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Influence of di-hydrogen phosphate ion on performance of polyamide reverse osmosis membrane for nitrate and nitrite removal

S. S. Madaeni · S. Koocheki

Abstract Reverse osmosis process has great potential in treatment of water and wastewater containing undesirable dissolved species. In the real world, the wastewater contains mixtures of ions. Generally, the presence of particular substances may affect the removal of specific ions and harmful substances in wastewater treatment. In this work, a Filmtec TW30HP-4641 RO element (polyamide, thin-film composite) with the capacity of 14.38 m^3/d was employed for wastewater treatment in Exir Pharmaceutical Co. (Borojerd, Iran). The rejections of individual nitrite, nitrate, and sulfite ions were around 91, 93, and 95%, respectively. However, the addition of KH_2PO_4 to the solution containing nitrite and nitrate ions improved the rejection up to 99%. Polyamide has electronic lone-pair in amino group that can make a resonance structure with carbonyl segment. The feed solution containing potassium and di-hydrogen phosphate ions may establish binding with membrane. The binding of potassium ions to the electronic lone-pair of membrane hold $H_2PO_4^-$ ions and provide a negative layer on the surface of membrane. Diffusion of anions through the membrane is minimized by establishment of the proposed negative layer. This improves the ion rejection capability of the membrane.

Keywords Reverse osmosis · Nitrate · Nitrite · Sulfite · Di-hydrogen phosphate · Wastewater treatment

1 Introduction

Deteriorating water quality influences human and has economic implications for various sectors including industry [1]. Today, agriculture and industry use 90% of the fresh water. Thus, it is very important to save as much water as possible. Industry should especially try to reduce the amount of process water [2].

The researchers have investigated alternative techniques such as membrane processes. Principal advantage of these techniques is the achievement of high-quality water [3] with confidence [4] compared to the traditional techniques including physical (such as sedimentation), chemical (e.g., ion exchange) and biological (such as activated sludge) procedures.

Reverse osmosis (RO) reduces dissolved salts [5] in waste water treatment. The spiral-wound membrane element is the most widely used with benefits including high membrane surface area to volume ratio, easy to replace, can be manufactured from a wide variety of materials and is prepared by several manufacturers. The membranes for RO systems are able to remove mono-valent salts [6].

The RO technology has great potential in treatment of drinking water supplies and wastewater containing undesirable dissolved species in the chemical industry [7]. The effect of salt type on mass transfer in reverse osmosis has been elucidated using transport equations [8].

A comprehensive study has been carried out by numerous researchers to exhibit the capability of membrane processes especially reverse osmosis process for removal of various ions from water and waste water. Nitrogenous compounds (ammonia, nitrite, and nitrate) are considered of major contaminants in wastewater treatment.

Ratanatamskul et al. [9] reported 70% nitrate removal using ultra low pressure nanofiltration membrane. An

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improved rejection was obtained by ultra low pressure reverse osmosis membranes [10].

Bohdziewicz et al. [11] obtained nitrate removal of 76% using cellulose acetate RO membrane for the removal of nitrate from groundwater. Ritchie and Bhattacharyya [12] reported >95% nitrate removal by means of a membrane-based hybrid process. Qin et al. [13] showed a spiral-wound RO membrane made of thin-film composite polyamide is capable of removing 90–97% of nitrogenous compounds.

Schoeman and Steyn [14] demonstrated that the RO process could be very effectively applied for water denitrification in a rural area. Nitrate-nitrogen could be removed from 42 mg/L to less than 1 mg/L (98% removal). Cevaal et al. [15] reported nitrate rejection about 97% using a commercial polyamide RO membrane (Dow-FilmTec).

Awadalla et al. [16] studied rejections of four membranes: PVA-NF, NF, DS5, FT-30, polyamide RO, and nitrate rejection was 43, 40, 97, and 92%, respectively. Qin et al. [17] reported 85% rejection for nitrate using RO polyamide membrane. Molinari et al. [3] showed nitrate rejection around 97% using RO membrane.

Sadr Ghayeni et al. [18] used a hollow fiber microfiltration membrane as a pretreatment prior to reverse osmosis for evaluation of the production of high-quality water from secondary effluent. Four different low operating pressure RO membranes (PVD, CTA, TFCL, and NF45) produced a target flux of 20 L/m^2 h at the relatively low operating pressures of 230, 750, 550, and 360 kPa, respectively. Conductivity measurements revealed rejections of ionic species of 99.2 and 41% for TFCL and NF45 membranes, respectively. However, nitrite/nitrate was only partially removed.

