

Studies on Rejection and Fouling of Polyamide Reverse Osmosis Membrane in the Treatment of Water Solutions Containing Humic Acids

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Abstract: Natural Organic Matter (NOM), which can be broadly divided into two fractions of hydrophobic and hydrophilic, is abundant in natural water resources and in many ways may affect the unit operations in water treatment. It plays an important role in membrane fouling in the water treatment process. Fouling of membranes decreases the applicability of the membrane process and thus a deeper understanding of membrane fouling is needed. The aims of this study were to investigate rejection NaCl and humic acid as hydrophobic fraction and flux decline behavior with a spiral wound RO membrane at a pilot scale and effect of water pH and conductivity (EC) on fouling and retention of RO membrane. The results showed that flux reduction increased with increasing ionic strength and humic acid concentration and lower pH. The rejection efficiency of organic and salt increased with an increase in pH and a decrease of ionic strength. Generally, rejection of humic acid and salt ranged 98-99.3% and 95.8-97.13% respectively. Permeate salt concentration was also significantly reduced immediately upon exposing membranes to humic acid. The different behavior is most probably caused by the differences in the fouling layers and foulant characteristics as well as by the electro neutrality effect. The improved salt rejection was likely due to Donnan exclusion by humic material close to membrane surfaces.

Key words: Natural Organic Matter (NOM) . humic acid . fouling . Reverses Osmosis (RO) . membrane . surface water

INTRODUCTION

The limited supplies of fresh water in many regions of the world and increasing population and improper industrialization practices have led to detrimental Surface and underground water pollution [1]. These phenomenon have raised concern in the public for stringent environmental legislation and alternative technology in water treatment. Membrane technology such as Reverse Osmosis (RO) and Nanofiltration (NF) membranes is now widely recognized as the best technologies for water treatment [2]. The membrane water treatment processes can remove multivalent ions, pesticides, toxins, endocrine disruptors and Natural Organic Matter (NOM) from surface water. The removal of Natural Organic Matter (NOM) from drinking water is of great importance due to its potential to form disinfection by-products when waters are disinfected with chlorine and to promote biofilm growth in water distribution networks. NOM is also considered one of the major

causes of NF fouling during the membrane filtration of surface waters [3].

NOM is abundant in natural water resources and in many ways may affect the unit operations in water treatment. NOM was derived both from natural degradation of some organic substances within the ecological systems and from human activities. Although, NOMs are considered harmless but they have been recognized Disinfection By-Products Precursors (DBPs) during the chlorination process. Formation of DBPs highly depends on the composition and concentration of NOM, which can be broadly divided into two fractions of hydrophobic (humic) and hydrophilic (non-humic) substances [4]. The Humic Substances (HS) are comprised of humic and fulvic acids and non-humic substances (non-HS) include carbohydrates, lipids and amino acids [5, 6]. NOM is typically dominated by humic materials, but proteins, polysaccharides and other classes of biopolymers also contribute to NOM. In addition to them, monomeric species such as simple sugars and amino acids are

present in water sources. The non-humic fraction of the NOM may generally more biodegradable and, as such, supports bacterial regrowth in water distribution systems. NOM cannot easily be removed using conventional water treatment processes. Therefore, they may enter the municipal water distribution network and reach to the points of use [7]. In comparison with conventional treatments, membrane processes are competitive and efficient in removing particulate and dissolved contaminants, including pathogenic microorganisms, hardness, small hazardous micro contaminants and DBPs. Specifically, RO membranes, demonstrates the best overall removal of TDS and organic compounds. Thus, RO membranes can be employed to produce high quality drinking water. However, membrane fouling resulting from the foulant accumulation on the membrane surface is the major cause of the RO system failure. RO membrane fouling is a complex phenomenon involving the deposition of organic, inorganic and biological material in the form of particulates or colloidal suspensions. Membrane fouling results in several deleterious effects, including a decrease in water production because of a gradual decline in flux, an increase in applied pressure required for a constant rate of water production, a gradual membrane degradation which results in a shorter membrane life and a decrease in the permeate quality [8]. Membrane fouling is still a major obstacle for efficient operation of RO and NF plants. Therefore, a fundamental understanding of fouling mechanisms and the influence of fouling on both quantity of flux and permeate quality of RO and NF product water is of paramount importance.

