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Fouling and Cleaning Characteristics of Reverse Osmosis (RO) Membranes

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Abstract

This work deals with fouling and successive cleaning of RO membrane fouled by an organic foulant, sodium alginate using a laboratory-scale cross flow test unit. First, spiral-wound RO membrane was fouled with sodium alginate solution up to 10% and 15%, respectively at an applied pressure of 1380 kPa with flow rate of 10 lit/min. An anionic surfactant, sodium dodecyl sulfate (SDS) was used as a chemical cleaning agent for cleaning of RO membrane. The effect of cleaning chemical dose and cross-flow velocity on the membrane chemical cleaning duration to achieve 100% cleaning efficiency (i.e., to get original water flux) was also investigated. As the SDS concentration increases, the membrane chemical cleaning time decreases due to increase in the solubility of the foulant (when the surface tension decreases by an increase in the SDS concentration). Furthermore, the membrane chemical cleaning time decreases with increasing cross-flow velocity of the cleaning chemical solution (SDS). Higher cross-flow velocity enhances the turbulence at the fouling layer and hence the mass transfer of the foulant from the fouling layer to the bulk solution is improved, then the SDS has weakened the structural integrity of the fouling layer. It is observed that better cleaning is occurred with higher concentration of SDS and flow rate. The obtained results clearly reveal that SDS cleaning is proved to be an efficient cleaning method for RO membranes fouled with organic foulant.

Keywords: Reverse osmosis; Fouling; Cleaning; SDS; Permeate flux

Introduction

In recent years, pressure driven membrane processes have been applied in a wide range of fields, such as chemical, medical, textile, petrochemical, electrochemical, water treatment, biotechnology and environmental industries. In particular, reverse osmosis (RO) process is widely used for desalination applications. RO is part of a fast growing market as the demand for clean fresh water around the world continues to increase. RO membrane modules are typically constructed as spiral-wound systems, consisting of multiple layers of membrane sandwiches separated by spacer sheets and coiled around a central perforated tube. RO provides several advantages among other separation technologies that includes high efficiency of the membranes in selective mineral rejection, high permeability to the water, decreased production costs, fulfillment of the most stringent regulations for public health, environment protection and separation process at room temperature [1]. In spite of its several advantages, the major drawback of the RO process is membrane fouling resulting in the reduction of water flux and degradation of membrane solute rejection over a period of membrane operation. Many research works have been performed to explain the mechanisms governing the fouling of RO membranes and also minimization of fouling rate by pretreating feed water, improving the antifouling properties of membranes and optimizing operating conditions [2,3]. In order to minimize membrane fouling in RO process, the feed water to membrane is treated continuously with fouling control chemicals such as antiscalants. Though antiscalants dissolve the substances accumulated near the membrane surface and reduce the rate of fouling, the high dosage of antiscalants leads to increase in RO membrane degradation. Therefore, controlled addition of antiscalants to achieve controlled membrane fouling leading to minimal membrane degradation and lower chemical consumption is desired. Despite these efforts, fouling still remains a key hindrance for energy efficient operation of RO membrane systems and leads to degradation of water flux and solute rejection.

To overcome this operational problem, the membrane maintenance activities are executed when membrane water flux and feed channel differential pressure cross beyond threshold limit. The typical membrane maintenance activities are: (i) membrane back washing with permeate water, (ii) membrane cleaning and (ii) partial replacement of membrane surface area i.e., membrane modules replacement. The membrane back wash is interim solution before perusing chemical cleaning process, where in low TDS and high velocity permeate water is passed through the feed channel to dissolve the deposited salts and flush out blocking content under turbulence condition. Thus the back washing leads to recovery of membrane flux from reversible fouling content and minimize the differential pressure across feed channel, and it may not be effective when membrane is affected by irreversible fouling. For the case of low level membrane degradation due to irreversible fouling, the chemical cleaning is most commonly used method among the various cleaning methods including physical, biological and enzymatic. In the case of high level membrane degradation due to irreversible fouling, the partial replacement of membrane surface is recommended to bring back original water flux of total membrane system.

