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Flux enhancement of thin film composite RO membrane by controlled chlorine treatment

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ABSTRACT

A major stumbling block in polyamide thin film composite RO membrane performance is its incompatibility with chlorine and oxidizing agents. The amide bond of the membrane is highly vulnerable to chlorine attack. Two reactions are possible with chlorine exposure i.e. N–H bond chlorination and/or aromatic ring chlorination. In this way, chlorine may cause degradation/modification in the membrane leading to deterioration in performance.
However, low concentration of chlorine up to a certain time may give synergistic effect on membrane and improve its performance. Chlorine solution, if exposed to membrane for certain time gives enhancement in trans-membrane flux of the membrane.
The same solution if exposed for more time deteriorates ultra-thin polyamide layer of TFC membrane. Conspicuously, the membrane with poor salt rejection and flux benefited more as compared to the membrane with better performance. In the present study, membranes with different salt rejection and flux were taken and exposed to the inorganic chlorine solution. The inorganic chlorine solutions were made by dissolving sodium hypochlorite in pH buffer. The different solutions were made by varying pH to investigate the pH dependence. The membrane samples were kept in solution for different time durations. The exposure time was monitored and the exposure level was taken in terms of ppm h (ppm chlorine solution exposed to membrane for a fixed time in h). With the same chlorine concentration, effect of varying pH was studied. Spiral wound TFC membrane modules were also subjected to chlorine solution to study its effect.

1. Introduction

The conventional membranes used for reverse osmosis application may be either cellulose acetate or thin film composite membrane. Both differ markedly in properties especially chlorine resistance. Cellulose acetate membrane is quite chlorine resistant but its applications are limited to water of relatively low salinity. Moreover the flux of such membranes is also low. Hence, the membranes of new generation are thin film composite polyamide membrane.

One of the major causes of the membrane failure is membrane–chemical interaction. Chlorine is used as disinfectant for control of bio-fouling but it reacts with membrane amine bond and converts it to N-chloro derivative. Feed water disinfection is an integral part of an RO plant processing natural or wastewater. The disinfectant of choice is chlorine and chlorine is notorious for performance failure of membrane.

Commercially available polyamide type membranes can be either fully aromatic or aromatic (cyclo) aliphatic.

Amide nitrogen is vulnerable to chlorine attack because of electron withdrawing effect of carbonyl group. Aqueous chlorine species react with amide nitrogen resulting in formation of N-chloro derivatives [1,2]. This reaction involves initial chlorination of amide oxygen followed by rapid rearrangement to the N-chloro product [3].

Aromatic rings are also susceptible to chlorine attack. Two pathways may be described as below. It can be either direct electrophilic aromatic substitution since aromatic rings bonded to N–H group of amide linkages are most vulnerable to chlorine attack or Orton rearrangement [3]. Initial chlorination of amide nitrogen resulting N-chloro amide then undergoes intermolecular rearrangement forming various aromatic substitution products. An explanation of this rearrangement suggests elimination of the N-bonded chlorine atom yielding molecular chlorine, which then rapidly attacks the aromatic ring via the Orton rearrangement, has been reported [4].

Chlorine attack to aromatic polyamide depends on the nature of amine present in the structure. Secondary amine linkage is vulnerable to chlorine attack whereas tertiary amine linkages are quite immune to chlorine attack.

Literature suggests the following conclusion regarding chlorine reaction with the membrane [5,11–16].

(1) Chlorine sensitivity is pH dependent. Most model compounds are more reactive for lower pH.
(2) Chlorine sensitivity is greatly enhanced when the aromatic group is linked to nitrogen in amide or urea.
(3) Urea is more reactive than amide.

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(4) Ester linkages are more chlorine resistant.
(5) Model compounds containing tertiary substituted nitrogen showed the highest level of chlorine resistance.

However, chlorine exposure to the thin film composite membrane may be a boon to the membrane and can be used for enhancing flux of the membrane. In this way chlorine plays dual role in membrane performance.

Post treatment of the polyamide membrane with solution of chlorine releasing solution e.g. sodium hypochlorite in order to improve performance of membrane has been investigated [6]. Treatment of certain thin film composite membrane based on polyamide obtained by condensation of mixtures of amine and particular triamine with chlorine or chlorine generating agent at pH 6–13 in order to improve solute rejection and flux has been worked out [7]. The treatment of polyamide thin film composite membrane employing triamino benzene as one monomer with an aqueous solution containing residual chlorine at pH of 10.3 to improve flux of membrane at the cost of rejection has been cited [8]. Evaluation of the effect of chlorine on TFC membrane vis a vis pH of the solution has also been done [9]. Mechanism of chlorination is studied in literature [10].

