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Water deoxygenation using hollow fiber membrane module with nitrogen as inert gas

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ABSTRACT

A pilot plant scale fiber membrane system was developed for the removal of dissolved oxygen from water via nitrogen vacuum. Feed water was introduced to the shell side; a nitrogen gas was applied to the lumen side, as an inert gas, of the hollow fiber. Outlet concentrations of oxygen in water depend on membrane module, inlet concentrations of oxygen in water, water flow, and nitrogen concentrations in inert gas and nitrogen flow. The effects of nitrogen purity on removal efficiency of dissolved oxygen were investigated. Equations for oxygen concentrations and efficiency due to nitrogen purity have been given.

Keywords: Water; Membrane module; Deoxygenation; Nitrogen purity

1. Introduction

Removal of dissolved oxygen in feed water is an important step for protecting the equipment (e.g. boiler or heat exchanger) from corrosion, poor heat transfer, and efficiency reduction [1]. With its high efficiency, energy, space, and cost savings, hollow fiber membrane contactors for oxygen removal from water have been widely used in the process for treated water in power plant, microelectronic, and other industrials. Recently, membrane contactors have been utilized to remove the dissolved gases in feed water. However, their use are still not commonly used compared with currently widely used technologies, such as chemical agents, vacuum tower, forced draft degasifiers, steam deareators, and oxygen scavengers [2]. Membrane process is very clean, does not produce any emission and does not use any fossil fuels. It is relatively new technology, hence, at the market there is only few producers and suppliers. Besides that, not so many engineers and technicians have knowledge and experience within this technology. But, with such significant advantages, popularity of using membrane for oxygen removal is going up. Membrane system is very modular and flexible. Plant can add membrane module in parallel connection in order to treat more water, quantity speaking. On the other side, plant can add membrane module in serial connection, in order to produce water with lower values of oxygen, quality speaking (this could applied if, for example, technology changed or low and regulations for boiler and pressure vessel).

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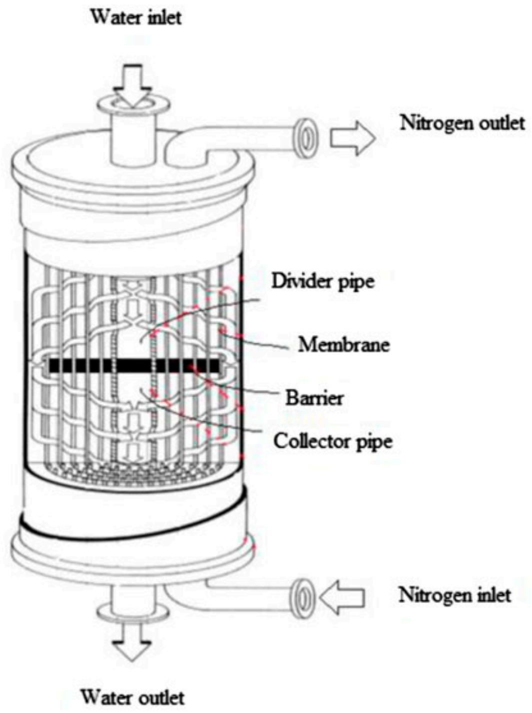

Fig. 1. Membrane module [3].

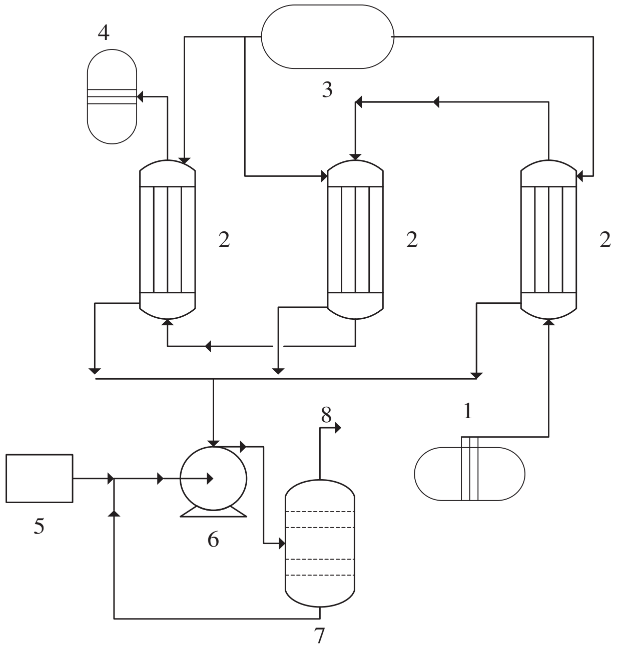

Fig. 2. Pilot plant scale for water deoxygenation: (1) feed water tank, (2) membrane module, (3) nitrogen storage, (4) treated water tank, (5) water's tank for vacuum pump, (6) vacuum pump, (7) phase separator, and (8) vent to atmosphere.