Chemical cleaning involves both chemical and physical interactions. Two chronological steps occur in chemical cleaning of the membrane: (i) chemical reaction between the cleaning chemical and the foulants in the fouling layer and (ii) mass transfer of the foulants from the fouling layer to the bulk solution, which is controlled by hydrodynamics. The efficiency of cleaning chemicals strongly depends on the chemical reactivity of the cleaning chemicals since the second step of mass transfer can take place only after the foulant-foulant interactions have been weakened by the chemical reaction [3]. Numerous studies have

been demonstrated that effective cleaning chemicals eradicate or reduce significantly the foulant-foulant adhesion forces which maintain the structural integrity of the fouling layer on the membrane surface [3,4]. Therefore, the selection of cleaning chemicals that display favorable chemical reaction with the target substances in the fouling layer is of vital importance. Moreover, the selected cleaning chemicals should have some characteristics such as chemical stability, safety, low cost and ability to be washed / removed with water. The cleaning chemicals must be able to dissolve most of the precipitated materials and remove them from the surface of membrane with no surface damage [5]. With the various cleaning chemicals (alkaline, acids, metal chelating agents, and surfactants) used for cleaning of organic fouled membranes, EDTA and anionic surfactant (SDS) have been proven to be effective in the cleaning of organic-fouled NF and RO membranes [3,4]. Surfactants are compounds that have both hydrophilic and hydrophobic groups, and are semi soluble in both organic and aqueous solvents. Surfactants can solubilize macromolecules by forming micelles around them and help to remove the foulant from the membrane surface. Zondervan et al. [6] studied cleaning behavior of ultrafiltration membranes fouled by surface water. The dynamic model for UF membrane cleaning phenomena is proposed and verified with experimental results. The proposed model is based on component balances and contains three parameters that can be determined by a simple experimental protocol that facilitates the possibility of online adaptation of model parameters at frequent intervals. Also the importance of dynamic model for the optimization of the cleaning process is briefed.

The current practice in RO process is that cleaning chemicals are added to clean the membrane at certain flow rate and concentration as suggested by the membrane manufacturer. Optimizing the chemical flow rate and cleaning cycle based on the membrane fouling state will reduce both energy and the cost of chemicals used for cleaning. This will also help in reducing the production off time due to cleaning and hence increases the RO permeate production. As described above, the membrane fouling/cleaning mechanism is not very well understood for RO membranes due to lack of physical understanding about interaction between (i) fouling material and membrane, (ii) among fouling materials, (iii) fouling material and cleaning chemicals, and (iv) between membrane and cleaning chemicals. The membrane cleaning chemistry and its hydrodynamics are vital to optimize the membrane cleaning process to minimize both chemical and energy consumption [7,8].

Al-Amoudi et al. [9] compiled different types of membrane fouling mechanisms and corresponding membrane cleaning methods applicable for nanofiltration membrane. The importance of different membrane cleaning methods and its intensifications in nanofiltration membrane cleaning efficiency is analyzed. In both academic and industry different methods are proposed and used to estimate membrane cleaning effectiveness. These methods either follow destructive and non-destructive type of measurement. The most common non-destructive method are flux and zeta potential measurements. Similarly destructive methods are atomic force microscopy (AFM) and Fourier transform infrared technique (FTIR). From industrial perspective, the method should able to measure membrane cleaning efficiency without disturbing the membrane system physically and in shorter duration. Also online/real time measurement of cleaning efficiency during membrane cleaning will be helpful operator to optimize the chemical, energy, and duration of cleaning etc. and that will improve over all plant efficiency. Therefore use of low cost non-destructive and online/real time membrane cleaning efficiency estimation method is very important. As described in ref. [9], both flux and zeta potential measurements methods are offline methods i.e., the measurements such as pure water flux and zeta potentials are measured before and after the membrane cleaning and those measurements are used to estimated one point chemical cleaning efficiency.

