



# Surface modification of thin film composite reverse osmosis membrane by glycerol assisted oxidation with sodium hypochlorite



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## ABSTRACT

Need for improvement in water flux of thin film composite (TFC) RO membrane has been appreciated by researchers world over and surface modification approach is found promising to achieve higher water flux and solute rejection. Thin film composite RO membrane was exposed to 2000 mg/l sodium hypochlorite solution with varying concentrations of glycerol ranging from 1 to 10%. It was found that there was a drop in concentration of sodium hypochlorite after the addition of glycerol because of a new compound resulted from the oxidation of glycerol with sodium hypochlorite. The water flux of the membrane treated with 1% glycerol with 2000 mg/l sodium hypochlorite for 1 h was about 22% more and salt rejection was 1.36% greater than that of only sodium hypochlorite treated membrane for the same concentration and time. There was an increase in salt rejection of membrane with increase in concentration of glycerol from 1% to 5%, however, increasing glycerol concentration further up to 10%, the salt rejection declined. The water flux was found declining from 1% glycerol solution to 10% glycerol solution. The membrane samples were characterized to understand the change in chemical structure and morphology of the membrane.

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## 1. Introduction

It is very well known that the most extensively used method for desalination of water over the globe is reverse osmosis (RO) [1]. Further, with growing population and industrialization, the installed capacity of desalination is growing at rapid pace. Reverse Osmosis is rather easy to operate, simple to design, modular and scalable and lower energy consuming as compared to thermal desalination [2].

A thin film composite RO membrane consists of three layers of which the bottom-most is nonwoven polyester fabric, the middle layer is of polysulfone membrane forming base for interfacial polymerization and the top-most layer is polyamide of 100–200 nm thickness which is responsible for salt rejection [3]. Many efforts have been made in improving the membrane materials by surface modification and other techniques world over; however, the energy consumption remains one of the major challenges in desalination and water reuse applications especially with growing capacity. The pressure required to overcome the osmotic pressure difference and push the water on the other side of the membrane needs significant

energy which leads to an equivalent green-house gas emission if the energy is produced by conventional thermal power plant. Thus, it is a need of the hour that the membrane should be the least energy intensive to reach the goal of thermodynamic minimum energy requirement for desalination [4].

It has been understood that thinner the top barrier layer of the TFC RO membrane, greater will be the water flux on account of lower resistance to flow [5].

To achieve higher permeability of the membrane, many approaches have been opted. As it is known that the top layer of the TFC RO membrane (polyamide) consists of amide group susceptible to oxidative degradation. Aqueous chlorine is found to react with the group resulting in the formation of *N*-chloro derivatives [6,7]. This reaction comprises of initial chlorination of amide oxygen followed by quick rearrangement to *N*-chloro products [8]. The aromatic rings are also equally susceptible to chlorine attack. There can be a direct electrophilic aromatic substitution as there are aromatic rings connected to amide linkages which are very likely to suffer chlorine attack or Orton rearrangement [9]. Initial chlorination of amide nitrogen may also result in the *N*-chloro amide structure and undergoes intermolecular rearrangement forming various aromatic substitution products [10].

However, the exposure to chlorine in controlled fashion i.e. controlled concentration for limited time at higher pH can be useful to enhance the water flux of the membrane [6]. Further, the mem-

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brane surface can be made more hydrophilic by a supramolecular assembly of chitosan over the sodium hypochlorite treated thin film composite RO membrane [11]. Surface modification is one of the most effective and easiest approaches to enhance the water flux of the membrane.

Also it has been observed that if the membrane is exposed to chlorine for longer period, it may degrade to form ultrafiltration like membrane [12]. The glass transition temperature of the polyamide barrier layer is found to decrease with increasing exposure of chlorine concentration and time [13]. Further the glass transition temperature has also been linked to pH value of the aqueous chlorine solution [14]. It is also observed that the effect of chlorine exposure under unpressurized condition has shown increase in flux with high pH while the water flux decreases under pressurized condition [15]. The decline in salt rejection and increase in flux due to chlorine exposure when correlated with the mechanical properties of the semi aromatic polyamide active layer used in RO membranes showed that there is an increased fragility of the fully oxidized aromatic polyamide network [16]. Moreover, chlorine exposure also results in decrease in biofouling of the membrane because of increased hydrophilicity [17]. The researchers have also found that the chlorination of membrane is a multistep process including reversible and irreversible steps [18]. Silane coated membrane has shown increased resistance to chlorine exposure by maintaining a salt rejection of 99% after exposure of 25,000 ppm h units [19]. The degradation of the polyamide membranes is found more to chlorine exposure when bromide ions are added to chlorine solution [20]. Moreover the degradation reaction of aromatic polyamide membrane due to sodium hypochlorite involved a reversible *N*-chlorination and an irreversible ring-chlorination. The *N*-chlorinated intermediate could be reversibly regenerated to initial amide by the treatment with alkaline solution before it rearranged to ring-chlorinated product, thus partially improved the membrane performance [21].

