Research of Oily Wastewater Treatment by means of Membrane Methods

N Makisha

1Moscow State University of Civil Engineering, Yaroslavskoye shosse, 26, Moscow, Russia, 129337

E-mail: nmakisha@gmail.com

Abstract. Membrane bioreactors nowadays are intensively applied in wastewater treatment worldwide. Such type of treatment systems has a large scope of implementation at facilities of different capacity. Undoubtedly, the use of MBR for the treatment of industrial wastewater greatly simplifies the process with significant fluctuations in the concentrations in the original wastewater and the presence of "volley discharges". BMR technology-bio-reactor with activated carbon and membrane separation is also of a certain interest. The use of this technology largely solves the issue of post-treatment of refinery wastewater, but returns us to the problem of high operating costs. An alternative to biological methods of wastewater treatment of the refinery can be the use of reverse osmosis plants for this purpose, providing the necessary degree of purification for a number of indicators. The method of reverse osmosis (RO) is already widely used in schemes of water treatment, drinking water supply and post-treatment of wastewater for reuse.

1. Introduction

The idea of MBR technology is to replace the secondary clarifiers with low-pressure Microfiltration (MF) or Ultrafiltration (UF) to achieve more intensive separation of activated sludge. MBR technology includes processing steps similar to the standard biological treatment process: bioreactor, return sludge, and excessive sludge removal. As the membranes (table 1) are used for sludge separation, MBR can provide a higher quality of purified water than traditional biological treatment.

The MBR process is a rapidly developing wastewater treatment technology (comparing to conventional methods) that promises high efficiency and greater compactness compared to traditional biological treatment. Due to the presence of an absolute barrier for suspended solids, MBR is able to maintain very high concentrations of solids (8,000 - 20,000 mg/L and even higher) in the aeration tank. MBR technology does not use the property of sludge deposition in order to preserve it in the biological process. Therefore, it can easily keep the active sludge in the system for a long time (10 - 40 days or longer). This allows to reduce the surplus or to achieve a higher level of treatment for BOD [1-3].

2. Materials and methods

Having many common features with the standard biological treatment process, MBR technology takes a different approach to the separation of activated sludge from wastewater. Membrane separation, preventing activated sludge from leaving the MBR system, provides significant advantages in the separation of water and biomass, making the process independent of the deposition properties of the
sludge. This allows the MBR operating and being managed in very wide ranges of sludge conditions and recycling concentrations, which are difficult to achieve in case of typical sedimentation process.

Table 1. Comparison of membrane features.

| Parameter                  | Hollow fiber | Type of membranes |
|----------------------------|--------------|-------------------|
| Material                   | Polymer      | Flat              |
| Placement density, m²/m³  | 300 – 600    | 50 – 150          | < 300 |
| Unit capacity              | Average      | High              | Low   |
| Mechanical properties      | Minimum      | Average           | Maximum |
| Clogging ability           | Average      | Maximum           | Minimum |
| Reverse washing resistance | Average      | Low               | Maximum |
| Replacement ability        | No           | No                | Yes   |
| Cost                       | Minimum      | Average           | Maximum |

Figure 1. Conventional and membrane treatment processes.

MBR operation with increased concentrations of active or allows the use of smaller size structures and reduce construction costs. Efficient economy of the MBR process requires a balance between the concentration of sludge, the size of the capacity and energy consumption for MBR systems. At higher concentrations, the biological process requires more air and higher energy consumption. This is because the oxygen transmission efficiency decreases with increasing concentration. Increasing the retention period of activated sludge allows a reduction in volume and lower construction cost, but at the same time, more energy may be required to provide the recycle [2,4].

Treatment systems with membrane submerged in the bioreactor operate at a lower flow of sewage and use significantly less energy (power consumption can be two orders of magnitude lower than that of separate systems). In the configuration with the submerged membrane, aeration is an important parameter that affects the process of water treatment. Aeration keeps solids suspended, cleans membrane surface and provides oxygen to the biomass for better biodegradability and cell synthesis.

