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Chemical Cleaning of Rofouled Module with Edta

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Abstract: In this work foulants, cleaning agent on the membrane surface were investigated. The obtained results showed that, EDTA-Na 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.

Key words: Hollow fine-fiber · Membrane · EDTA-Na

INTRODUCTION

A membrane is a thin barrier or film through which solvents and solutes are selectively transported. A study carried out by Beckman *et al.* [1] on sewage contaminated surface waters proved that "BIZ" enzyme detergent, sodium perborate and EDTA are promising cleaning agents. They restored the membrane coefficient to about 80 to 85% of the initial level.

W.R Grace and Co. [2] reported the efficiency of several chemical agents used for cleaning fouled RO membranes. The EDTA-NH_4HCO_3-zonyl FSA formulation out-performed all other chemicals tested with regard to gypsum scale dissolution. NH_4HF_2 was the most effective chemical tested for the dissolution of SiO_2 scales, whereas sodium dithionite ($Na_2S_2O_4$) was the most effective chemical tested for the dissolution of Fe-containing scales.

Cleaning strategies for removal of biofilms from RO membranes were evaluated by Whittaker, *et al.* [3]. A variety of compounds was examined using a screening procedure to determine appropriate and potentially effective cases of chemicals that could be employed in cleaning spirally wound (SW) cellulose acetate membrane modules. The study indicated that the anionic agents and combination-involving enzyme containing preparations were the most effective in biofilms removal. Furthermore, membranes receiving influent with high levels of combined chlorine were easier to clean but more susceptible to structural damage from prolonged exposure to combined chlorine. No treatment or combination of treatments, however, was completely effective or effective at all stages of biofilms removal.

Hatch and Workman, [4] reported that 70% of the calcium-based deposits were removed from the large RO plant at Cape Coral (USA) when citric acid stabilized by ammonia was used as a cleaning agent. For chemical cleaning of fouled membrane module, the first step is identification of foulants' types on the membrane surfac[4]. Results show that more than 98% of the main compounds, which cause fouling, are salts and metal oxides of iron, calcium and magnesium. Iron compounds in internal parts of the module are more than of outside parts. The solid particles of iron's oxides are magnitude (Fe_3O_4 formed of mixture of FeO and $Fe\ O_2)_3$which is resulted from the systems's corrosion (pipes, control valves, pumps and etc.).

Hatch and Workman, [4]. 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.

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: 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.

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Cleaning Agents: Ethylene diamine tetra acetic 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

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.

The obtained results showed that, EDTA-Na 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 Edta-na Concentration: This effect was evaluated in the former section up to 0.1% (wt) for cleaning agent EDTA-Na. 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 (3-2) shows the effect of various concentrations of EDTA-Na solutions at pH=8 on permeate stream flow rate increament after cleaning in 10 bar applied pressure.

This figure shows that the efficient concentration for removal of foulants from membrane surface is 0.1% (wt) at pH=8.

Effect of Cleaner Stream Flow Rate: This effect was evaluated instead of the crossflow velocity. Crossflow velocity is described by the following equation (3-1). 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 3-1).

$$V = Q_c / A \qquad (3-1)$$

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 EDTA-Na (0.1%, pH=8) solution at 22-24°C for 10 minutes were tested. The result is shown in Figurs 3-3.

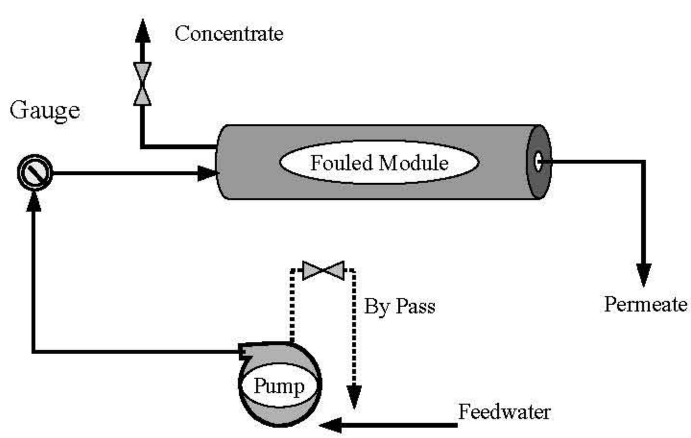

Fig. 3-1: Schematic of Module Cleaning System Figure 3-2: Effect of EDTA Concentration on Permeate Stream Flow Rate Increament (ÄP=10 bar, pH=8)

