EFFECT OF PROCESS FACTORS ON THE PERFORMANCES OF REVERSE OSMOSIS PROCESS IN AN AQUEOUS RADIOACTIVE WASTE TREATMENT PLANT

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This paper has aimed at studying the effect of process factors on the performances of the reverse osmosis (RO) process in an aqueous low and intermediate level radioactive waste treatment plant. The experiments were performed using actual aqueous radioactive waste (ARW) containing various radionuclides and nonradioactive chemical species. Feed ARW pressure (2-4 MPa), pH (4.8-8.2) and temperature (25-45°C) were considered as process factors. Performances of polyamide Hydranautics SWC1-4040 membrane were evaluated in terms of its productivity and efficiency. Membrane productivity was expressed as permeate flux (20-140 L/(m²·h)) and its efficiency as permeate conductivity (150-270 μS/cm) and salt rejection (79-87%), as well as permeate cobalt concentration (0.1-0.9 mg/L) and cobalt rejection (43-95%).

Keywords: reverse osmosis, aqueous radioactive waste, permeate flux, salt rejection

1. Introduction

Due to a high efficiency, easy operation, compact equipment, simplicity in the process control, low capital and operating expenses, membrane technology is being used extensively for various separation and purification processes [1-10]. Reverse osmosis (RO) as a feasible separation process is a relatively young technology. Osmosis is a natural phenomenon in which a solvent (usually water) passes through a semipermeable barrier from the side with lower solute concentration to the one with higher solute concentration (Fig. 1a). Water

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continues to flow until the chemical potential equilibrium of the solvent is established (Fig. 1b). Osmotic pressure is the pressure required to stop water flow and reach the equilibrium.

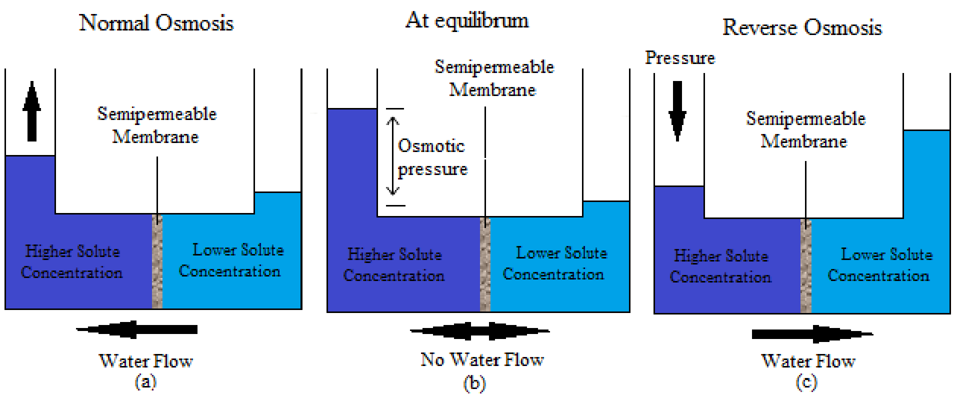


Fig. 1. Schematic of normal osmosis (a), equilibrium (b) and reverse osmosis (c) phenomena

If a pressure difference greater than the osmotic pressure difference is applied, the flow of water (solvent) is reversed, as it can be seen in Fig. 1c; as a result, separation of water from the solution occurs as pure water flowing from the high concentration side to the low concentration side. This phenomenon is termed reverse osmosis.

A RO membrane acts as a semipermeable barrier allowing a selective passage of a particular species (solvent) while partially or completely retaining other species (solutes). Chemical potential gradients across the membrane provide the driving forces for solute and solvent transport across the membrane. The solute chemical potential gradient is usually expressed in terms of concentration, whereas the water (solvent) chemical potential gradient is generally expressed as pressure difference across the membrane [11].

Three streams (and associated variables) of the RO membrane process are involved: *the feed water* enters the RO membrane under pressure (enough pressure to overcome osmotic pressure), the water molecules pass through the semi-permeable membrane resulting in the *permeate* (or *product*) *stream* while the salts and other contaminants are not allowed to pass and are discharged through the *concentrate* (or *reject*) *stream*, which goes to drain or can be fed back into the feed water supply to be recycled through the RO system. A few important parameters of RO proccess are further highlighted.