2. Experimental

Thin film composite membrane is made by interfacial polymerization of Metaphenylene diamine and Trimesoyl chloride on polysulfone base. Hence, it is polysulfone–polyamide composite membrane. Interfacial polymerization is an instantaneous reaction which leads to coating of ultra-thin barrier layer over polysulfone membrane [17]. The polysulfone base membrane and polyamide barrier layer was made in-house in a pilot plant and the spiral wound membrane module was made outside through external agency. Thin film composite RO membrane was exposed to sodium hypochlorite solution at different concentration and pH to study chlorine exposure to TFC membrane. The mode of chlorine exposure is by soaking the membrane with the solution and (not by filtering through the membrane to avoid unwanted reaction of chlorine with the polysulfone below polyamide barrier layer) made by dissolving sodium hypochlorite in pH buffer solution. The average temperature during experiment was 25 °C. It is seen that the reaction with chlorine is pH dependent; hence the experiments were carried out at different pH in order to study the pH dependence. The chlorine exposure level was measured in terms of ppm h. The effect of chlorine exposure on membrane characteristics i.e. solute rejection and flux was evaluated. The membrane flux and solute rejection were determined on the standard membrane testing kit by dead-end filtration method at 300 psi pressure and ambient temperature. The membrane samples were cut in the 4.9 cm diameter circular shape and placed in the testing kit. The testing is done in standard testing kit and mode of filtration is dead-end filtration. The saline water solution was made with a concentration of 2000 ppm NaCl. The pressure was kept at 450 psi for 20 min for bringing the membrane in its normal functioning and then pressure was kept at 300 psi and stabilized. The permeate was collected for 20 min. Conductivities of feed as well as permeate were measured. Four such samples were tested in a kit and the average of them was taken in consideration. The membrane flux was measured in terms of m^3/m^2 day.

100 g of sodium hypochlorite (LR grade) with 4% active chlorine was dissolved in pH buffer to make 1 l solution having 4000 ppm effective concentration of active chlorine in the solution. pH buffer solution preparation is as shown in Table 1. The thin film composite membrane was cut in the size 10 cm width, 15 cm length and stuck on the glass-plate. The membrane was washed with distilled water and dipped in the solution containing chlorine for the specified time. i.e. 15 min, 30 min, and 45 min so that reaction can be accomplished. The membrane was washed with distilled water soon after the treatment. The following table shows different experimental conditions in the study.

Sodium hypochlorite (4% active chlorine) is an efficient chlorinating agent used in the present study. In the present work, the hypochlorite solution has been subjected to TFC membranes as well as spiral wound modules of membrane to enhance their characteristics. The term solute rejection refers to salt (NaCl) rejection in this study.

2.1. Module experiments

The experiments were done with 8 in. diameter spiral wound TFC membrane module of the effective membrane surface area of 39.1 m^2. The module was subjected to 2000 ppm chlorine solution having pH 10 with 36 l/min flow rate with re-circulating flow from the tank for 15 min. During experiment, the reject valve is kept fully open and pressure of the system is 1.2 kg/cm^2. Afterwards, the module was thoroughly washed with water for 1 h. Subsequently, flux and rejection were evaluated. The flux and rejection were evaluated before the treatment in order to compare the performance after chlorine treatment. Moreover, the flux and rejection data were monitored at the specific time duration after the treatment for evaluating the long-term effect of chlorine on TFC membrane.

3. Results and discussions

Results of the experiments done to study chlorination of thin film composite reverse osmosis membrane and their analysis are presented below (Table 2).

Membrane with high flux was taken to investigate whether chlorine can still enhance flux of membrane. It can be seen from the above results that rise in flux at the cost of solute rejection is achieved in all three cases. 41% rise in flux is observed at the cost of 7.5% loss in solute rejection in cases of 2000 and 3000 ppm h chlorine exposure level respectively at pH 8.5.

At pH 10.00, a substantial rise of 78% in flux, supplemented by 9% rise in rejection was observed by exposing 4000 ppm chlorine at pH 10 for 15 min i.e. 1000 ppm h. 18% rise in flux and 6.5% rise in solute rejection were observed at 2000 ppm h level whereas 4.4% rise in solute rejection and more or less same flux was observed at 3000 ppm h level while comparing the original membrane.

It is explicit from the results that there is rise in flux by 34% and rise in solute rejection by 10% when exposing membrane to chlorine for 1000 ppm h at pH 12.00. 81% rise in flux was obtained by exposing the membrane to chlorine to the extent of 2000 ppm h. Around 8% rise in solute rejection with the same flux was achieved by exposing the membrane to 3000 ppm h chlorine at pH 12.00.

At pH 12.5, it is seen from the above results that 23.7% rise in flux with almost same solute rejection has been observed with 1000 ppm h

Table 1
Experimental arrangements to study chlorine exposure on TFC membrane.

Experiment	Chlorine concentration	Time of exposure (min)	Exposure level (ppm h)	pH	pH buffer
A	4000	15, 30, 45	1000, 2000, 3000	8.50	1 l 0.025 M $Na_2B_4O7 \cdot 10H_2O$ + 304 ml 0.1 M HCl
B	4000	15, 30, 45	1000, 2000, 3000	10.0	1 l 0.05 M $NaHCO_3$ + 214 ml 0.1 M NaOH
C	4000	15, 30, 45	1000, 2000, 3000	12.0	1 l 0.05 M Na_2HPO_4 + 538 ml 0.1 M NaOH
D	4000	15, 30, 45	1000, 2000, 3000	12.5	1 l 0.2 M KCl + 816 ml 0.2 M NaOH