Another important contaminant in waste water treatment is phosphate ion. Balannec et al. [19] studied phosphate rejections of three RO membrane: Desal 3SF (Polyamide/Polysulfone), TFC-HR (Composite polyamide), and BW30 (Composite polyamide). Phosphate removals of 99.6, 100, and 99.8% were obtained, respectively.

Vourch et al. [20] used a model of nanofiltration and reverse osmosis and reported rejection of phosphate as high as 95%.

Generally, the presence of particular substances may affect the removal of specific ions and harmful substances in wastewater treatment. In this work, the influence of di-hydrogen phosphate ion on performance of Filmtec reverse osmosis element for rejection of nitrite and nitrate ions was evaluated.

2 Materials and methods

2.1 Apparatus

A pilot plant reverse osmosis (Aqua-Cleer MFP/3-800-Culligan Company, Italy) with two elements (spiral-wound module) operating in series was used for all trials (Fig. 1). Permeate and concentrate were returned to the tank. The feed tank was stainless steel, with a capacity of 1000 L and two walls which allowed the feed temperature to be kept constant using the circulation of cooled water or steam. Volume of permeate was measured using a calibrated volume counter. For measuring the time, a calibrated chronometer was used.

All the hydraulic components used in Aqua-Cleer MFP/3 plants consist of corrosion-resistance materials and are designed to withstand the operating condition as follows:

- The elements upstream of the high-pressure pump are resistant to a nominal pressure of 8 bar (114 psi).
- The elements of the high-pressure circuit (membrane inlet and reject lines) withstand a nominal pressure of 16 bar (228 psi).

Some parts of the line made of stainless steel, other parts were high-pressure hoses. The system consisted of a valve to control the applied pressure and flow.

2.2 Membrane

The thin-film composite polyamide membrane (Filmtec TW30HP-4641) was employed in the spiral-wound modules with the 128 ft^2 (11.89 m^2) active area. Polyamide has electronic lone-pair in amino group that can make a resonance structure with carbonyl group [3].

2.3 Feed

Feed solutions were prepared using deionized water at the pH between 5.5 and 6. For preparation of feed the following reagents, all from Merck, were employed: sodium

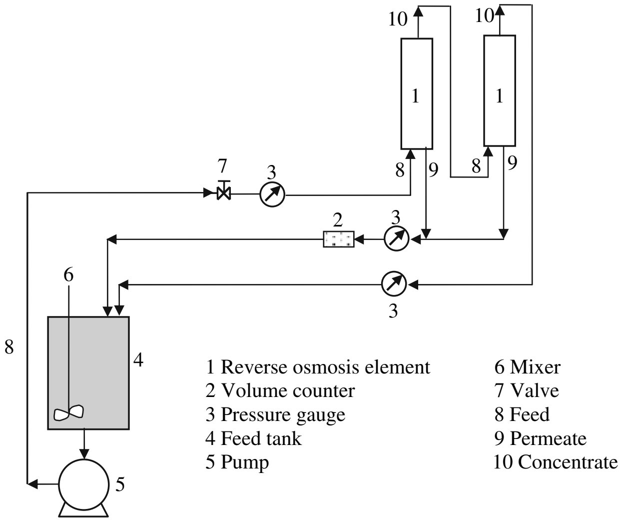

Fig. 1 Schematic diagram of reverse osmosis system

nitrate, sodium nitrite, potassium di-hydrogen phosphate, and sodium sulfite. The KH_2PO_4 was used in the solution together with other ions.

2.4 Ion rejection

Concentrations of ions were measured on the basis of standard methods [21] as follows:

The colorimetric method was employed for nitrite determination. After adding color reagent to samples and standards, absorbance was measured at 543 nm. The color reagent was prepared by adding 800 mL water to 100 mL 85% phosphoric acid and 10 g sulfanilamide. After complete dissolution of sulfanilamide, 1 g *N*-(1-naphtyl)-ethylenediamine dihydrochloride was added and mixed to dissolve. This was diluted with water to 1 L. For nitrate determination, the ultraviolet spectrophotometric screening method was applied at the wavelength of 220 nm. Sulfite determination was carried out by iodometric titration. Di-hydrogen phosphate was determined by vanadomolybdo-phosphoric acid colorimetric method. In this procedure, 35 mL of sample containing 0.05–1.0 mg P was placed in a 50-mL volumetric flask. Ten milliliters vanadate-molybdate reagent was added and diluted to the mark using distilled water. The absorbance of sample versus a blank at a wavelength of 400–490 nm was measured after 10 min.