The aim of this paper is to study water filtration containing humic acid as hydrophobic fraction and flux decline with a spiral wound RO membrane at a pilot scale and their relation with feed water background, in particular with water pH and Conductivity (EC).

MATERIALS AND METHODS

RO membrane characteristics: The RO membrane used in this study was designated by the manufacturer as TW30-1812 (Dow-Film Tec Corp). It was made with a polyamide thin-film composite membrane in spiral wound configuration; the size was: outside diameter 1.75 inches and length 11.74 inches. Module performances, from factory tests, were: 12l/h permeate rate, 96% minimum saline rejection and 98% typical saline rejection, as obtained in permeation test with 250ppm softened tap water, 50PSI, 25°C and pH = 8, maximum operating pressure 300 psig (21 bar), pH range in continuous operation 2-11. The effective membrane surface area was 5.5 ft².

Membrane filtration experiments: Experiments were conducted using a cross-flow pilot-scale membrane unit as shown in Fig. 1. It was equipped with a feed and permeate container, a pressure vessel containing the membrane module, an alternative circulation and pressurization pump with a security valve, two pressure gauges, a tap water heat exchanger for temperature control, three flow-meters on feed water, permeate and Retentate pipes. Full circulation mode was used during the experiment where the Retentate and permeate were returned to the feed tank, its volume was 35L, in order to maintain constant concentration [9]. Each membrane filtration test was conducted at room temperature ($22 \pm 1^\circ\text{C}$) by a heat exchanger.

Before all experiments the membrane was cleaned by means of standard procedures to remove preservatives and rinsed with deionized water until the conductivity of the permeate remained below $2 \mu\text{S cm}^{-1}$. The experiments were carried out with the following protocol; for the first 30 min the membrane was rinsed with DI water followed by measuring the pure water permeability as a reference. Then an

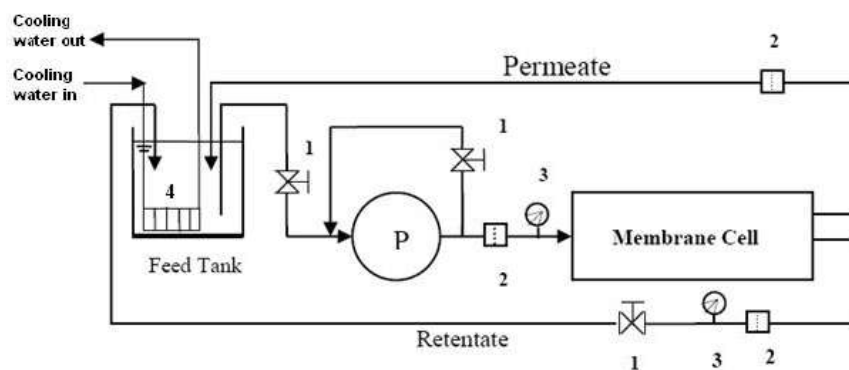


Fig. 1: Schematic diagram of experimental apparatus. 1: Regulating valves, 2: Flow meters, 3: Manometers, 4: heat exchanger, P: high-pressure pump

experiment with a particular feed solution was carried out until a steady state was reached. For the fouling experiments, permeate samples were taken at the start, at the end and at several predetermined time intervals (15 min) during the fouling experiment. The feed concentrations were measured midway in every 15min period or in every one-hour period. Samples were analyzed for conductivity, pH and TOC concentration. Retention solute of TOC and conductivity was calculated according to Eq. (1) [10]:

$$R\% = \frac{C_f - C_p}{C_f} \times 100 = 1 - \frac{C_p}{C_f} \times 100 \quad (1)$$

Where R% is the retention percent, C_f and C_p are solute concentration in feed and permeate respectively. Permeate flux decline is used in this study to describe the fouling extent of membranes.