The objectives of this study were to develop a pilot plant scale hollow fiber membrane deoxygenation system, and to investigate the effects of nitrogen purity on the oxygen removal. While nitrogen purity is changing, outlet oxygen concentrations and process efficiency also changes. The aim of this study is to present in which way it is affecting.

The pilot plant scale was provided by Liqui-Cel Membrane Contactors Company. The type of the membrane is X-IN. The dimensions of the fibers, outer and inner diameter are 300 and 200 μm, respectively. The schematic diagram of the membrane module with elements is shown in Fig. 1 [3]. Maximum water flow is 450 m^3/h [3]. Minimum oxygen concentration in treated water is 7.5 ppb [3]. Membrane module beside oxygen removal can be used for carbon dioxide removal.

2. Experimental setup

The schematic diagram of the pilot plant scale deoxygenation system is shown in Fig. 2. Water from the reservoir was pumped by a centrifugal pump to the hollow fiber membrane module at the shell side. Nitrogen under vacuum was exerted on the lumen side of the membrane module by vacuum pump to pull oxygen out from the membrane. Water flow is 20 m^3/h with inlet temperature of 12°C. Pilot plant scale consists of three membrane modules in serial connection because of demanded lower concentration of oxygen at water outlet. Flow of nitrogen is fixed at 6 m^3/h per each membrane module, or 18 m^3/h overall. Vacuum level is 150 mm Hg. Vacuum pump size is 107 m^3/h and it is negligible chance during the process (less than 0.3%). Oxygen concentration in inlet water is 10.98 ppm. Phase separator does not interfere with the process, it is only used for recirculation of water in vacuum pump.

3. Results and discussion

3.1. Measurement values

All of the previously mentioned parameters are fixed during the experiment. The only variations were made with nitrogen purity at inlet. Starting from the values of 99.99% and ending with only 50% purity. The other ingredient with nitrogen is air. Measurements of oxygen concentration for each case are in Table 1.

Table 1
Measurement of oxygen concentration due to nitrogen purity

C_{N_2} (%)	C_{out} (ppb)	C_{N_2} (%)	C_{out} (ppb)
99.99	147.4	91	1419.1
99.9	160.2	90	1561.1
99	287.5	85	2268.6
98	429.0	80	2976.0
97	570.5	75	3683.7
96	712.0	70	4391.2
95	853.5	65	5098.7
94	995.0	60	5806.2
93	1136.5	55	6513.8
92	1278.1	50	7221.3

3.2. Deoxygenation process efficiency

The oxygen removal efficiency was calculated from the concentrations of the dissolved oxygen present at the inlet and outlet of the deoxygenation module as the following:

$$\eta = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \tag{1}$$

where C_{in} is the oxygen concentration at inlet water. C_{in} is the constant during the experiment with value 10.98 ppm. C_{out} is the oxygen concentration at outlet water, obtained by measurement, in ppb. Calculated efficiency is presented in Table 2.

Using statistics regression analysis [4], the following equations for oxygen concentrations in outlet water (C_{out}, ppb) due to nitrogen purity are given:

$$C_{out} = 13316 - 118.8 \times C_{N_2} - 0.1314 \times C_{N_2}^2 \tag{2}$$

where C_{N_2} is the nitrogen purity in %.

Table 2
Calculated removal efficiency due to nitrogen purity

C_{N_2} (%)	η (%)	C_{N_2} (%)	η (%)
99.99	98.72	91	87.66
99.9	98.59	90	84.83
99	97.95	85	75.72
98	96.77	80	74.00
‘97	94.95	75	65.80
96	93.81	70	63.37
95	92.31	65	52.65
94	90.98	60	47.89
93	90.60	55	43.94
92	89.23	50	34.23

Using the same tool, equation for efficiency (η, %) due to nitrogen purity (C_{N_2}, %) is given:

$$\eta = -21.275 + 1.0824 \times C_{N_2} + 0.0011969 \times C_{N_2}^2 \tag{3}$$

Eqs. (2) and (3) are shown in Figs. 3 and 4, respectively, as lines. These figures show the calculations errors made by regression analysis [4]. At the next chapter, statistical formulas and parameters are presented, which are been used for configuration of Figs. 3 and 4.

