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Chemical Cleaning of Fouled Polyethersulphone Nanofiltration Membranes with Ethylenediaminetetraacetic Acid

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ABSTRACT

This study mainly investigated the potential use of ethylenediaminetetraacetic acid (EDTA) as the chemical cleaning agent to restore the permeate flux of organically fouled polyethersulfone (PES) nanofiltration (NF) membranes under varying applied pressures. The cleaning efficiency was quantified based on flux recovery rate. The results showed that the optimum EDTA concentration is 1.0 wt%, within the range investigated, which proved that higher concentration does not necessary enhance the cleaning efficiency. The results also demonstrated that the highest flux recovery was achieved at the applied pressure of 14 bar regardless of EDTA concentration. Overall, the maximum flux recovery that could be achieved is only 35.03%, implying EDTA is not very effective in removing foulants from the PES NF membranes.

Keywords: EDTA, flux recovery, pressure, nanofiltration

1.0 INTRODUCTION

Water reclamation and desalination of seawater or brackish water are the well-known solutions to tackle the difficulties of protecting a reliable freshwater supply [1]. This is when the significant of membrane technology arisen. However, the further development of the membrane technologies has been hindered by its major obstacles, the membrane fouling. The ongoing of filtration process causes blockage of membrane pore due to high amount of foulants which eventually decrease the rate of final permeate production but however, increases the complication of the membrane system.

Membrane cleaning methods is the only option to mitigate the membrane fouling instead of replacing the membrane. However, the selection of membrane cleaning method might be difficult due to increase in complexity of fouling layer.

During the process of membrane filtration, membrane fouling is unavoidable [2]. Despite adequate pretreatment, the increase complexity of membrane fouling mechanism has been a major issue for membrane cleaning. There are several factors which contribute to the types and amounts of the foulants. These factors are the quality feed water, type of membrane, membrane materials and finally, process design and control. The most recognised fouling types are colloidal fouling, organic fouling, inorganic fouling and microbial fouling. Fine suspended particles are major contribution of colloidal foulants. Meanwhile, organically fouling is due to high content of natural organic matters (NOM) of the water source water such as lake. Furthermore, organic fouling is reported as the major factor which

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contributes to the decline performance of the membrane filtration which also known as the flux decline [3, 4].

Membrane cleaning is the most vital counter measures for membrane fouling in terms of both economical and scientific points of view. This is due to effective membrane cleaning might restore the performance of the membrane filter whereby frequently replacing the fouled membrane may not economical for large scale municipal applications. Forward flushing, backwashing, chemical cleaning, air flushing and any merging of these methods are the available membrane cleaning solutions. Nonetheless, the selection of inappropriate cleaning methods may consequence in ineffective membrane cleaning as well as damages the membrane itself. Hence, it is significant to first analyse precisely the type of foulants that attached on or within the membrane before proceeds to any membrane cleaning.

In chemical cleaning, most commercially available chemical agents are mixtures of compounds and recommended based on their targeted type of foulant by membrane manufactures [5]. Basically, there are two categories of chemical cleaning solutions which are the acid and alkaline solutions. Generally, acidic solutions such as phosphoric or nitric are normally used to remove inorganic or precipitate fouling. Meanwhile, chelating agents such as EDTA and alkaline solution such as sodium hydroxide are suitable for organic and biological fouling removal. This is because organic substances such as protein and polysaccharides usually hydrolyze at lower pH of acids and chelating agents.

In fact, the effectiveness of chemical cleaning on fouled membrane depends greatly on several parameters such as pH, concentration, hydrostatic conditions, temperature, applied pressure, duration and frequency of membrane cleaning. The cleaning efficiency of ethylenediaminetetraacetic acid (EDTA) and sodium dodecyl sulfate (SDS) were previously investigated under various feedwater pHs [5-8], cleaning time [6-7], concentrations [6], water fluxes [8] and temperatures [6, 8] by several researchers. Ang *et al*. [5] revealed that cleaning efficiency increased from 25% to 44% as the increasing of pH from 4.9 to 11 because all carboxylic functional groups of EDTA are fully deprotonated (become negatively charged) at pH 11 compared to pH 4.9. Moreover, the foulant structure was broken down easily at higher pH. It is also reported that increasing in concentration of EDTA and SDS does increase the cleaning efficiency because sufficient chemical reaction between the chemicals and foulants in order to break down the fouling layer structure [5]. On the contrary, Masse *et al*. [6-7] discovered that increasing concentration of EDTA ranging from 0 to 20 mM brought no effect on membrane permeability.