For mixture of ions, electrical conductivity (μs/cm) was employed as the basis for calculation of ion concentration. The rejection (R_Ω) was calculated as:

$$R_\Omega = [1 - \Omega_P/\Omega_F] \times 100 \qquad (1)$$

where Ω_P and Ω_F are the conductivity of permeate and feed, respectively.

3 Results and discussion

The rejections were tested for four solutions, each of which contained one of the following anions: di-hydrogen phosphate (80 ppm), sulfite (50 ppm), nitrite (50 ppm), and nitrate (80 ppm). The selected ranges of ion concentrations are three times higher than the ion concentrations in the raw waste water of a typical pharmaceutical plant. The rejection results are presented in Fig. 2 for various transmembrane pressures.

The rejection of anions obtained in this work was as follows:

$$H_2PO_4^- > SO_3^{2-} > NO_3^- > NO_2^-$$

Di-hydrogen phosphate anion exhibited the highest rejection. The rejection sequence was independent of the transmembrane pressure (see Fig. 2 for various pressures).

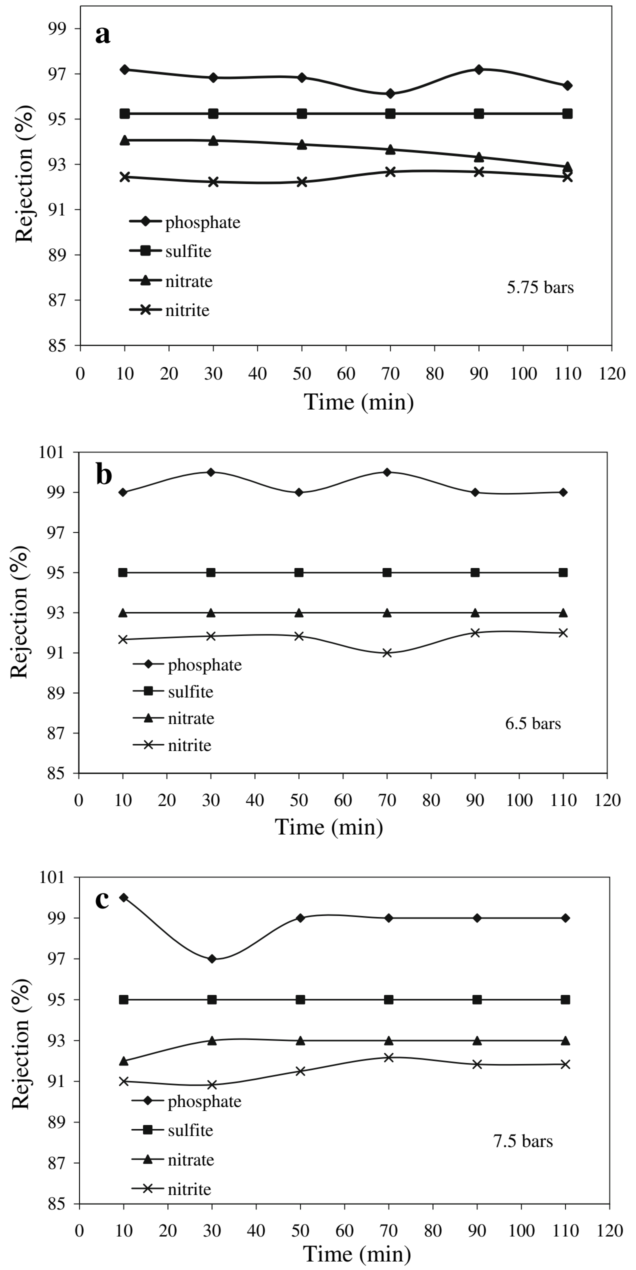

Fig. 2 Rejection of individual di-hydrogen phosphate, sulfite, nitrate, and nitrite ions using Filmtec TW30HP-4641 reverse osmosis element versus time **a** 5.75 bars, **b** 6.5 bars, and **c** 7.5 bars

The rejections of nitrate and nitrite ions were almost independent from the ionic concentration in the short period time (see Fig. 3 for details). The data indicate that the rejections of nitrate and nitrite ions (regardless of concentration) are around 94 and 92%, respectively.