Another economic factor is the power consumption, considering which provides the improvement of the bioreactors. Another key step in the recent development of membrane bioreactors the idea was to use a two-phase fluid for contamination control. This led to automation of cleaning processes. Low operating costs achieved within the application of submerged membrane bioreactor, along with a steady reduction in the cost of membranes has led to a significant increase of implementation of
facilities since the mid 1990-ies. Since that time permanent research how to modify the design, to create improved types of membranes, to select of optimal flow rates of wastewater and the aerated air in order to increase the lifetime of the membrane are under way. The result of this research is smoothly operated process with implemented back flushing, which allows stable operating of membrane bioreactors and consuming less energy for the process.

**Table 2.** Comparison of membrane features.

| Parameter                        | Membrane methods | Conventional treatment |
|----------------------------------|-------------------|------------------------|
| Transmembrane pressure (TMP) [kPa] | 10-50             | NA                     |
| Flow (average) [L/(m²*h)]        | 15-25             | NA                     |
| Energy consumption [kWh / m³]    | 1-3.5             | 0.9-2.9                |
| MLSS [g/L]                       | 10-25             | 3-6                    |
| HRT [h]                          | 12                | 24                     |
| SRT [days]                       | 6-60              | 6-20                   |
| BOD removal efficiency [%]       | 95-99             | 90-95                  |
| COD removal efficiency [%]       | 95-99%            | 90-95%                 |
| TKN removal [%]                  | 40-95%            | 40-80%                 |
| Period of membrane replacement [year] | 5-8              | NA                     |
| Membrane module price [USD/m²]  | 50-100            | NA                     |

Undoubtedly, the use of MBR for the treatment of industrial wastewater greatly simplifies the process with significant fluctuations in the concentrations in the original wastewater and the presence of "volley discharges". The above scheme makes it possible to obtain purified water in the conditions of the refinery, corresponding to the standards for discharge into the fishery water for nitrogen compounds, suspended solids, COD and BOD, but it is impossible to achieve the required concentration for oil products (0.05 mg/l) even with an increase in the concentration of activated sludge to the limit values of 8 g/L [5]. This circumstance forces to apply additional measures of post-treatment.

An alternative to biological methods of wastewater treatment of the refinery can be the use of reverse osmosis plants for this purpose, providing the necessary degree of purification for a number of indicators. The method of reverse osmosis (RO) is already widely used in schemes of water treatment, drinking water supply and post-treatment of wastewater for reuse [6-9]. The RO process is carried out in the apparatus schematically shown in figure 2.

![Figure 2. Reverse osmosis treatment of wastewater.](image-url)
In work [9] efficiency of application of this method for oil-containing waters of a surface drain from territories of the industrial enterprises, and the sewage, which are formed on car washes, is studied and proved. Application of the most modern membrane installations with devices with "open channel" allows receiving up to 90% of filtrate [10-12].

The studies show that the use of devices based on RO technology is the most promising direction of development of wastewater treatment technology containing petroleum products, surfactants, phenols and other oil refining pollution.

The study of membrane units operating on wastewater of the refinery and petrochemical, and elaboration of the most optimal schemes for oil-containing wastewater treatment using RO technology is a very important task.

3. Results
Combined wastewater from an oil refinery (refinery) was used as examples of oily wastewater. Sources of formation of industrial oily waste water: condensed steam after distillation columns; water contained in the initial oil (up to 0.5% of the total oil) after settling and separation of the phases "oil-water"; water released from petroleum products or intermediates during processing; water after technological flushing (purging) of boiler plants; runoff after electro-desalination of hydrocarbons using water; surface runoff from the refinery.

The purpose of the experimental studies was to determine the maximum possible yield of different types of filtrates – for discharge into reservoirs for fishery purposes, for supply to steam generators of the boiler house and to determine the main parameters of the plant. To simulate the operating conditions of the reverse osmosis unit, an experimental stand was used, shown in Fig. 3.

Figure 3. Bench-scale reactor: 1 – capacity of source and concentrated water; 2 – reverse osmosis membrane; 3 – capacity of pure water (filtrate); 4 – pump; 5 – sampling valve; 6 – filtrate; 7 – concentrate; 8 – supply of source water; 9 – discharge of filtrate; 10 – pressure gauge; 11 – supply of source water.