Al-Amoudi et al. [9], has identified key parameters which are affecting nanofiltration membrane chemical cleaning efficiency: (i) Effect of cleaning solution pH, (ii) Effect of ionic strength of the cleaning solution, (iii) Effect of cleaning solution concentration, (iv) Effect of cross-flow velocity (hydrodynamic shear), (v) Cleaning duration, (vi) Cleaning frequency, (vii) Effect of temperature, (viii) Effect of pressure. Theses parameter can be categorized into groups such as, offline parameters which are optimized offline fixed for given cleaning process and online parameters which are optimized in real time during cleaning process such (i) cleaning solution concentration, (ii) cross flow velocity (iii) cleaning duration. Other parameters are fixed offline and they are constant during cleaning process. In general, the membrane manufactures use to provide recommended optimal value for all eight parameters identified by Al-Amoudi et al. [9], that include combination of cleaning chemical to be used for given feed and membrane properties. However the above said online parameters varies with respect to nature of membrane fouling occurred during regular operations, that leads operator choose trial and error method to estimate optimal cleaning duration, cross flow velocity, cleaning chemical concentration profile during cleaning process.

Therefore the present study is focused on estimation of membrane cleaning efficiency in regular intervals during cleaning operation by manipulating cleaning duration, cross flow velocity, cleaning chemical concentration profile and other offline parameters are fixed with respect to membrane and foulant properties. The analysis of online data will enable operator to perform optimal cleaning operations in real time. In pilot study, the spiral wound RO membrane was fouled using sodium alginate up to 10 and 15%, respectively. The fouled RO membrane was chemically cleaned with SDS. The effect of SDS dose and flow rate on cleaning time to get original flux recovery was investigated.

Modeling of Membrane Cleaning Process

Experimental

Organic foulant: The organic foulant used in this work was sodium alginate (Merck (I) Ltd, Mumbai). Alginate has been extensively used in membrane fouling research to represent polysaccharides that constitute a major fraction of soluble microbial products in wastewater effluent. A required concentration of sodium alginate solution (200 ppm) was prepared by dissolving sodium alginate (powder form) in Millipore water (model: Elix 3 make: Millipore). To obtain complete dissolution, the solution was stirred for 24 hr. The pH of the above prepared foulant solution was in the range of 7-8.

Cleaning chemical: It is well documented that the chemical cleaning by caustic and acidic cleaning reagents results in noteworthy variations in the membrane charge, hydrophobicity, permeability and rejection. In particular, caustic cleaning causes conformational changes in the membrane polymeric matrix and hence it increases the membrane permeability and solute passage [10,11]. In view of the above, sodium dodecyl sulfate (SDS) (Merck (I) Ltd, Mumbai) was selected as a cleaning agent for cleaning of RO membrane. In addition, it is inexpensive compared to other traditional cleaning chemicals. The SDS solution was prepared by dissolving the required quantity of SDS in Millipore water. The concentration of SDS was measured using standard technique reported elsewhere [12]. The titrant was hyamine 1622 (Merck, Germany) and the indicator was an acidic mixture

of dimindium bromide (Merck, Germany) and disulfine blue VN (Merck, Germany). The titration was carried out in a water-chloroform medium. At the end point, the pink color of the chloroformic phase was discharged first and then turned to blue. SDS concentration was determined using the following equation:

$$SDS\,concentration = \frac{a \times molar\,concentration\,of\,hya\min e \times 288.38}{5ml\,of\,sample}$$

where *a* is the volume (ml) of hyamine 1622 required for titration.