3.3. Statistical comparison of the equations

The statistical comparison of the equations can be done by the following procedure [4]:

(1) calculate the oxygen concentrations in outlet water C_C by Eq. (2);

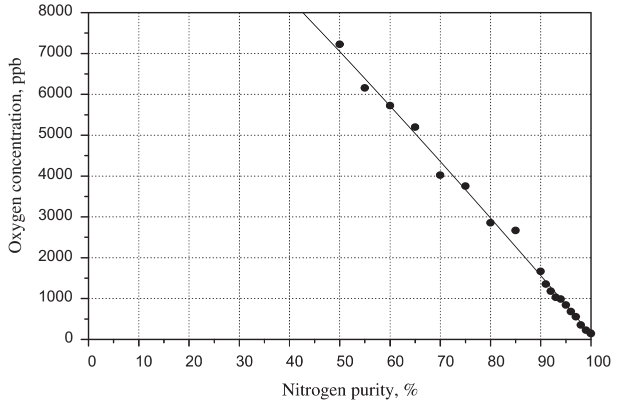

Fig. 3. Oxygen concentrations in outlet water and nitrogen purity.

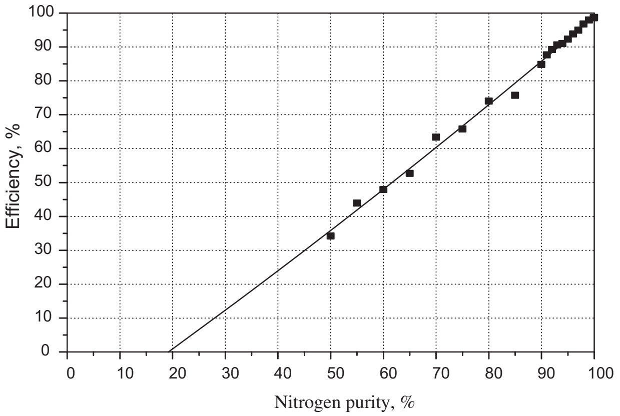

Fig. 4. Efficiency and nitrogen purity.

(2) the oxygen concentrations in outlet water C_{pred} by measurement; and
(3) calculate the following parameters:

- the mean relative error:

$$\text{mean RE} = \frac{1}{n} \times \sum_{i=1}^{n} \frac{\left|C_{\text{C},i} - C_{\text{pred},i}\right|}{C_{\text{C},i}} \tag{4}$$

- the maximal positive error:

$$\max \text{RE}^{+} = \max\left(\frac{C_{\text{C},i} - C_{\text{pred},i}}{C_{\text{C},i}}\right) \tag{5}$$

- Θ, correlation ratio:

$$\Theta = \sqrt{1 - \frac{\sum_{i=1}^{n}\left(C_{\text{C},i} - C_{\text{pred},i}\right)^2}{\sum_{i=1}^{n}\left(C_{\text{C},i} - C_{\text{C,av}}\right)^2}} \tag{6}$$

where $C_{\text{C,av}}$ is the average value of C_{C} for complete set of nods.

$$C_{\text{C,av}} = \frac{\sum_{i=1}^{n} C_{\text{C},i}}{n} \tag{7}$$

According to Table 3, each of the used parameters has good statistical values. Maximal positive error for Eq. (2) is 18.64% which is acceptable error for this kind of studies (according to some authors it should not be above 20%). For Eq. (3), value of the maximal positive error is only 4.83%, which is excellent. In the design phase of the membrane units with this configuration (membrane type, nitrogen purity, etc.) engineers should use mean relative error. Both equations have more than acceptable results.

3.4. Benchmarking between membrane and conventional thermal process

One of the most conventional techniques for water deoxygenation is thermal degasification process. It is shown in Fig. 5. There are two cylindrical vessels, one horizontal, and other vertical. Treated water from minerals (example: reverse osmosis) enters at the top of the vertical cylinder, and via tray, sleeve down to the horizontal cylinder. Water steam enters at the top of the horizontal cylinder, in such quantity to maintain the temperature in the system around 105 ℃. At that temperature, the optimal oxygen removal is achieved from the water. Water steam with dissolved oxygen leaves the units at the top nozzle of the vertical cylinder. The main cost beside units itself is the water steam. Hence, the cost of the treated water depends on produced steam, efficiency of the boiler, and the price of the fuel for the boiler (natural gas, oil, coal, etc.). Some plants use technological or secondary steam from the process, for them, cost of the treated water is insignificant.