The initial wastewater (the production drain selected at the entrance to the refinery treatment facilities) is placed in a tank 1 with a volume of 200 liters. From the tank 1, the initial water is pumped 4 to the membrane unit 2. In the membrane unit, the initial water is divided into filtrate (purified water passed through the membranes) and concentrate (water flow, which contains all the pollution retained by the membrane). The speed in the channel of the device is maintained at the level of 0.1 m/sec, which provides a minimum deposition rate on the membranes of suspended solids. The filtrate is collected in the filtrate tank 3, and the concentrate is returned to the tank 1. Table 3 shows the results of analyses of the selected samples during the experiment are presented.
Table 3. Results of bench-scale research.

| Parameter                  | Influent | Effluent for discharge into a river | Effluent for reuse | Limitation |
|----------------------------|----------|-------------------------------------|-------------------|------------|
| pH                         | 7.434    | 6.004                               | 5.404             | 6.5-8.5    |
| TSS, µg/L                  | 21.0     | --                                  | --                | 3.0        |
| Phenol, µg/L               | 0.21     | 0.0008                               | 0.002             | 0.001      |
| SAA, µg/L                  | 0.147    | 0.05                                | 0.05              | 0.50       |
| Petrochemicals, µg/L       | 16.89    | 0.05                                | 0.05              | 0.05       |
| Fe<sub>tot</sub>, µg/L     | 2.860    | 0.043                               | 0.028             | 0.1        |
| Cl, µg/L                   | 395.86   | 11.82                               | 23.63             | 300.0      |
| SO<sub>4</sub>, µg/L       | 43.26    | 0.236                               | 0.02              | 100.0      |
| NH<sub>4</sub>, µg/L       | 3.65     | 0.1                                 | 0.1               | 0.40       |
| NO<sub>2</sub>, µg/L       | 0.02     | 0.001                               | 0.002             | 0.02       |
| NO<sub>3</sub>, µg/L       | 0.343    | 0.118                               | 0.1               | 9.0        |
| PO<sub>4</sub>, µg/L       | 0.05     | 0.05                                | 0.05              | 0.15       |

4. Conclusions
1. Membrane methods proved to be among the most efficient for the treatment of oily wastewater.
2. The numerous studies show that the use of devices based on RO technology is the most promising direction of development of wastewater treatment technology containing petroleum products, surfactants, phenols and other oil refining pollution
3. The efficiency of treatment achieved within the bench-scale research was lower than limitation level at all the indicators.

5. References
[1] Madaeni S S, Eslamifard M R J. of Hazard. Mater. 174 1–3 404-409
[2] Petrinic I, Korenak J, Povodnik D 2015 Hélix-Nielsen Journal of Cleaner Production 101 292-300
[3] Bennett A Filtration & Separation 44(8) 16-19
[4] Wenten I G Khoiruddin Desalination 391 112-125
[5] Rahmanian B, Pakizeh M, Maskooki A 2010 Journal of Hazardous Materials 184(1–3) 261-267
[6] Babilas D, Dydo P 2018 Separation and Purification Technology 192 419-428
[7] Saeid Hosseini S, Nazif A, Shahmirzadi M, Ortiz I 2017 Separation and Purification Technology 187 46-59
[8] Boricha A G, Murthy Z V P 2009 Separation and Purification Technology 65 282-289
[9] Lan J, Ren Y, Lu Y, Liu G, Luo H, Zhang R 2019 Chemical Engineering Journal 359 1139-1149
[10] Pervov A G 2017 Petroleum Chemistry 57(6) 532-535
[11] Pervov A, Tikhonov K, Dabrowski W 2018 Desalination and water treatment 110 1-9
[12] Galkina E, Vasyutina O 2018 IOP: Materials Sci. and Eng. 365(2) 022047

Acknowledgement
This work was financially supported by Ministry of Science and Higher Education of the Russian Federation (#MK-519.2019.8).