The water flux through the membrane, J_w, is defined by Eq. (1), where G_w is the volumetric or mass flow rate of water and A_m the membrane surface area.

$$J_w = \frac{G_w}{A_m} \qquad (1)$$

The solute mass flux, J_{ms}, is given by Eq. (2), where G_{ms} is the mass flow rate of solute.

$$J_{ms} = \frac{G_{ms}}{A_m} \qquad (2)$$

The solute rejection, R, is expressed by Eq. (3), where C_P is the permeate solute concentration and C_F the feed solute concentration.

$$R = 1 - \frac{C_P}{C_F} \qquad (3)$$

The quantity of water that passes through the membrane (the permeate) is evaluated in terms of water recovery, r, defined by Eqs. (4) and (5) for a batch and a continuous RO system, respectively, where V_F is the feed volume, V_P the permeate volume, F_F the feed flow rate, F_P the permeate flow rate and Δt the operating time.

$$r = \frac{\sum J_w A_m \Delta t}{V_F} = \frac{V_P}{V_F} \qquad (4)$$

$$r = \frac{J_w A_m}{F_F} = \frac{F_P}{F_F} \qquad (5)$$

The concentration factor, CF, is defined by Eq. (6) as the ratio between the solute concentration in the concentrate stream (C_C) and its concentration in the feed stream (C_F).

$$CF = \frac{C_C}{C_F} \qquad (6)$$

RO is used industrially for the production of drinking water from saline or brackish waters and is increasingly being used for the treatment of wastewaters. RO membranes have been recently applied to process the liquid radioactive waste from commercial nuclear power plants [12-14]. Because nearly all contaminants from a solution (dissolved gases and tritium being two exceptions) are rejected by RO, the high purity product water is usually of such low activity (sometimes after ion exchange polishing) that it is suitable for discharge into the environment. A RO system in the nuclear industry is usually a part of an integrated liquid waste treatment system and is used to replace or improve the existing evaporation and/or ion exchange technology.

Experiments were conducted at Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering (IFIN-HH) in a low and intermediate level radioactive waste (LILRW) treatment plant. Aqueous radioactive waste (ARW) was treated in order to determine the influence of different parameters, *i.e.*, feed pressure, pH and temperature, on membrane productivity and efficiency. Membrane productivity was evaluated by permeate volumetric flux and its efficiency was assesed by measuring permeate conductivity and Co (radioactive species) concentration in permeate (representing a measure of rejection of all salts and Co, respectively).

2. Materials and method

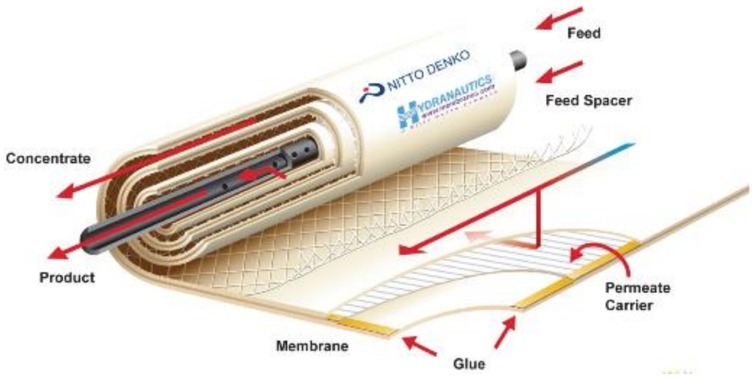
RO membrane element (Hydranautics SWC1-4040, Italy) used in this experiment is presented in Fig. 2 and its main characteristics are summarized in Table 1. The membrane consists of a compact base of 30–60 nm polyamide (PA), whose microstructure is shown in Fig. 3. Initial pH of ARW was adjusted using concentrated nitric acid and 30% sodium hydroxide solution.