At first, permeate flux that shown with J and J_0 (as LMH) was calculated by the ratio between the permeate flux (QP) and the membrane surface area as following [11]:

$$J = \frac{Q_p}{A} \quad (2)$$

Then, permeate flux decline is defined as the percentage of reduced permeate flux compared to initial permeate flux as following [12].

$$PFD\% = \left(1 - \frac{J}{J_0} \right) \times 100 \quad (3)$$

Where J_0 is the initial permeate flux at filtration start time and J is the permeate flux at filtration time t .

After each experiment the membrane was rinsed with DI water for 30 min and the pure water permeability was measured. The difference between the pure water permeability before and after each experiment was used to characterize the extent of reversible fouling, if the water permeability after the rinsing was too low (<95% of the initial flux) chemical cleaning was carried out. The chemical cleaning involved storage in acid solution (Citric acid, pH = 4) and base-solution (TSP, pH = 10) for at least 15 min, followed by rinsing with DI water for 15 min. The difference between water permeability before and after the chemical cleaning characterized the extent of irreversible fouling. After the experiments the membrane was stored in DI water [9].

Feed solutions: Deionized water (DI) was used for the preparation of all stock solutions and membrane performance experiments. NaOH and HCl were used for adjusting the pH solution. Salt stock solutions were prepared using certified analytical grade sodium chloride (NaCl) and calcium chloride (CaCl_2) salts dissolved in deionized water (DI). Humic Acid (HA) (Humic acid sodium salt from Rohm&Haas Co) is used as model Natural organic matter. In all filtration experiments, background electrolyte solution contained NaCl with varying conductivity and also pH was changed at 6.5, 7.5 and 8.5 by using NaOH and HCl solutions.

Analytical methods: The humic acid content of the feeds, the permeates and the retentates were analyzed by measuring the UV_{254} (UV absorbance at a wavelength of 254nm) and DOC (dissolved organic carbon, mg L^{-1}). DOC measurements were performed using a Total Organic Carbon (TOC) analyzer (Shimadzu, Japan, Model: TOC-VCSH, Serial No: 3993668) in accordance with the Standard Method 5310C. UV absorbance at 254 nm was analyzed in accordance with the Standard Method 5910 B by using a Lambda 25 UV/Vis spectrophotometer. Potassium hydrogen Biphthalate (KHP) was used to check the precision of the spectrophotometer. And also the Conductivity ($\mu\text{S cm}^{-1}$) and pH of the feeds, the permeates and the retentates were measured according to Standard Methods [13].

RESULTS AND DISCUSSION

Effect of ionic strength: The common monovalent ions or salt, which can be easily found in a variety of water and wastewater, was NaCl salt. Therefore, to investigate the influence of ionic strength or conductivity on the membrane fouling process; fouling experiments were performed at three different ionic concentrations of an indifferent electrolyte 250, 500 and 1000 $\mu\text{S cm}^{-1}$. Figure 2 shows that the fouling behavior is plotted in the form of the permeate flux decline vs. time. Table 1 and 2 show the rejection of humic acid and salt with ionic strength as well as pH. As Fig. 2 shows clearly that membrane fouling becomes more visible as the ionic strength of the feed solution increases. And also as shows in Table 1 and 2, increasing of the ionic strength of the feed solution decreases slightly retention of dissolved organic carbon and conductivity. The DOC retention of all tested conditions varied from 98 to 98.73% that is not significant. The salt retention varied from 95.9 to 96.96%.

Table 1: Dissolved organic carbon retention at varying pH and conductivity. Test conditions: Applied pressure at 170 PSI, 3 mgC L⁻¹, T = 22°C

EC (μS cm ⁻¹)	250		500		1000	
	Concentration*	Rej (%)	Concentration	Rej (%)	Concentration	Rej (%)
pH = 6,5	49.0	98.37	54.0	98.20	60.0	98.00
pH = 7,5	45.5	98.48	49.5	98.35	54.5	98.18
pH = 8,5	38.0	98.73	41.5	98.62	44.5	98.52