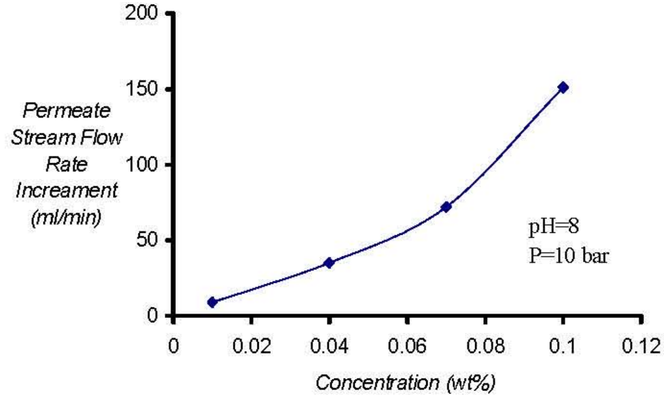

Fig. 3-2: Effect of EDTA Concentration on Permeate Stream Flow Rate Increament (ΔP=10 bar, pH=8)

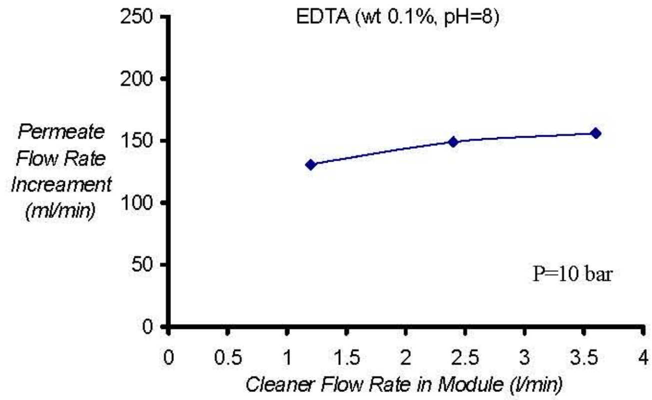

Fig. 3-3: Effect of EDTA Cleaner Flow Rate

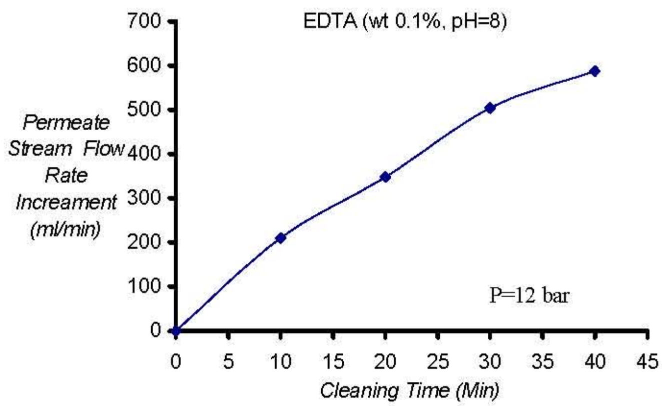

Fig. 3-4: Effect of Four Times Cleaning by EDTA Solution

Figure 3-3 show that when, cleaner stream flow rate is high, cleaning is more efficient. Probably, when cleaner stream flow rate is high, fluid turbulency is high which provide conveninent condition for separation of fouling depisits from the membrane surface.

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.

