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# Chemical Cleaning of RO Fouled Module with Oxalic acid

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**Abstract:** In this work, the effect of foulants cleaning agent on the membrane surface were investigated. The obtained results showed that, oxalic acid solution is suitable for chemical cleaning of the fouled module. Optimization of conditions (concentration, rinsing time and flow rate in the module was investigated and it showed a suitable cleaning program.

**Key words:** Hollow fine-fiber · Membrane · Oxalic acid

## INTRODUCTION

A membrane is a thin barrier or film through which solvents and solutes are selectively transported. A field test was performed by Wilf and Gluechkstern, [1] to restore commercial RO membranes used a low-pressure alkaline solution followed by dosing a colloidal solution of high molecular weight polymers at high pressure. This program was conducted on 8" and 10" hollow fine fiber (HFF) elements and on 8" polyamide spirally wound (SW) elements. The procedure for 8" and 10" HFF elements consisted of flushing with 2% citric acid (pH 4) followed by flushing with NaOH solution (pH 10.5). Tannic acid solution (100 ppm) at a pressure of 20 bar was then circulated for 10 minutes. The salt passage was reduced from an average of 14% to a level of 6-10%. This was associated with a tolerable (10%) decrease in productivity. The same procedure was applied to 8" polyamide SW elements that had a salt passage in the range of 14-24%.

An average reduction of 43% was obtained by circulating 1 ppm tannic acid for 15 minutes circulation. It was concluded that some RO membranes can be restored using alkaline solution followed by circulation of high molecular weight polymers at high pressures.

Ebrahim and Malik, [2] summarized experiences gained in cleaning different types of seawater RO membranes at the Doha RO Plant in Kuwait. They concluded that cleaning with the DuPont recommended procedure of 2% citric acid at pH 4 and 1.5% Ultrasiel 10 (detergent from Henkel, W.G.) followed by polyvinyl methyl ether (PTA) and tannic acid (PT-B) treatments proved to be effective in restoring B-10 polyamide membranes. The UOP recommended procedure of citric acid cleaning to remove acid-soluble foulants, followed by cleaning with a solution of borax, EDTA and trisodium phosphate to remove non-acid soluble foulants did not always succeed in restoring the performance of UOP-PA membranes. Cellulose acetate membranes were successfully restored by citric acid and Utrasiel 50 (detergent from Henkel, W.G.) cleaning, followed by treatment with agent from Bevaloid, U.K.. This agent, however, proved to be instable at pH = 6.0, which required frequent membrane cleaning and regeneration.

For chemical cleaning of fouled membrane module, the first step is identification of foulants' types on the membrane surfac[3]. Results show that more than 98% of the main compounds, which cause fouling, are salts and metal oxides of iron, calcium and magnesium. The second step is finding suitable chemicals in a cleaning and rinsing program. In this step stability of membrane properties must be considered. The third step is evaluation the cleaning efficiency in a real module. This work was carried out to the make-up water for the boilers at the Tabriz power plant in Iran is treated by a reverse osmosis (RO) process.

## MATERIALS AND METHODS

**Membrane Module:** Membrane modules are hollow fine-fiber modules. DuPont Company manufactures these modules.These asymmetric membranes are made from polyaromatic amide (Aramid). They can operate continuously at temperature in the range of 0°C to 35°C and pH in the range of 4 to 11, not susceptible to biological attack and excellent chemical stability. These modules include of the two types of hollow fine-fiber (B-9:

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fibers 42 μm ID X 85 μm OD and B-10: fiber 42 μm ID X 95 μm OD). In Tabriz Power Plant water required for boilers is treated by these RO modules.

**Cleaning Agents**

**Oxalic acid (Merck), distilled water**

**Module Cleaning Technique:** Suitable chemical cleaning agents may be chosen based on the information of foulant types and membrane chemical stability. Cleaning agents in different concentration, various velocity and several time and temperatur were tested in the fouled modules without applying any pressure. For evaluation of the cleaning efficiency, water flux before and after cleaning at high pressure (28 bar) was measured.

The modules are very voluminous and heavy. Therefor, for choosing the suitable cleaning agents, firstly the fouled membranes were washed by floating in various chemicals. The obtained solutions were analyzed using atomic absorption. This technique provideds information for choosing the suitable cleaning agents which may be tested in real modules.

## RESULTS AND DISCUSSION

**Identification of Foulant Types:** The precipitates on the membrane surface were analyzed and the results indicate thatmore than 99% of the main compounds that precipitate on themembrane surface are iron, calcium and magnesium (iron = 56%,calcium = 28% and magnesium = 15%) compounds. Other ionswere investigated, such as Ba2+, Co3+, Ni2+, Pb2+ and Bi3+, butnone were present in the foulant.