*Concentration in permeate is μgC L⁻¹

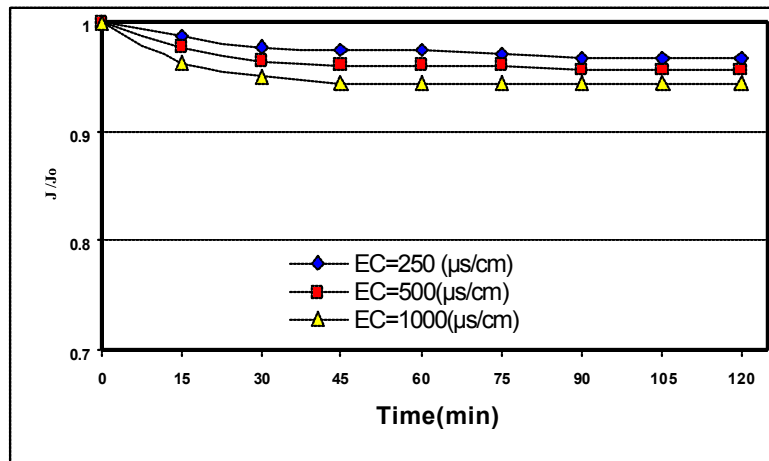


Fig. 2: Effect of conductivity on flux reduction and RO membrane fouling. Test conditions: pH = 7.5, applied pressure at 170PSI, 3mgC L⁻¹, T = 22°C

Table 2: Retention of conductivity at varying pH and conductivity. Test conditions: Applied pressure at 170PSI, 3 mgC L⁻¹, T = 22°C

EC (μS cm ⁻¹)	250	500	1000
pH = 6,5	96.88	96.48	96.00
pH = 7,5	96.88	96.40	95.90
pH = 8,5	96.96	96.68	96.47

It was observed that the relative flux declines (J/J₀) were estimated about 3.3, 4.4 and 5.6% for 250, 500 and 1000 μS cm⁻¹ ionic strength respectively. At higher ionic strength, the charges of the humic acids and the membrane are reduced due to double layer compression, leading to a decrease in electrostatic repulsion among humic acid molecules and between the humic acid molecules and the membrane surface. As a result, humic acid molecules deposition and concentration polarization onto the membrane surface increases and the membrane fouling layer becomes thicker. In addition, due to reduced electrostatic repulsion at high ionic strength, humic acid molecules become more coiled and form a more compact fouling layer. The resulting fouling layer provides an additional hydraulic resistance to permeate flow through the membrane and leads to visible flux decline. In contrast, the strong electrostatic repulsion among organic molecules and between organic molecules and the

membrane surface at low ionic strength, prevents significant the humic acid molecules accumulation on the membrane surface. Similar trends of decreased flux decline with increasing ionic strength for charged NOM were observed by Lee *et al.* [14].

When ionic strength is changed from 250 to 1000 μS cm⁻¹ (at pH 7.5), the rejection of humic acid and salt is decreased from 98.48 to 98.18% and 96.88 to 95.9% respectively. This amount of decreasing efficiency is not significant. Tang *et al.* [14] showed that higher ionic strength has the effect to increased charge density slightly, it also shielded the charges due to increased concentration of counter ions, leading to a net reduction in the electrostatic repulsion between humic acid molecules. Consequently, more flux reduction occurred at higher ionic strength [14].

Jarusutthirak *et al.* (2005) were investigated the NF membrane fouling due to monovalent cation, reported that the experimental results were fitted with pore blocking model (at low ionic strength of 0.01 M), possibly due to reduced charge repulsion between positively charged Na⁺ and negatively charged membrane, thus affecting membrane surface and/or pores. At high ionic strength of 0.05M NaCl, the results were followed with cake formation. This was possibly dominated by reduced charge repulsion between positively charged Na⁺ and negatively charged NOM, thus resulting an increase of NOM accumulation on the