RO membrane: An aromatic polyamide thin-film composite RO membrane (M/s Permionics Membranes Pvt. Ltd., Vadodara, India) was used in this study. RO membrane module (size: 2.5" × 20") was typically assembled as spiral-wound systems consisting of multiple layers of membrane sandwiches separated by spacer sheets and coiled around a central perforated tube. The effective membrane area was 1 m². The average value of hydraulic permeability of RO membrane was found to be 7.8×10^{-12} m³/m² Pa.s.

Cross-flow membrane setup

For fouling and cleaning experiments, a laboratory-scale cross flow test unit was used with spiral-wound RO membrane. The membrane fitted pressure vessel was connected with feed tank through a centrifugal pump. Two rotameters were connected with the outlet line showing the concentrate and permeate flow rate. There was a by-pass line before the membrane pressure vessel to manipulate the feed flow rate and pressure to membrane by recycling the part of feed to the feed tank. A cooling tank was also provided to cool down the high temperature concentrate stream due to heat loss from feed pump. The schematic diagram of spiral wound RO membrane set up is shown in Figure 1.

Fouling and cleaning procedure

Before start of the fouling experiment, the pure water permeability of the RO membrane was evaluated using Millipore water. After that, spiral wound RO membrane was fouled by filtration of 200 ppm sodium alginate solution at an applied pressure of 1380 kPa with flow rate of 10 lit/min. The fouling experiment was performed up to 10% and 15% fouling, respectively. The percentage of fouling was measured by considering the pure water flux and the permeate flux of the foulant with time. The permeate flux (*J*) was estimated from the following equation.

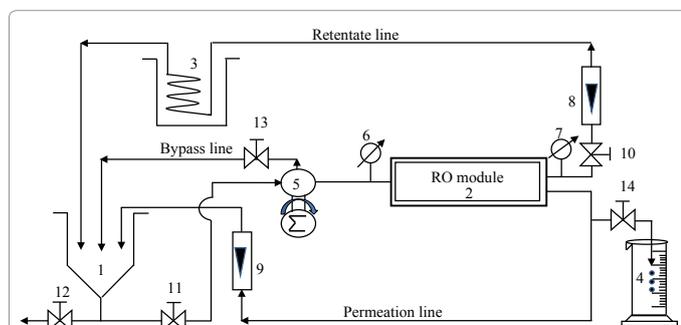$$J = \frac{\ddot{A}V}{\ddot{A}t} \qquad (1)$$

Figure 1: Schematic diagram of spiral wound RO membrane: (1) Feed tank, (2) RO spiral wound membrane module, (3) Cooling tank, (4) Measuring cylinder, (5) Plunger pump, (6) Inlet pressure gauge, (7) Outlet pressure gauge, (8) Retentate flow rate, (9) Permeate flow rate, (10) Retentate control valve, (11) Feed control valve, (12) Drainage valve, (13) Bypass valve, (14) Sampling valve.

Where A is the surface area of membrane, ΔV is the volume of permeate collected and Δt is the sampling time.

Once the fouling was achieved to predefine level (i.e., 10 or 15%), the fouling (sodium alginate) solution in the feed reservoir was disposed of and SDS solution (cleaning chemical) was added to the feed reservoir to clean the fouled membrane. To investigate the influence of cleaning chemical concentration and flow rate on cleaning time to get 100% efficiency, the cleaning experiment was carried out at an applied pressure of 101.43 kPa with various concentrations of SDS (0.1-0.3 mM) and cross-flow velocity (4-11 lit/min). It is important to state that high pressure chemical cleaning of fouled RO membranes is not common in practice. In view of this, all the cleaning experiments were operated at 101.43 kPa. After completion of cleaning experiments, the SDS solution in the reservoir was discarded, and both the reservoir and membrane cell were rinsed with Millipore water to flush out the residual SDS solution. Finally, the cleaned RO membrane was subjected to the pure water flux measurement. All the cleaning experiments were conducted at temperature of 30 ± 1 C. Few fouling/cleaning experiments were performed twice to check the reproducibility. Zondervan et al. [6] studied the cleaning behavior of UF membrane by measuring pH and turbidity of cleaning concentrate. The UF process separates bigger than ~ 0.01μm particle size and same will be coming along with cleaning concentrate while cleaning the membrane. Therefore turbidity measurement is good enough to measure cleaning behavior/state in case of UF. However, in case RO/NF process, it does molecular separation and measurement of individual foulant molecule concentration will be very difficult and expensive in real process. Therefore in this work, concentration of cleaning chemical (SDS) in cleaning concentrate was measured in frequent interval; the interval size is fixed based on cleaning dynamics. The concentration of foulant is expected to increase in cleaning concentrate and reach to asymptotic value. Similarly the concentration of cleaning chemical is expected to decrease and reach to asymptotic value. The cleaning process is stopped when concentration of cleaning chemical reached to asymptotic value.