No researcher has attempted to study the effect of glycerol on oxidation of polyamide layer by sodium hypochlorite. The present paper investigates for the first time that addition of glycerol to sodium hypochlorite while its exposure to thin film composite RO membrane has the synergistic effect as compared to only sodium hypochlorite treated thin film composite RO membrane.

## 2. Experimental

### 2.1. Materials

Thin film composite RO membrane was purchased from Hydranautics, USA. Glycerol (>99%, Thermo Fisher Scientific India Pvt. Ltd., India), sodium hypochlorite (laboratory reagent grade with available chlorine of 4%–6% w/v from RFCL Limited, India), sodium thiosulphate (Thermo Fisher Scientific India Pvt. Ltd., India), sodium *m*-bisulfite (RFCL Limited, India), potassium iodide (analytical reagent from RFCL Limited, India), Acetic acid glacial (ThermoFisher Scientific India Pvt. Ltd., India), starch soluble (High Purity Laboratory Chemicals, India).

### 2.2. Method

Polyamide TFC RO membrane was first cut into a strip of 10 cm × 20 cm. The surface of the membrane was thoroughly cleaned with deionized water. The membrane strip was then carefully stuck on a glass plate to ensure that only the top layer was subjected to treatment and the other components remained air tight and free of any chemical contact. This membrane was treated with the solution of sodium hypochlorite and glycerol. The sodium hypochlorite solution of 2000 mg/l was made in deionized water;

the concentration of sodium hypochlorite was measured by standard iodometric titration. A total of 1%, 2%, 3%, 4%, 5% and 10% glycerol was added in 2000 mg/l sodium hypochlorite solution, respectively, stirred for 15 min and used for treating thin film composite RO membrane. Control experiments were done by exposing TFC RO membrane to 1%, 2%, 3%, 4%, 5% and 10% aqueous glycerol solution.

The membrane was dipped in the solution for 60 min. After that the membrane was taken out with proper care. The membranes were dipped in sodium *m*-bisulfite solution of 6000 mg/l for 30 min to neutralize the presence of active chlorine. Thereafter, they were washed with deionized water and tested. The samples were retained for characterization.

An experiment was carried out to study the effect of only complex formed between sodium hypochlorite and glycerol due to reaction without the effect sodium hypochlorite on TFC RO membrane. A solution of 2000 mg/l sodium hypochlorite and 1% glycerol was made and stirred for 1 h. A volume of 6000 mg/l sodium *m*-bisulfite was added and the solution was stirred to neutralize free chlorine. TFC RO membrane was exposed to it for 1 h and then washed carefully with deionized water.

### 2.3. Membrane performance

The membrane coupons were tested in the standard test kit at 250 psig pressure in brackish water of 2000 mg/l sodium chloride. The membrane coupons used in test kit were circular in shape with area 19.625 cm<sup>2</sup>. Salt rejection and water flux were monitored after pressurizing the membrane samples for 20 min.

### 2.4. Membrane characterization

Membrane characterization was done using Scanning electron micrographs (JSM-7100F Scanning Electron Microscope, Jeol, Japan) to study the surface morphology, attenuated total reflectance infrared spectroscopy (ATR FTIR-Spectrum GX FTIR Spectrometer, PerkinElmer, USA) and powder X-ray diffraction (Empyrean, PAN-analytical X-ray diffractometer with CuK $\alpha$  radiation) to understand the chemical structural change, atomic force micrographs (NTEGRA Aura, NT-MDT Instruments, Russia) to study the surface roughness features and contact angle (drop shape analyser—DSA 100 provided by Krüss Optronic—Germany) analysis for measuring surface hydrophilicity and infrared spectroscopy (Spectrum GX FTIR Spectrometer, Perkin Elmer) analysis for understanding the compounds occurring in the liquid solution.

### 2.5. Kinetic study

A study was done for finding out the rate of reaction of glycerol with sodium hypochlorite. The sodium hypochlorite solution was made of 2000 mg/l and then taken into two separate flasks. After that 5% and 10% glycerol was added, respectively, in both the flask and then the concentration of sodium hypochlorite was measured after stirring it for 15 min. The concentrations of the solutions were measured periodically over 5 h and a graph was plotted showing the consumption of sodium hypochlorite over the period.

## 3. Results and discussion

Table 1 shows the decline in sodium hypochlorite concentration with time with glycerol concentration 5% and 10%.

Table 1 shows that the decline in sodium hypochlorite concentration is higher with higher glycerol concentration, which demonstrates that glycerol gets reacted with sodium hypochlorite and reduces its concentration. The concentration at the end of first

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