Applied pressure in membrane cleaning is also a significant factor as it often relates to hydrodynamics of a membrane system. Minimum applied pressure should be adjusted as membrane cleaning is conducted. This is to avoid further compression of the fouling layer and results in further flux reduction, especially in forward flushing method. For instance, it is reported that if surface deposits present in or within the membrane surface, any pressure applied to the membrane cleaning will not able to achieve in maximum cleaning efficiency [9]. On the other hand, some researchers also reported that increasing applied pressure caused the NF membrane surface fouling becomes more severe.

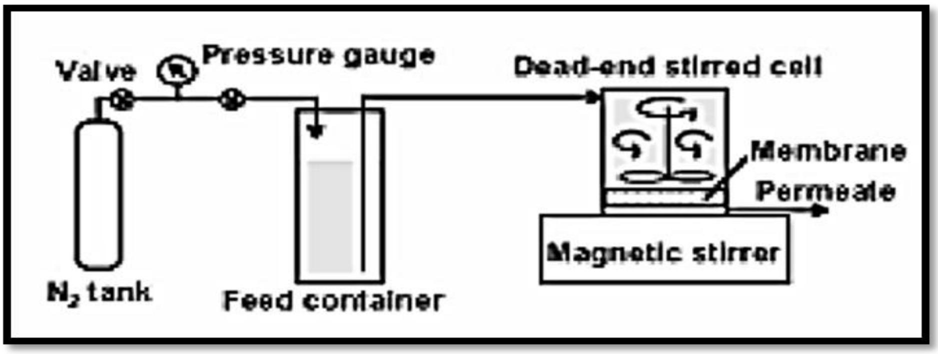

Figure 1 Schematic Diagram of the filtration apparatus used for permeation and cleaning experiments

However, chemical cleaning using EDTA subject to different applied pressures has never been explored to date; so this will be the principal contribution of this work. In short, the significance of this study is aimed to provide the optimum concentration of EDTA along with cleaning pressure in order to achieve better cleaning efficiency for organically fouled nanofiltration membrane.

This paper attempts to investigate the effect of EDTA concentration on cleaning efficiency of organically fouled nanofiltration (NF) membranes under varying applied pressures.

2.0 MATERIALS AND METHODS

2.1 Filtration Apparatus and Experiments

The schematic diagram and photograph of the filtration apparatus used for permeation and cleaning experiments are illustrated in Figure 1 and 2, respectively. This dead-end filtration apparatus used in this experimental works consists of a stirred cell (Sterlitech HP4750), nitrogen gas cylinder, pressure regulator, feed container, magnetic stirrer and electronic balance. The effective membrane area of the stirred cell is 0.00146 m^2. The high pressure nitrogen gas cylinder was used as pressure supply. Filtration experiments were conducted via distilled water before and after the fouling process to measure the differences of their pure water fluxes. The water fluxes before fouling and after fouling were labled as J_{wi} and J_{wf}. respectively. The applied pressure to measure the water flux was fixed at 14 bar. The system was operated under pressures of 12, 14, 16 and 18 bar which used pressure gradient as a driving force. All filtration experiments were conducted at room temperature of about 25 °C at 400 rpm stirring speed and repeated for at least twice to ensure the results were reproducible.

