shift system. Water quality analysis and sludge shipment are performed during the daytime (08:00 to 16:00); beyond this period, only equipment running checks are required. To reduce labor costs, four workers are arranged for running the treatment plant. Electricity expenses mainly arise from the pumps and blower, and the daily chemical input
includes urine and phosphates. The daily total watt-hours are 542 kWh with electricity expenses of 0.21 per m$^3$ treated wastewater ($0.03/\text{m}^3$, exchange rate $1 = \text{RMB} 6.9$). The daily chemical regent expenses are 0.067 per m$^3$ treated wastewater ($0.0097/\text{m}^3$, exchange rate $1 = \text{RMB} 6.9$). The daily running cost is estimated as RMB 0.73 per m$^3$ treated wastewater ($0.1/\text{m}^3$, exchange rate $1 = \text{RMB} 6.9$), of which the labor costs contribute half of the total running cost (Figure 6). It is important to note that the human expenses have been increasing in recent years.

![Pie chart showing daily running cost breakdown](image.png)

**Figure 6.** Daily running cost during steady running period (treatment capacity of 1500 m$^3$/day).

4. Conclusions

The full-scale biological process including ABR, SBR, and SF demonstrated robustness in treating WORS. Even under varying influent concentrations, the treated WORS met the national standards.Seed sludge from municipal wastewater treatment plants could adapt to the WORS following the cultivation. The biological process is recommended for full-scale WORS treatment plants due to the experience of the study.

**Author Contributions:** W.Z. conceived and designed the experiments; Y.W. performed the experiments and analyzed the data; Y.J. wrote the paper.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

**References**


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