The black particles on the membrane surface were attracted bya magnet. Considering the analysis that more than 50% of foulants are iron compounds, we conclude that the iron is in theform of magnetite (i.e. Fe3O4, or mixture of FeO and Fe2O3). Our conclusion is supported by the finding that it was difficult to dissolve the precipitates in different acids. Furthermore, the pH of the feed water is acidic (pH = 5.44), which indicates that the formation of iron hydroxides (Fe(OH)2 and Fe(OH)3) on themembrane surface was not possible. This conclusion is confirmed by their solubility product constant table (1).

**Chemical Cleaning of Fouled Module:** For chemical cleaning of the fouled module, the used modules which had been employed in Tabriz Power Plant for 4 to 5 years in water treatment system were tested. For chemical cleaning and optimization of cleaning conditions, the following system was set up.

Table 1: Solubility Product Constant of Ca, Fe and Mg precipitations [4]

| Compound | $K_{sp}$ | Compound | $K_{sp}$ |
|---|---|---|---|
| $MgCO_3$ | $1 \times 10^{-5}$ | $CaCO_3$ | $4.8 \times 10^{-9}$ |
| $MgSO_4$ | Soluble | $CaSO_4$ | $1.2 \times 10^{-6}$ |
| $Mg(OH)_2$ | $1.8 \times 10^{-11}$ | $Ca(OH)_2$ | $5 \times 10^{-6}$ |
| $Fe(OH)_2$ | $8 \times 10^{-16}$ | $Fe(OH)_3$ | $4 \times 10^{-38}$ |

The obtained results showed that, oxalic acid solution is suitable for chemical cleaning of the fouled module. In this work for optimization of conditions (concentration, rinsing time and flow rate in the module) and to show a suitable cleaning program, variouse parameters were tested. For evaluation of cleaning efficiency, the increase in permeate stream flow rate in constant pressure was measured. During cleaning of the module, no pressure was applied.

**Effect of Cleaning Agent Concentration:** This effect was evaluated in the former section up to 0.1% (wt) for cleaning agent oxalic acid. In this section lower concentrations were tested. The operation conditions were rinsing time 10 minutes, temperature 22-24 °C and stream flow rate in the module 3.6 lit/min.

Figure 2 shows the effect of various concentrations of oxalic acid solutions in increament of permeates stream flow rate after cleaning in 10 bar applied pressure.

This figure shows that the efficient concentrattion for removal of foulants from the membrane surface is 0.1% (wt).

**Effect of Cleaner Stream Flow Rate:** This effect was evaluated instead of the crossflow velocity. Crossflow velocity is described by the following equation 1. In this equation "A" is the membrane surface area. In this module, surface area is unknown. However, this does not cause any problem because the surface area is constant for each test. This effect was controled using by passes valves (figure 1).

$$V = Q_c / A \quad (1)$$

V: crossflow velocity (m/s)

$Q_c$: cleaner stream flow rate ($m^3$/s)

A: membrane surface area ($m^2$)

The effect of cleaner flow rate, on increament of permeate flow rate was investigated. In these trials oxalic acid (0.1%) solutions at 22-24 °C for 10 minutes were tested. The result is shown in Figurs 3.