2.2 Fouled Membrane and Cleaning Protocol

The organically fouled membranes were produced by passing clean NF polyethersulfone (PES) membranes with a 10 mg/L Aldrich humic acid (AHA) (Sigma Aldrich) solution. Table 1 presents the properties of the membrane used in this study [10]. The important physical and chemical characteristics of AHA employed in the study can be retrieved from [10]. This study mainly concentrates on the cleaning efficiency of EDTA on organically fouled NF based on flux recovery of the membrane. Firstly, the permeate flux of fresh NF membrane was measured by filtering distilled water, J_{wi}. After the fresh membranes

Figure 2 Photograph of the filtration apparatus used for permeation and cleaning experiments

were fouled with a 10 mg/L AHA solution, the fouled NF membranes were filtered with distilled water to determine their permeate flux after fouling, J_{wf}. The membranes were subsequently cleaned with different concentrations of EDTA at varying cleaning pressures for 30 minutes and the permeate flux after cleaning, J_{wc} were determined afterwards. The concentrations of EDTA adopted were 0.5, 1.0, 2.0 and 3.0 wt%, while the cleaning pressures applied were 12, 14, 16 and 18 bar. The optimum concentration and applied pressure were identified based on the highest flux recovery.

The percentage flux recovery (FR) of EDTA can be determined by using Equation (1) [5].

$$FR = \left(\frac{J_{wc} - J_{wf}}{J_{wi} - J_{wf}} \right) \times 100\% \quad (1)$$

where J_{wc} is permeate flux after cleaning (L/m^{2}h), J_{wf} is permeate flux after fouling (L/m^{2}h) and J_{wi} is permeate flux before fouling (L/m^{2}h).

3.0 RESULTS AND DISCUSSION

3.1 Effect of EDTA Concentration on Membrane Cleaning

Figure 3 shows the flux recovery of organically fouled NF membranes subject to different concentrations of EDTA (0.5, 1.0, 2.0 and 3.0 wt%) at the applied pressure of 12, 14, 16 and 18 bar, respectively. The flux recovery was inconsistent with the concentration of EDTA in which high flux recovery was observed at 1.0 wt% EDTA concentration for all applied pressures investigated in this study. The flux recovery was found in a decreasing trend when higher EDTA concentrations (i.e., 2.0 wt%) was adopted.

The fouled NF membranes cleaned with 1.0 wt% EDTA at the applied pressure of 14 bar exhibited the highest flux recovery of 35.03% among all the cleaning protocols investigated.

Table 1 Properties of the membrane used in this study [10]

Product code	**NF1**
Manufacturer	Amfor Inc.
Membrane type	Flat sheet
Material	Polyethersulfone (PES)
Solute rejection (%)	98 [a] ($MgSO_4$)
Contact angle (°)	31.1 ±1.2 [c]
Wettability	Hydrophilic
Ionizable group (charge)	Negative [d]
Water permeability, L_p (LMH/bar)	7.9 [e]

[a] Pressure applied at 150 psi for 2000 mg/L of $MgSO_4$.
[c] Determined through EasyDrop contact angle measuring instrument.
[d] Given by manufacturer.
[e] Permeability test carried out with ultra-pure water at 25 °C.

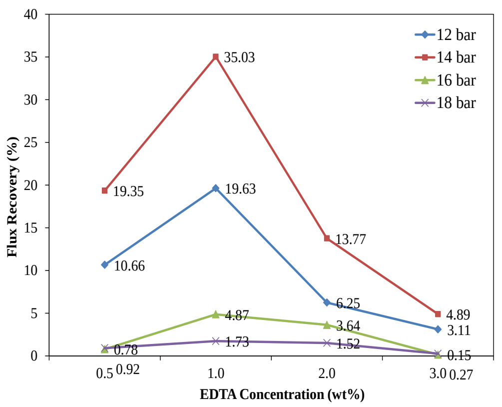

Figure 3 Flux recovery (%) at different EDTA concentration

The flux recovery was found in a decreasing trend with the increasing concentration of EDTA greater than 1.0 wt%. This phenomenon is supported by Li *et al.* [12] who investigated the effect of solution concentration have proven that increasing cleaning solution does not necessary enhance the cleaning efficiency. In their study, they discovered that increased concentration of surfactant cetyltrimethyl ammonium bromide (CTAB) from 0.1 to 0.5 wt% does not results in improvement of cleaning efficiency but deteriorate the cleaning efficiency. This is attributed to the possibility of excess surfactants adsorption into the membrane surface during cleaning process.