Table 1

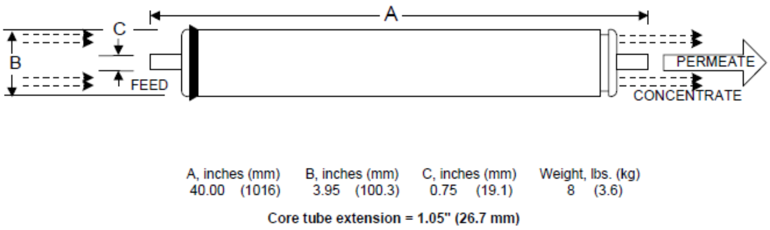
Membrane characteristics

Membrane type	Spiral wound
Membrane material	Composite polyamide
Membrane surface area	6.5 m^2
Permeate flowrate	4.5 m^3/day
Salt rejection capacity	Min. 99.5%
Working pressure	Max. 6.9 MPa
Permeate chlorine concentration	Max. 0.1 ppm
Operating temperature	Max. 45 °C
pH range	3-10
Feed water turbidity	1.0 NTU
Concentrate:permeate flow rate ratio	Min. 5:1

(a)



(b)



(c)

Fig. 2. Hydranautics SWC1-4040 RO membrane element (a), membrane structure (b) and geometric dimensions (c) [15].

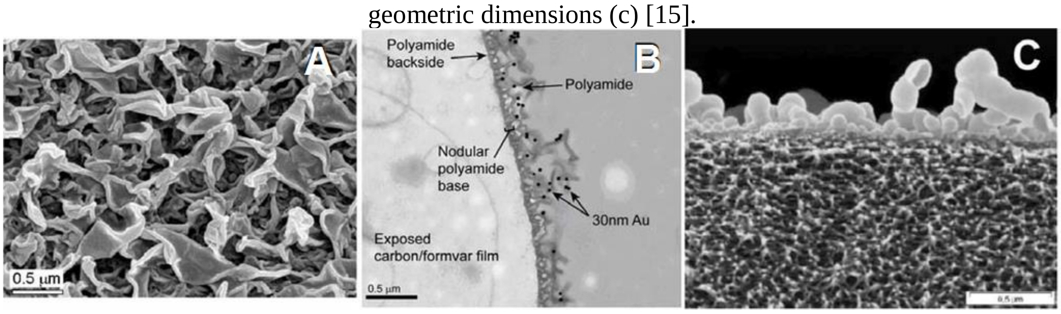


Fig. 3. Electron micrographs of the polyamide (PA) layer:
(**A**) structure of the PA surface [16]; (**B**) TEM cross section of an isolated PA layer [17];
(**C**) SEM cross section of a PA layer [18].

Feed, permeate and concentrate flow rates were measured with flowmeters. Conductivity was measured with Schott Lab 960 conductivity meter equipped with two conductivity cells, LF413T and LF313T, for high and low values, respectively. Co concentration was measured using Co^{60} as tracer. Co^{60} activity was determined by gamma spectrometry using a high resolution gamma-ray spectrometer, Canberra type, GENIE 2000 version 3.2 software and

Laboratory **SO**urceless **C**alibration **S**oftware (LabSOCS). RO process studied in this paper is included in the technological scheme shown in Fig. 4.