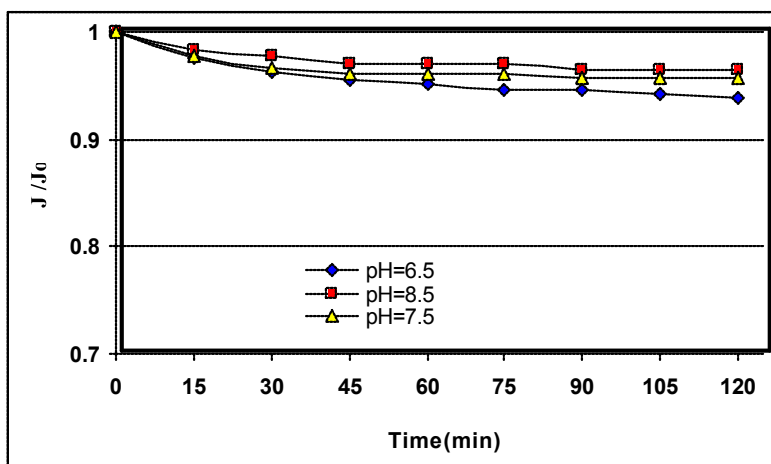


Fig. 3: Effect of pH on flux reduction and RO membrane fouling. Test conditions: Conductivity = 500 ($\mu\text{S cm}^{-1}$), applied pressure at 170PSI, 3 mgC L^{-1} , $T = 22^\circ\text{C}$

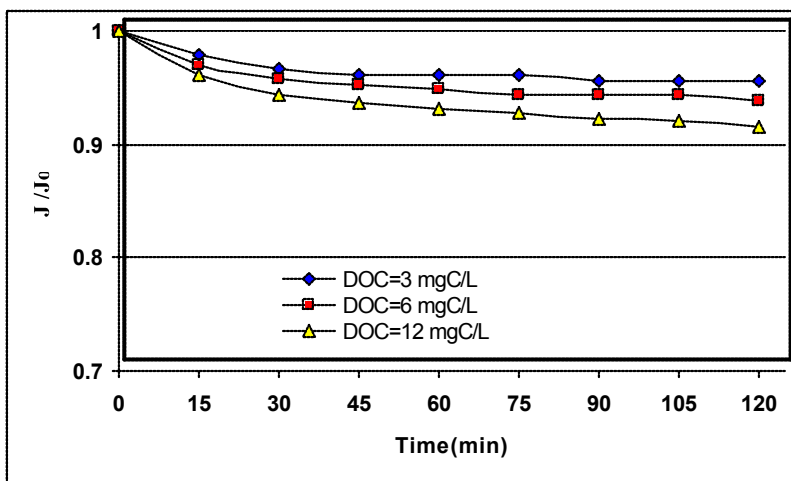


Fig. 4: Effect of Humic acid concentration on flux reduction and RO membrane fouling. Test conditions: Conductivity = 500 ($\mu\text{S cm}^{-1}$), pH = 7.5, applied pressure at 170PSI, $T = 22^\circ\text{C}$

membrane surface. However, an increase of ionic strength from 0.01 to 0.05M can also decrease charge repulsion between positively charged Na^+ and negatively charged membrane. They observed that the rejection of conductivity decreased from 25.3% to 13.7% with increasing ionic strength from 0.01 to 0.05 M, possibly due to decrease double layer thickness on membrane matrix. The rejection of Dissolved Organic Carbon (DOC) was about 94.9-95.3% [15].

Effect of solution pH: Figure 3 shows the influence of solution pH on membrane fouling and also Table 1 and 2 shows the dissolved organic carbon rejection of humic acid and salt retention with pH as well as ionic strength. The rejection efficiency of organic and salt increased with an increase in pH. The possible

explanation is that the membrane surface charge and humic charge were been more negatively due to deprotonation functional groups under alkaline condition. Under these conditions, humic accumulation on the membrane surface decrease and it is not substantial.

It was observed that the relative flux declines (J/J_0) were about 6.1, 4.4 and 3.4% for pH 6.5, 7.5 and 8.5 respectively (Fig. 3). A more significant decline in permeate flux is observed at pH 6.5 compared to pH8.5. This behavior is attributed to the less electrostatic repulsion among the humic acid molecules and between the humic acid molecules and the membrane surface at this pH. In generally, flux decline at pH 6.5 to 8.5 is very small because all the functional groups are already deprotonated and the membrane is negatively charged. As a result, humic accumulation on the membrane

Table 3: Dissolved organic carbon and conductivity retention at varying humic acid concentration. Test conditions: Conductivity = 500 ($\mu\text{S cm}^{-1}$), pH = 7.5, applied pressure at 170PSI, T = 22°C