Figure 4 EDTA residuals on the membrane surface after chemical cleaning process

In our study, some EDTA residuals were observed on the membrane surface after chemical cleaning process, as shown in Figure 4. This residual could possibly one of the contributions that cause to fouling of the membrane and limit the favorable chemical reaction [9]. Overall, recovery of flux only reached the maximum of 35.03%, implying EDTA is not an effective cleaning agent for organically fouled NF membranes.

3.2 Effect Applied Pressure on Membrane Cleaning Process

The flux recoveries of organically fouled NF membranes subject to different applied pressures of 12, 14, 16 and 18 bar at the EDTA concentrations of 0.5, 1.0, 2.0 and 3.0 wt% are illustrated in Figure 5. As can be seen from Figure 5, at the lowest concentration of EDTA (0.5 wt%) among the studied concentrations, the highest flux recovery of 19.35% was achieved after the organically fouled NF membrane was cleaned under the applied pressure of 14 bar. Surprisingly, the highest flux recovery of 35.03% was also obtained at 14 bar applied pressure for cleaning using 1.0 wt% EDTA. Meanwhile, similar results were observed again for 2.0 wt% ad 3.0 wt% EDTA whereby the highest flux recoveries were 13.77% and 4.89%, respectively.

This has drawn a conclusion that the highest flux recovery occurred at 14 bar among all the applied pressures and the flux recovery began to drop dramatically at pressure greater than 16 bar especially for the concentrations of 0.5 and 1.0 wt%. This adverse effect is probably attributed to the applied pressures of 16 and 18 bar are not effective to allow adequate chemical reaction between EDTA and the foulants to break down the absorbed organic foulants [5]. This statement

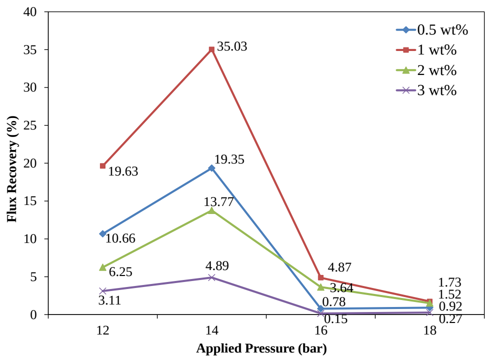

Figure 5 Flux recovery (%) at different applied pressures

was supported by Li and Elimelech [13] who revealed that chemical cleaning of fouled membranes is realized through chemical reactions between the foulants and the chemical agents.

Some researchers also reported that increasing applied pressure would cause the NF membrane surface fouling become more severe [14]. This decreasing phenomenon is probably attributed to the applied pressures of 16 bar and 18 bar are too high with inappropriate cleaning duration adopted which hinder the effectiveness of performing the favourable chemical reaction between EDTA and the foulant [9]. Bartlett *et al.* [9] also highlighted that for the deposits present in or within the membrane surface, any applied pressures to the membrane cleaning will not be able in restoring the flux effectively.

4.0 CONCLUSION

In this study, the cleaning efficiency of organically fouled NF PES membranes was investigated using EDTA at varying concentrations and applied pressures. The results showed that the optimum EDTA concentration is 1.0 wt%, within the range investigated, which proven that higher concentration does not necessary enhance the cleaning efficiency. Observed EDTA residual deposited on the membrane surface could possibly cause to fouling of the membrane and limit the favourable chemical reaction during chemical cleaning. The results also demonstrated that the highest flux recovery was achieved at the applied pressure of 14 bar regardless of EDTA concentration. Overall, recovery of flux only reached the maximum of 35.03%, implying EDTA is not an effective cleaning agent for organically fouled NF membranes.

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