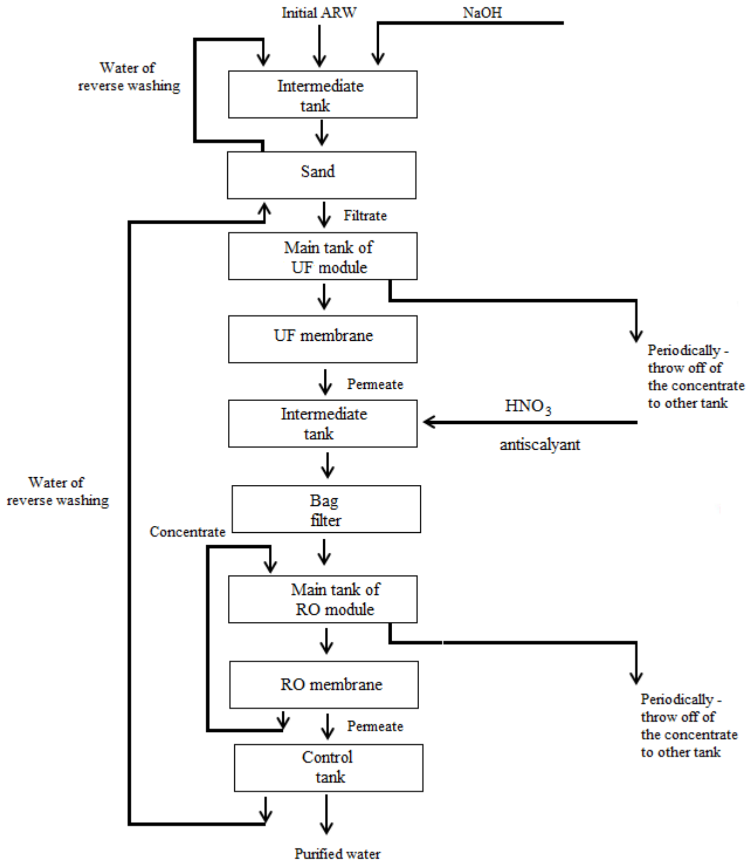


Fig. 4. Technological scheme for treating the ARW.

The permeate obtained after ultrafiltration module represented the RO module feed. It was characterized and its parameters are shown in Tables 2 and 3.

Table 2

. **Radioactivity concentration of RO module feed**

Radionuclide	Activity, Bq/L
Co-60	10.68
Cs-137	1.62
Am-241	1.90

Table 3

Physico-chemical parameters of RO module feed

No.	Parameter	Value	No.	Parameter	Value
1	pH	7.1	17	Al^{3+}	<0.01 mg/ dm^3
2	Conductivity	1240 μS/cm	18	S^{2-}	<0.1 mg/ dm^3
3	TDS	720 mg/dm^3	19	SO_3^{2-}	<1 mg/ dm^3
4	NH_4^+	<0.01 mg/ dm^3	20	As^+	<0.01 mg/ dm^3
5	NO_3^-	3.56 mg/ dm^3	21	Pb^{2+}	<0.01 mg/ dm^3
6	NO_2^-	<0.01 mg/ dm^3	22	Cd^{2+}	0.09 mg/ dm^3
7	SO_4^{2-}	137.1 mg/ dm^3	23	Cr^{3+} + Cr^{6+}	0.02 mg/ dm^3
8	Cl^-	100 mg/ dm^3	24	Fe^{2+} + Fe^{3+}	0.48 mg/ dm^3
9	Br^-	<0.01 mg/ dm^3	25	Cu^{2+}	0.46 mg/ dm^3
10	F^-	0.39 mg/ dm^3	26	Ni^{2+}	0.34 mg/ dm^3
11	PO_4^{3-}	3.43 mg/ dm^3	27	Zn^{2+}	0.16 mg/ dm^3
12	Ca^{2+}	76.13 mg/ dm^3	28	Hg^{2+}	<0.01 mg/ dm^3
13	Mg^{2+}	35.61 mg/ dm^3	29	Ag^+	<0.01 mg/ dm^3
14	Na^+	238.86 mg/ dm^3	30	Mo^{2+}	<0.01 mg/ dm^3
15	K^+	14.64 mg/ dm^3	31	Mn	0.21 mg/ dm^3
16	Li^+	0.03 mg/ dm^3	32	Co^{2-}	1.59 mg/ dm^3

The working pressure in the RO module ranged from 2 to 4 MPa, the temperature from 25 to 45°C and the pH values from 4 to 9. The permeate was collected in a tank and its flux was continuously monitored.

After each purification experiment, permeate samples have been taken and the conductivity and radioactivity of Co^{60} were measured.

3. Results and discussion

Effect of feed waste pressure

The most important operational parameter in a RO system is the feed pressure. The effect of pressure on the membrane performance was studied keeping all other parametres constant (pH=6.2, t=25 °C). Plots of permeate flux depending on operating time and pressure are illustrated in Fig. 5. The influence of feed pressure on conductivity and Co concentration of permeate, as well as on salt and Co rejection is shown in Figs. 6 and 7, respectively.

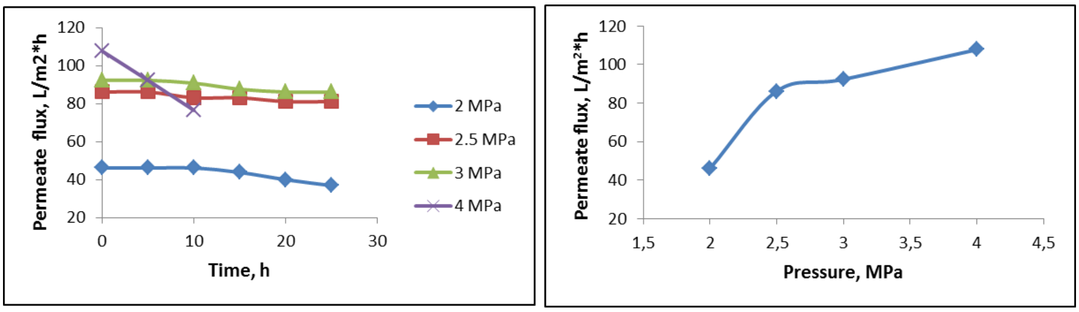


Fig. 5. Permeate flux depending on operating time and feed pressure.