To elucidate the effect of ions mixture on rejection, $H_2PO_4^-$, NO_3^-, and NO_2^- ions were mixed at different concentrations of 50, 80, and 110 ppm. The concentrations of three ions were equal for all cases. The results for rejection of the ions mixtures are depicted in Fig. 4.

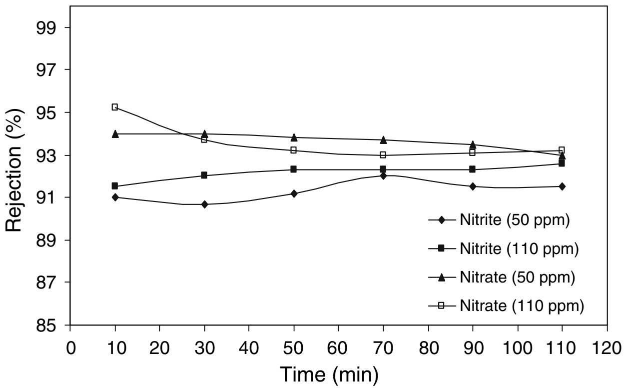

Fig. 3 Rejection of individual nitrite and nitrate ions using Filmtec TW30HP-4641 reverse osmosis element versus time for different concentrations

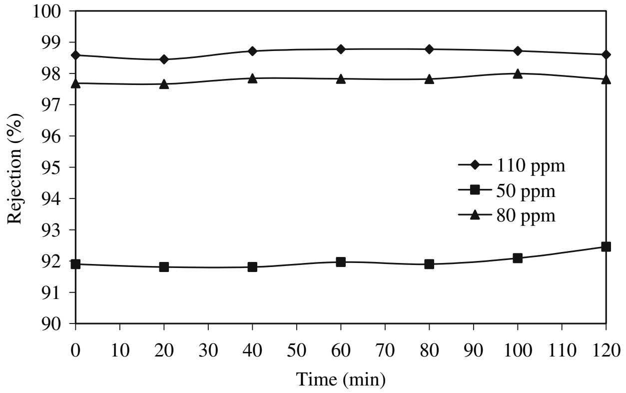

Fig. 4 Rejection of mixed ions using Filmtec TW30HP-4641 element versus time (equal concentration for all ions, 6 bars, 25 °C)

Apparently, the rejection is a function of ions concentration in the mixture (Fig. 5). The graphs indicate that at low (50 ppm) concentration there is no pronounced effect for the mixtures, i.e. the rejection is around 92% similar to the rejection for nitrate and nitrite (Fig. 5). However, at higher concentrations (80 and 110 ppm) the rejection was improved to 98% (for 80 ppm) and 99% (for 110 ppm). We demonstrated that the alteration of nitrate and nitrite concentrations exhibits no effect on rejection (see Fig. 3). This means the improvement in rejection of NO_3^- and NO_2^- ions is due to the presence of $H_2PO_4^-$. In other words when nitrate and nitrite ions were mixed with di-hydrogen phosphate at an appropriate concentration, the rejection was improved to 99%. This is an important conclusion as the removal of nitrate and nitrite ions from wastewater is a vital requirement for water and wastewater treatment.

Rejection is a function of solute molar flux which depends on solute permeability and presence of other solutes (Eq. 2).

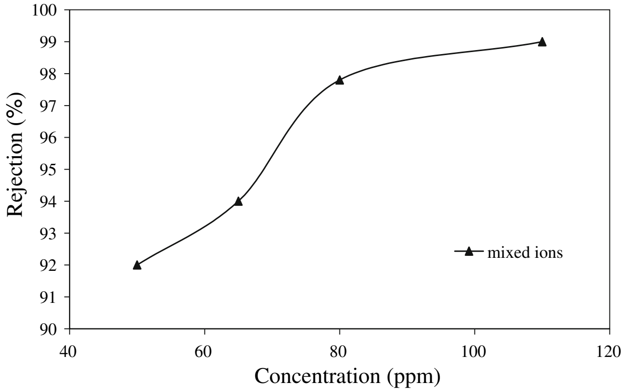

Fig. 5 Rejection of solution containing di-hydrogen phosphate, sulfite, nitrate, and nitrite ions using Filmtec TW30HP-4641 element versus average concentration (equal concentration for all ions, 6 bars, 25 °C)

$$J_S = (C_m)_{av}(1-\sigma)J_W + \frac{P_S}{l}(C_m - C_P) \tag{2}$$

where J_S is solute molar flux, $(C_m)_{av}$ is average of solutes concentration, σ is reflection coefficient, J_W is solvent flux, P_S is solute permeability, l is thickness of membrane, C_m is solute concentration, and C_p is solute concentration in permeate.