Results and Discussion

Fouling of RO membrane

Figure 2 depicts the flux behavior of the foulant with time for 10 and 15% fouling experiments. It is evident from the Figure 2a that the flux declines quickly in the initial stage and then declines slowly (see Figure 2b). It means that the foulant, sodium alginate, gel layer becomes denser and more compact which leads to a considerable increase of hydraulic resistance. Hence the time required for 15% fouling of RO membrane is increased when compared with 10% fouling. These results are consistent with results reported by Ang et al. [3] for fouling of RO membranes.

Cleaning of RO membrane

When considering the cost and environmental impact of cleaning chemicals, pumping energy, plant down time aspects of membrane cleaning cycle, the optimization of cleaning cycle time is very important for membrane separation process. Hence finding minimum cleaning cycle time is another crucial parameter for determining the optimal cleaning efficiency. An optimum membrane cleaning time reduces the operational cost and also plant down time. Cleaning with different concentration of SDS solution was performed to investigate the influence of concentration on cleaning time to get optimal cleaning efficiency. The effect of various concentration of cleaning chemical (SDS) was performed and the results are shown in Figure 3. It is clearly
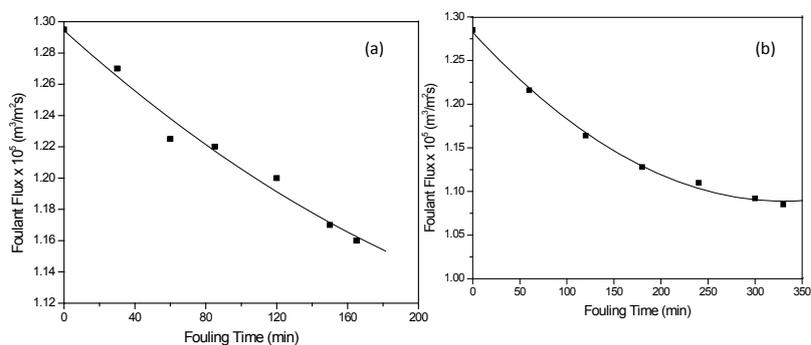
Figure 2: Flux behavior during fouling experiment with sodium alginate solution (a) 10% fouling, and (b) 15% fouling.
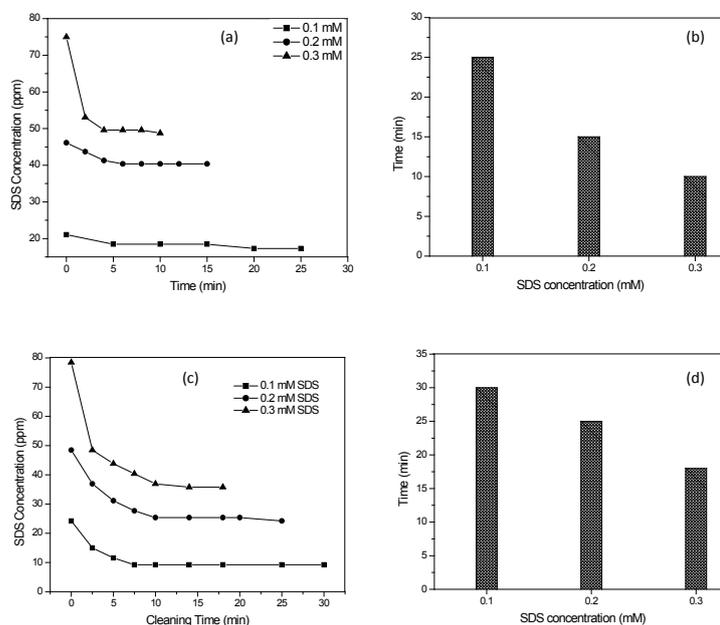