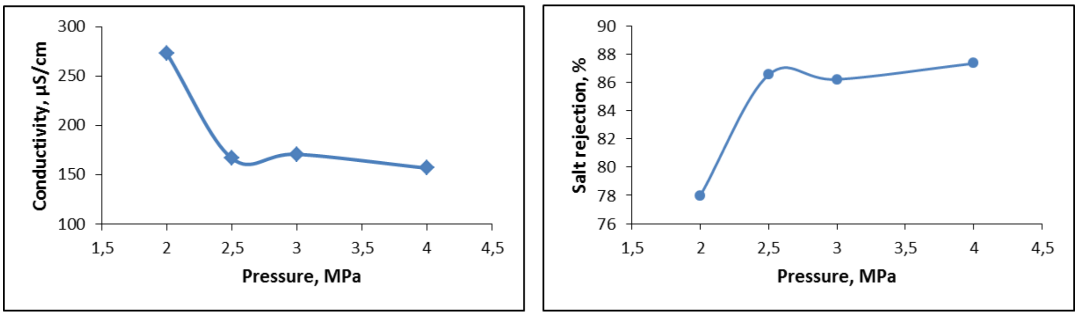


Fig. 6. Effect of feed waste pressure on permeate conductivity/salt rejection.

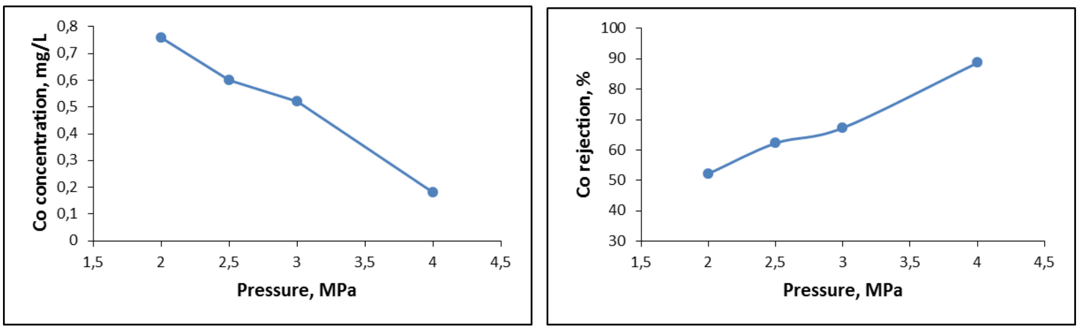


Fig. 7. Effect of feed waste pressure on Co concentration in permeate/Co rejection.

As depicted in these Figures, the permeate flux increases as the work pressure increases, but at higher pressure a more rapid decline in the flux occurs because the higher permeate rates at higher pressures led to enhanced transport of foulants to the membrane, greater compaction of the fouling layer and increased hydrodynamic resistance. Regarding the conductivity and Co concentration of permeate as a measure of salt rejection, their values decreased with an increase in the pressure. Pressure increases the driving force for the solvent and decreases osmotic pressure hence more amount of water can pass through the membrane resulting in an increase in salt rejection [19].

From these graphs it can be seen that maximum flux and salt rejection were obtained at 4 MPa, but the permeate flux decreases rapidly at this pressure value. No considerable effect can be observed if pressure varied in 2.5-3 MPa range. RO is a pressure-driven process and the main energy consumers in any membrane desalination plant are the high pressure pumps. An operating pressure of 2.5 MPa was selected in order to reduce the energy required for processing the feed waste.