Table 3
Statistical parameters for the observed equations

Eq. no.	mean RE (%)	max RE^{+} (%)	Θ (%)
(2)	8.52	18.64	0.997
(3)	2.30	4.83	0.998

According to [5], comparison of the price between thermal and membrane degasification process are shown in Table 4.

The prices are shown in euros per one m^3 of water. Each plant has been producing water steam with coal and heavy fuel oil. Membrane process gives lower price for oxygen removal from water of more than 50% than thermal process.

The biggest advantage of the membrane process is price, which is shown in Table 2. Beside the price itself, membrane process is very clean in ecological way and does not produce any emission. On the other side, thermal process use water steam, and almost every plant use fossil fuels for steam production.

Limitation for membrane process is needed for nitrogen. Plant has possibility to buy or to install unit for nitrogen production (feed itself is free air, but unit needs energy for nitrogen removal from air). Either way, nitrogen produce cost. Other limitation for plant is the need for skilled work force for membrane units. Quantity limitation for membrane unit is water flow

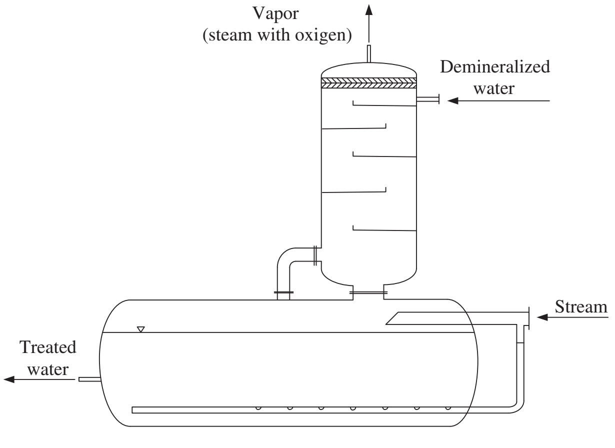

Fig. 5. Thermal degasification unit.

Table 4
Price of the treated water

Process	Plant I	Plant II	Plant III
Annual capacity of the plant, m^3/year	87,600	72,871	40,697
Thermal degasification, EUR/m^3	2.70	2.75	2.99
Membrane degasification, EUR/m^3	1.58	1.62	1.86

of 450 m^3/h, while thermal unit does not have limit (depends on the volume of cylinders and fluid's flow).

4. Conclusion

A pilot plant scale hollow fiber membrane deoxygenation system was developed and found to be efficient in removing the dissolved oxygen from feed water at the appropriate operating conditions. All parameters were constant during the process; the only variable was nitrogen purity as inert gas. As it was expected, with lower nitrogen purity, oxygen concentrations in outlet water were increased, and oxygen removal efficiency was decreased. This paper gave quantitative and qualitative expression for previously mentioned oxygen concentrations and efficiency.

Eq. (2) can be used to determine the oxygen concentrations in outlet water. Eq. (3) can be used to determine the oxygen removal efficiency. These equations are recommended only for similar operational conditions (water flow, oxygen inlet concentrations, membrane module, etc.)

In Table 4, price in euros per one m^3 of oxygen removed from water is presented. With membrane process, price can be as low as 1.58 EUR/m^3, while for thermal process the same can be as high as 2.99 EUR/m^3. With big notes, thermal process depends mostly on the price of the produced steam. Some plants have technology with waste steam, in that case membrane process, of course, should not be used.

Acknowledgments

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Nomenclature

C_{in} — oxygen concentration at inlet water (ppm)
C_{out} — oxygen concentration at outlet water (ppb)
C_{N_2} — nitrogen purity (%)
η — oxygen removal efficiency (%)
C_C — oxygen concentration in outlet water calculated by Eq. (2) (ppb)
$C_{C,av}$ — average value of C_C (ppb)
C_{pred} — oxygen concentrations in outlet water by measurement (ppb)
mean RE — mean relative error (%)
max RE^+ — maximal relative error (%)
Θ — correlation ratio (%)

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