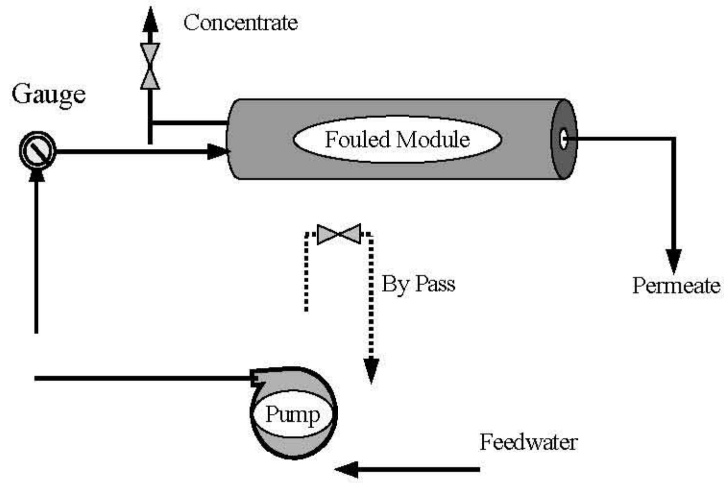


Fig. 1: Schematic of Module Cleaning System

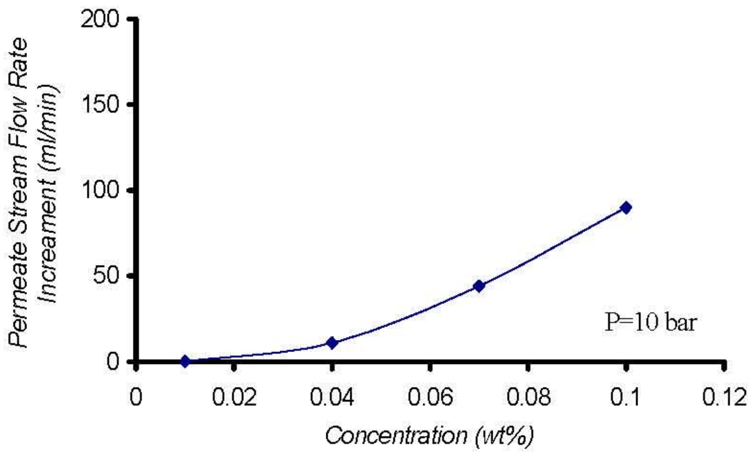


Fig. 2: Effect of Oxalic Acid Concentration on Permeate Stream Flow Rate Increament

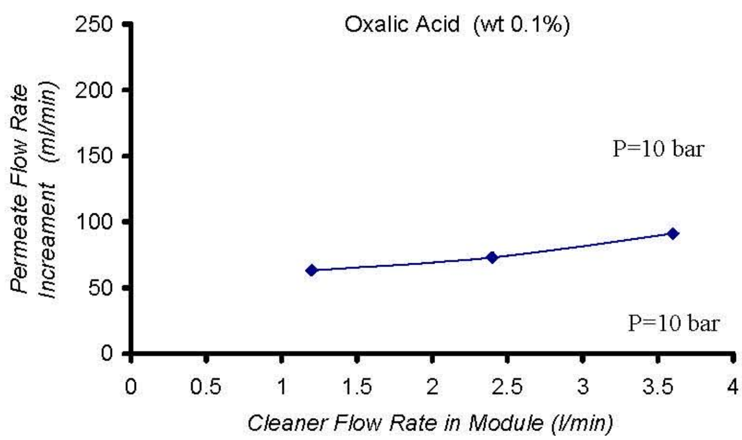


Fig. 3: Effect of Oxalic Acid Flow Rate

Figure 3 show that the effect of oxalic acid is higher. Oxalic acid is used for removal of iron compounds. These compounds (particles) at high pressure stuck on the membrane surface. High turbulency of the cleaner (oxalic acid) fluid helps to separate these compounds from the membrane surface.