Effect of feed waste pH

Experiments were conducted at p=2.5 MPa and t=25 °C under different pH levels of feed waste. The pH was ajusted with concentrated nitric acid and 30% sodium hydroxide solution and the feed waste was recirculated 2 h for homogenization. The variations of permeate flux depending on time and initial pH are shown in Fig. 8.

The effect of pH on conductivity and Co concentration of permeate, as well as on salt and Co rejection is shown in Figs. 9 and 10, respectively.

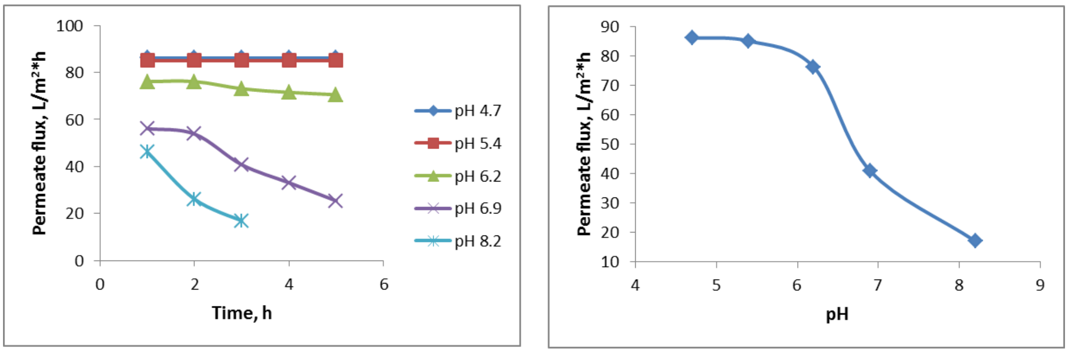


Fig. 8. Permeate flux depending on time and pH.

The results obtained have shown a decrease in time of the RO module treatment capacity in the case of feed waste with neutral or high pH. For a low pH (acidic conditions), the permeate flux remained almost constant. This finding could be explained by the fact that the low pH conditions prevent the precipitation of Ca^{2+}, SO_4^{2-} and CO_3^{2-} ions.

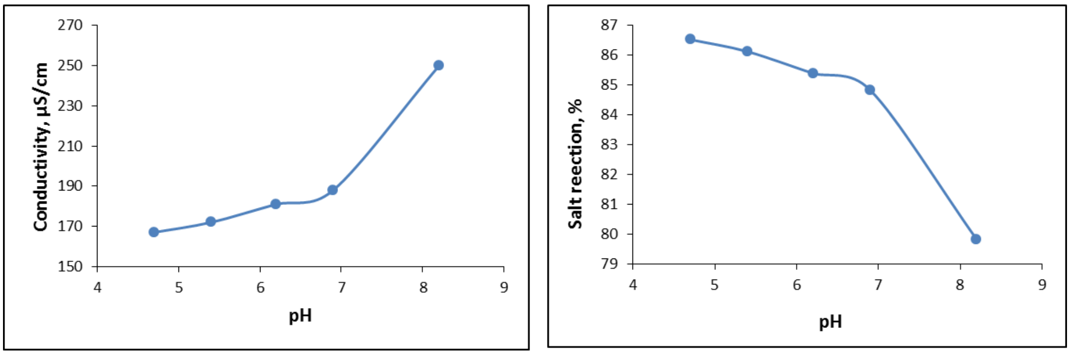


Fig. 9. Effect of feed waste pH on permeate conductivity/salt rejection

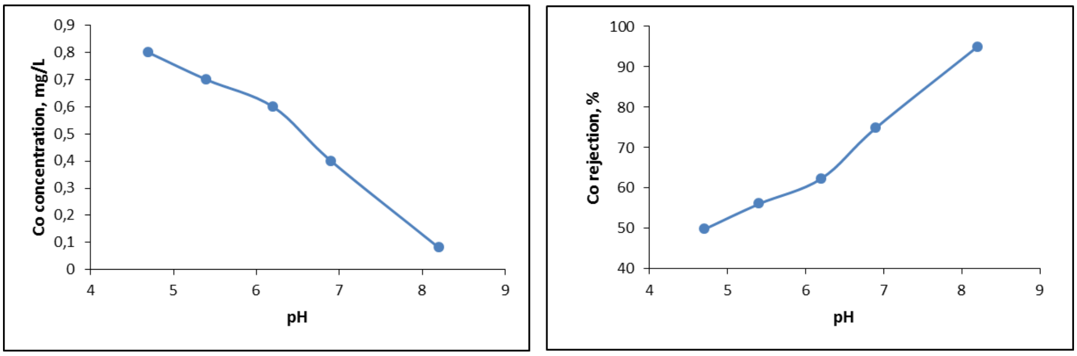


Fig. 10. Effect of feed waste pH on Co concentration in permeate/Co rejection.