In summary, solute permeability depends on the properties of ions and membrane. The interaction between membrane and species may affect the membrane performance. Molinari et al. [3] studied the interactions between polyamide RO membrane and nitrate ions. They observed that copper nitrate was absorbed on reverse osmosis polyamide membrane during treatment a solution containing copper nitrate. The process was described principally to copper ion binding to the electronic lone-pair of membrane amino-groups by means of Lewis acid–base interaction which holds NO_3^- ions. The other salts like sodium nitrate did not exhibit the same interaction with membrane.

In the current study, a polyamide thin-film composite membrane was used for treatment of wastewater containing nitrate and nitrite ions. Polyamide has electronic lone-pair in amino group that is able to make a resonance structure with carbonyl segment (Fig. 6). The feed electrolyte solution containing potassium and di-hydrogen phosphate ions provide binding with membrane. The experimental data confirm this conclusion. The RO membrane was washed with purified water. This was followed by washing the membranes with 2.5% HNO_3. In the analyzed samples, di-hydrogen phosphate ions were detected. The strength of the complexation is a function of both the donor atom and the metal ion. Qualitative predictions about the strength of donor acceptor complexation can be made on the basis of the hard-soft-acid-base concept. The better matched the donor and acceptor, the stronger is the complexation. Moreover, the binding of potassium ion to the electronic

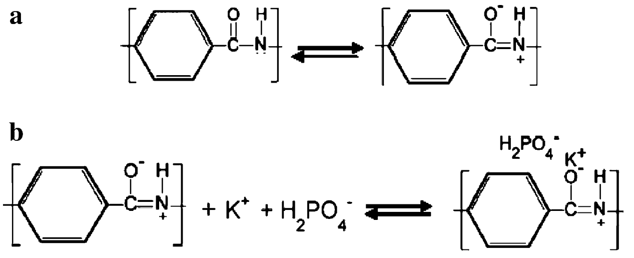

Fig. 6 Binding mechanism of potassium di-hydrogen phosphate on polyamide membrane

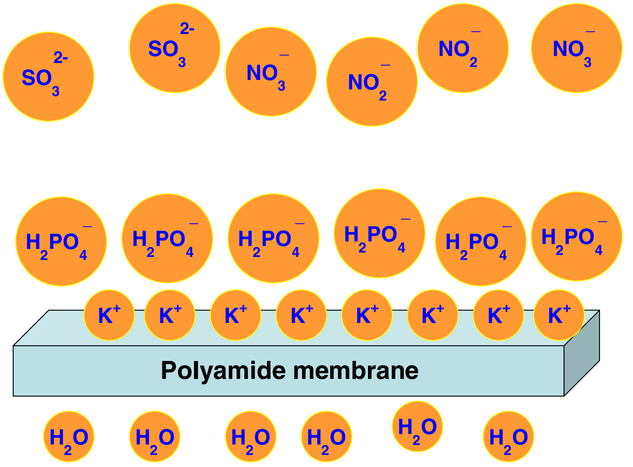

Fig. 7 Establishment of a negative layer on the surface of polyamide membrane

lone-pair of membrane holds $H_3PO_4^-$ ions on the basis of reported mechanism in Fig. 6. This provides a negative layer on the surface of the membrane (Fig. 7). The formation of this layer requires sufficient quantity of di-hydrogen phosphate. We demonstrated that the low concentration of this ion (50 ppm) has no effect on the rejection of nitrate and nitrite ions (Figs. 4 and 5). This means the proposed layer has not been established at 50 ppm. Diffusion of anions toward the membrane is reduced due to the electrostatic effects by this negative layer. This layer prevents the passage of anions through the membrane leading to an improvement in ion rejection.

4 Conclusion

Removal of individual nitrite, nitrate, and sulfite ions was around 91, 93, and 95% using Filmtec TW30HP-4641 reverse osmosis element. The presence of KH_2PO_4 increased the rejection of nitrite and nitrate ions up to 99%. The potassium ion in the feed solution provides binding with polyamide membrane. Subsequently the potassium ion binding to the electronic lone-pair of membrane holds di-hydrogen phosphate ion. This establishes a negative layer on the surface of the membrane. Diffusion of similarly charged anions through the membrane is diminished by the formed layer.

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