Figure 3: Variation in SDS cleaning time with SDS concentration. (a) and (b) are the results of cleaning experiments for 10% fouled RO membrane; (c) and (d) are the results of cleaning experiments for 15% fouled RO membrane. SDS cleaning experiments were carried out at 101.43 kPa with flow rate of 4 lit/min.

seen that SDS is very effective in removing the fouling layer. When the SDS concentration increases from 0.1 to 0.3 mM, the cleaning time reduces noticeably for both 10 and 15% fouled membranes due to augmentation of physical and chemical aspects of cleaning.

For 15% fouled RO membrane, the foulant concentration is more on the membrane surface than that of 10% fouled membrane. As a result the cleaning time for 15% fouled RO membrane is increased. While the SDS concentration increases, the intermolecular adhesion force decreases because of which the cleaning time decreases; solubility of the foulant increases when the surface tension decreases by an increase in the SDS concentration. The obtained results clearly demonstrate that the cleaning chemical dissolves the foulant which is deposited on the membrane surface and also removes it at faster rate with higher SDS concentration. Further, consumption of cleaning chemical increases with concentration and in general, it leads to increased plant operating cost. On the other hand, as the cleaning time comes down, plant down time also comes down resulting decreased operating cost. Therefore understanding chemistry of chemical cleaning process is very important to estimate optimal cleaning chemical concentration for given membrane separation process.

As we know, surfactants are compounds that have both hydrophilic and hydrophobic structures. SDS decreases the surface tension of adjacent molecules and hence it improves the membrane cleaning. The interaction between the membrane and SDS is controlled by hydrophilic/hydrophobic reaction. As sodium alginate is hydrophobic, hydrophobic tail of the surfactant is preferably adhered to the membrane surface and hydrophilic head is orientated towards aquatic phase (water) [13]. In the work of Ang et al. [3], they reported that SDS cleaning was able to remove over 90% of the alginate gel layer formed on the RO membrane. However, it is evident from this work that SDS is so effective to remove the foulant completely. During the chemical cleaning of the fouled membranes, a chemical reaction between the cleaning chemical and the foulant is occurred and followed by transport of the reaction products away from the membrane surface. It is apparent from these data that a favorable chemical reaction between the surfactant and alginate gel layer is involved. The decrease in cleaning time with increasing SDS concentration implies that this chemical reaction is controlled by the stoichiometry between the SDS dose and the amount of alginate gel layer on the membrane surface.
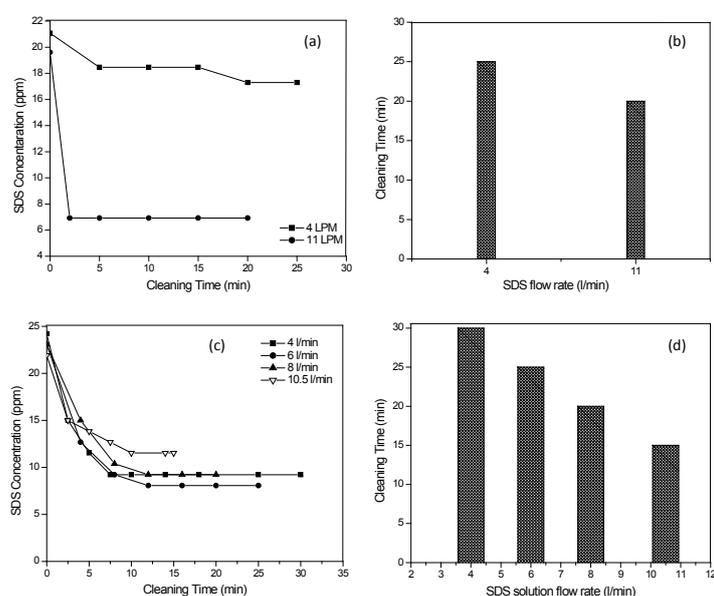
Figure 4: Variation in SDS cleaning time with SDS flow rate. (a) and (b) are the results of cleaning experiments for 10% fouled RO membrane; (c) and (d) are the results of cleaning experiments for 15% fouled RO membrane.