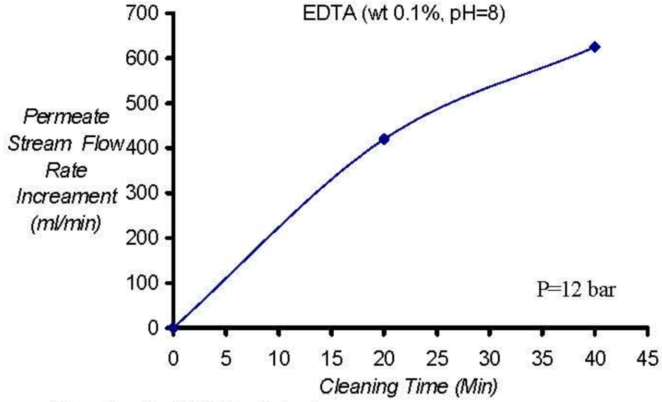

Fig. 3-5: Effect of Two Times Cleaning by EDTA Solution

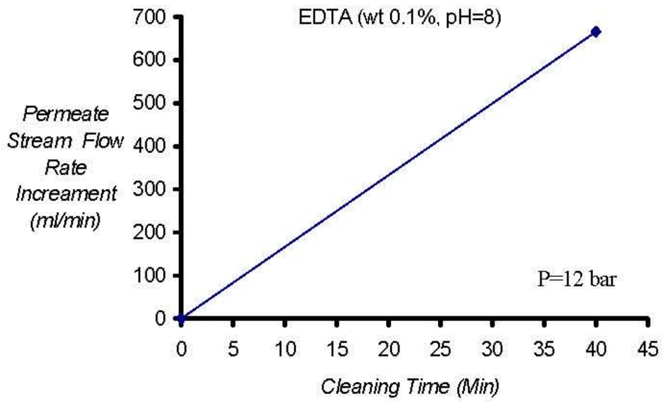

Fig. 3-6: Effect of One Time Cleaning by EDTA Solution

Comparison of the results obtained in Figures 3-4 to 3-6 are shown in Figure (3-7).

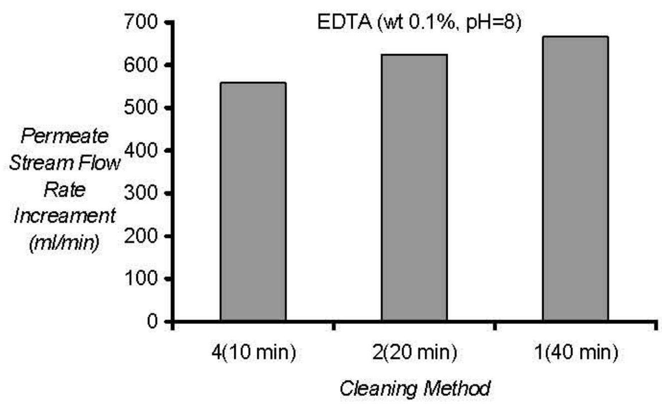

Fig. 3-7: Results of the Cleaning Time Programs (EDTA Solution)

In this work, for EDTA cleaner, three experiments were performed. In the first set of experiment, the module was cleaned four times and each time for 10 minutes. In the second set of experiment, the module was cleaned two time and each time for 20 minutes. In the third set of experiment, module was cleaned once for 40 minutes. After each cleaning module was washed by distilled water for 10 minutes. After each washing, permeate stream flow rate increament was measured, at 12 bar. Figures 3-4 to 3-6 show the results.

This figure shows that complete cleaning in one time is more efficient compare to the cleaning in partial times even if the total cleaning times are equivalent. When EDTA solution is in contact with the fouling materials, EDTA molecules loosened the fouling composite by formation of complexes with Ca^{+2} and Mg^{+2} ions.

Table 3-1: Stability Constants for Metal Complexes of EDTA

Metallic Ion	Log K	Metallic Ion	Log K
Ba^{2+}	7.86	Mg^{2+}	8.79
Ca^{2+}	10.69	Mn^{2+}	13.87
Cu^{2+}	18.80	Ni^{2+}	18.62
Fe^{2+}	14.32	Pb^{2+}	18.04
Fe^{3+}	25.10	Zn^{2+}	16.5

Cleaning Mechanism: Cleaning mechanisms are different for each of the cleaning agents. EDTA molecule is a powerful complex donor with metallic cations (Table 3-1) [5]. EDTA molecules have four acidic protons, that merely in alkaline medium, lose their acidic protons to form complexes with metallic cations. EDTA as a cleaner, with the same mechanism form complexes with the metallic cations (Ca^{2+} and Mg^{2+}) in the surface of fouled membrane. With the formation of complexes, catoins (Ca^{2+} and Mg^{2+}) of the solid phase (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.

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