Concentration* (mgC L ⁻¹)	Organic matter		Conductivity	
	Concentration	Rej (%)	Concentration	Rej (%)
3	49.5	98.35	18.0	96.40
6	77.5	98.71	15.8	96.84
12	83.0	99.30	14.4	97.12

*Organic matter concentration in permeate as $\mu\text{gC L}^{-1}$ and conductivity as $\mu\text{S cm}^{-1}$

surface is not substantial. In addition, the shape of humic acid molecules are different with pH, due to increased electrostatic repulsion between negatively charged neighboring carboxyl groups and thus form a sparser fouling layer. Similar trends of increased flux decline with decreasing pH for charged natural organic matter (NOM) molecules were observed by others [16, 17].

Yoon *et al.* reported that the negative charge of humic acid as well as the negative zeta potential of the membrane surface fouled membrane with humic acid increased with higher pH and the deposition of humic acid on the membrane surface was expected to decrease with higher pH because of larger repulsive forces. The number of negatively charged functional group of humic acid would be increase with pH [18].

Effect of humic acid concentration: When the concentration of the feed water was increased approximately from 3 to 12 mgC L⁻¹, The DOC retention increased from 98.35 to 99.3%. It was observed that the relative flux declines (J/J_0) were about 4.4, 6.2 and 8.5% for 3, 6 and 12 mgC L⁻¹ respectively (Fig. 3). Increasing humic acid concentrations increased the rate and extent of flux reduction greatly because of the accumulation of a fouling layer on the membrane with the membrane fouling; therefore it hinders organic transport through the membrane. The adsorption of organic foulants on the membrane surface may also increase the negative charge of the membrane surface and thus increase the repulsion (electrostatic) forces and consequently retention. Water molecules are small and almost without charge and they pass through the fouled membrane more easily than organic molecules [18]. Tang co-workers reported that the rate at which humic acid molecules accumulate on a membrane surface is determined primarily by the collision frequency of humic acid molecules onto the membrane surface, which increases at higher feed concentrations and the

collision efficiency, which is defined as the ratio of the number of molecules deposited onto the membrane surface over the total number of collision events. As a result, more humic molecules are generally deposited onto a membrane when the feed concentration increases [14].

As Table 3 shows, increasing humic acid concentrations increased conductivity rejection. Salt rejection increased from 96.4 to 97.12% when humic acid concentrations increased from 3 to 12 mgC L⁻¹. Humic acid deposits on membranes can improve salt rejection by two possible mechanisms: size exclusion and Donnan exclusion. Donnan exclusion is likely the dominant mechanism in the current study, where Cl⁻ anions are repelled by negatively charged humic acid. Meanwhile, counter ions Na⁺ are retained to maintain solution neutrality. If size exclusion were the dominant mechanism, salt rejection improvement due to the formation of much denser and less porous foulant layers [14]. Size exclusion mechanism is weak here because it is important when divalent cation i.e. calcium (Ca²⁺), is present but background electrolyte is monovalent cation, i.e. sodium (Na⁺) [15]. Similar results were observed by Xu *et al.* [12]. Liikanen *et al.* (2005) reported that an increased feed water organics concentration caused an increased retention of organic matter, most probably due to the formation of a denser DOM foulant layer on the membrane surface and DOM molecule aggregation to bigger, less permeable particles [17].

CONCLUSIONS

The chemical composition of feed water greatly influences membrane fouling of RO membranes.

It is accelerated at lower pH, higher ionic strength and in the presence of high humic concentration. Permeate salt concentration was also significantly reduced immediately upon exposing membranes to humic acid. The improved salt rejection was due to several mechanisms such as size exclusion and Donnan exclusion. The main mechanism in this was likely Donnan exclusion by humic material close to membrane surfaces. In addition, the adsorption of organic foulants on the membrane surface may also increase the negative charge of the membrane surface and thus increase the repulsion (electrostatic) forces and consequently retention.

An increased feed water organics concentration caused an increased retention of organic matter, most probably due to the formation of a denser foulant layer on the membrane surface and molecule aggregation to bigger, less permeable.

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