It is well understood that the cleaning time can be reduced noticeably by employing favorable physical conditions such as cross-flow velocity, for effective transport of foulant from the fouling layer to the bulk solution after the chemical reaction between the cleaning chemical and deposited foulant that has weakened the structural integrity of the fouling layer. In view of this, the influence of SDS flow rate (turbulence) on cleaning time to achieve 100% cleaning efficiency (i.e., to get its original flux) was investigated with SDS concentration of 0.1 mM at an applied pressure of 101.43 kPa for 10% and 15% fouled RO membrane, and the obtained results are illustrated in Figure 4.

With increasing the flow rate of the cleaning chemical (SDS), the time required to get 100% cleaning efficiency is reduced drastically for both 10 and 15% fouled membrane. This is due to enhancement of disruption of the fouling layer and the mass transfer of the foulant from the fouling layer to the bulk solution with an increase in cross-flow rate. It is noteworthy to mention that the cleaning time is reduced with increasing the cross-flow velocity merely when the chemical reaction between the foulant and cleaning chemical is high enough to produce a favorable reaction. Otherwise, an increase in cross-flow velocity which results in increase of shear rate does not augment the mass transfer of fouling material to the bulk solution [13]. From Figure 4a and 4b, the SDS concentration for 10% fouled membrane is decreased from 21 to 7 ppm within 2 min while for 15% fouled membrane, it decreased from 24 to 15 ppm only though the flow rates are almost same (~ 11 lit/min). This is because of the concentration of SDS is constant (at 0.1 mM) which is governing the reaction with foulant. Therefore it can be concluded that for the reduction of membrane cleaning duration, chemical reaction between the cleaning chemical and foulant as well as the coupled mass transfer phenomena are very essential.

In another aspect, the energy required for pumping is directly proportional to cleaning flow rate while chemical flow rate is inversely proportional to plant down time. For example, in case of 10% fouled membrane, by increasing flow rate from 4 to 10.5 lit/min, the cleaning time reduced form 20 min to 2 min. This result concludes again that the membrane cleaning chemistry and its hydrodynamics are crucial to optimize the membrane cleaning process to minimize both chemical and energy consumption and decrease the plant downtime.

Conclusions

We have successfully demonstrated the fouling and subsequent cleaning of RO membrane with sodium alginate and SDS, respectively using a laboratory-scale cross flow test unit. SDS cleaning is found to be very effective in cleaning of RO membrane fouled by organic foulant. While increasing the SDS concentration and the cross-flow velocity of the cleaning chemical solution (SDS), cleaning time decreases due to increase in the solubility of the foulant and enhancement of disruption of the fouling layer and the mass transfer rate, respectively. It is observed that better cleaning is occurred with higher concentration of SDS and flow rate. Further, the relative reduction in cleaning time with respect to increase in SDS concentration is observed to be more when compared to increase in its cross flow velocity. It is evident that during cleaning of RO membranes, the duration of cleaning could be reduced noticeably by optimizing the cleaning chemical dose and cross-flow velocity.

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