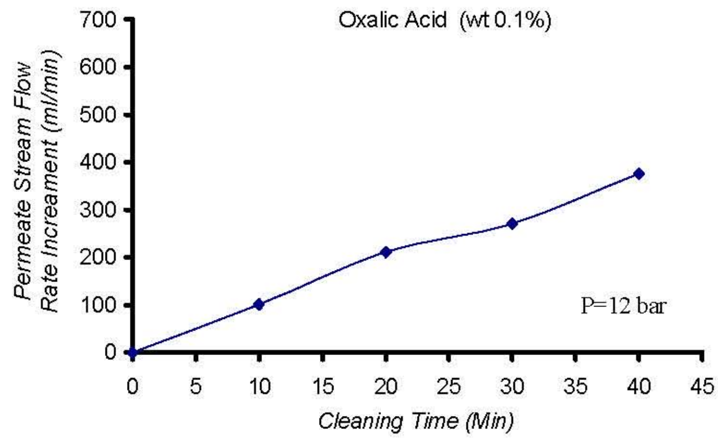


Fig. 4: Effect of Four Times Cleaning by Oxalic Acid Solution

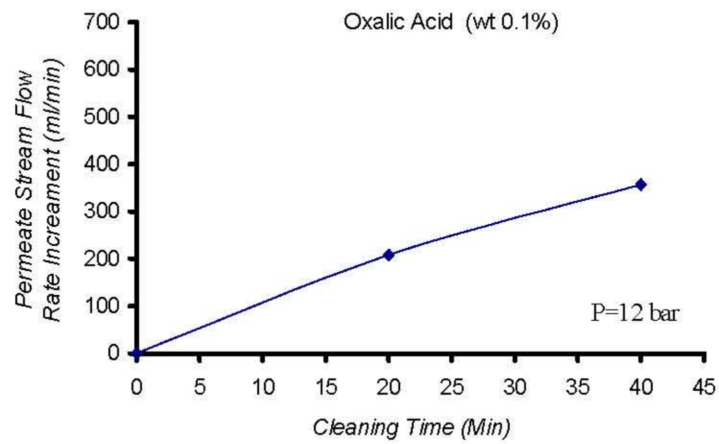


Fig. 5: Effect of Two Times Cleaning by Oxalic Acid Solution

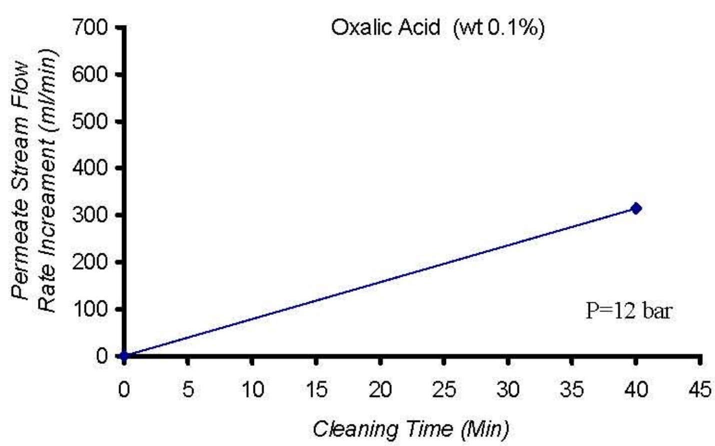


Fig. 6: Effect of One Time Cleaning by Oxalic Acid Solution

**Effect of Cleaning Time:** In this work, the effect of washing the membrane by distilled water for various cleaning times was studied. For this purpose, after cleaning the module by cleaner solution in a specific times, the module was washed by distilled water for 10 minutes. The module was cleaned by the same cleaner solution again. Ultimately, module was cleaned by cleaner solution in a specific time, without washing by distilled water. For evaluation of the cleaning time, the increament in the permeate stream flow rate was measured.

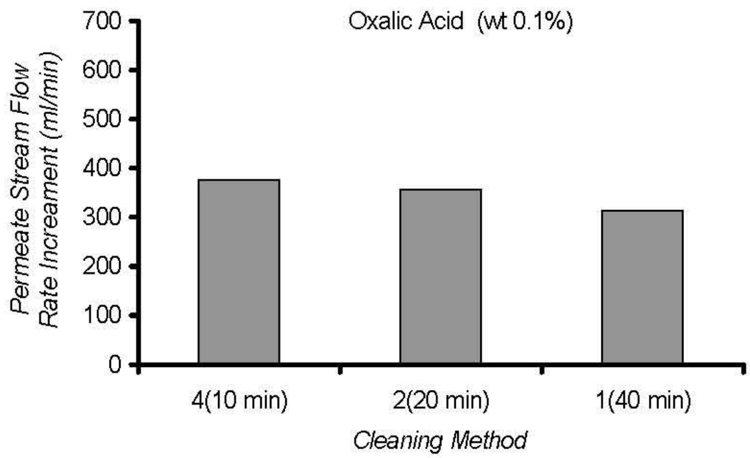


Fig. 7: Results of the CleaningTime Programs (Oxalic Acid Solution)

For investigation of the effect of time programs for oxalic acid solution, three experiments were performed. Figures 4 to 6 show the results.

Comparison of the results obtained in Figures 4 to 6 are shown in Figure 7.

This figure shows that complete cleaning in four time is more efficient compare to the cleaning in once time even if the total cleaning times are equivalet. This result may be was communicated to the surface washing and separated iron compounds of the membrane surface by oxalic acid solution. Washing with distilled water, between each time cleaning, helps to the this performance.

**Cleaning Mechanism:** (precipitation on the membrane surface) transfer to the liquid phase (medium of the cleaner solution). This transfer provides condition for dissolution of precipitation on the membrane surface, which results in membrane cleaning.

probably oxalic acid solution cleans the membrane surface physically. Oxalic acid is not a powerful solution to dissolve magnitude ($Fe_3O_4$). These compound are merely dissolved hardly in powerful acids at high temperature. By chemical and physical interactions between membrane surface and solution medium, oxalic acid provide condition for separation of magnitude molecules from the membrane surface. Therefore membrane surface is cleaned.

## CONCLUSION

In this work, the effect of foulants cleaning agent on the membrane surface were investigated. The obtained results showed that, oxalic acid solution is suitable for chemical cleaning of the fouled module.

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