It was observed that as feed pH increased, permeate conductivity and Co rejection also increased, while permeate Co concentration decreased.

The pH affects the separation performance by influencing the hydration and absorption capacity of solution on membrane. When a charged membrane is placed in a salt solution, a dynamic equilibrium is established [20-22]. The counter-ion of the solution, opposite in charge to the fixed membrane charge, is present in the membrane at a higher concentration than that of the co-ion (same charge as the fixed membrane charge) because of electrostatic attraction and repulsion effects. This creates a Donnan potential which prevents the diffusive exchange of the counter-ion and co-ion between the solution and membrane phase. When a pressure driving force is applied to force water through the charged membrane, the effect of the Donnan potential is to repel the co-ion from the membrane; since electroneutrality must be maintained in the solution phase, the counter-ion is also rejected and salt rejection occurs. As the fixed charge in polyamide membranes has the isoelectric point of the charged groups at a range of pH 3-4 [23], the membranes are negatively charged at pH>4 and the rejections of positive charged ions (see Table 2) decrease.

The rejection of Co ions at pH=4 significantly falls compared with pH>8. Co is present in feed waste as dissolved cobalt (Co^{2+}) and gives $Co(OH)_2$ at pH

>8. $Co(OH)_2$ stays in colloidal phase and is easily rejected by membrane. Therefore Co rejection increases at higher pH.

Effect of feed waste temperature

The effect of varying temperature on performance of RO membrane while keeping other parameters constant (*p*=2.5 MPa, pH=6.2) is shown in graphs from Figs. 11-13.

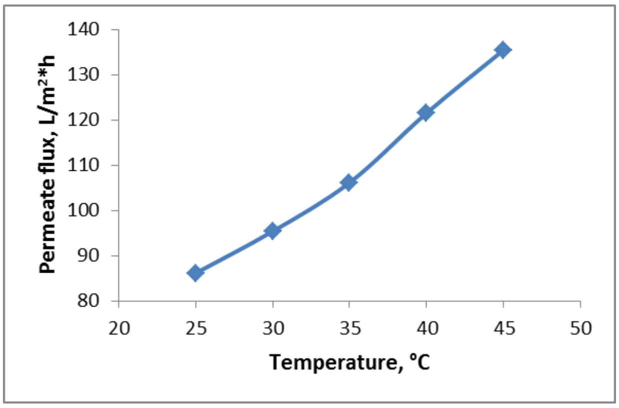


Fig. 11. Effect of feed waste temperature on permeate flux.

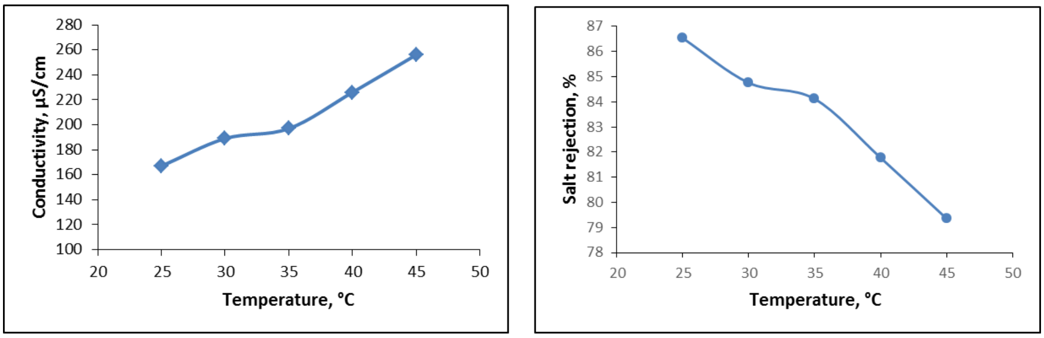


Fig. 12. Effect of feed waste temperature on permeate conductivity/salt rejection.

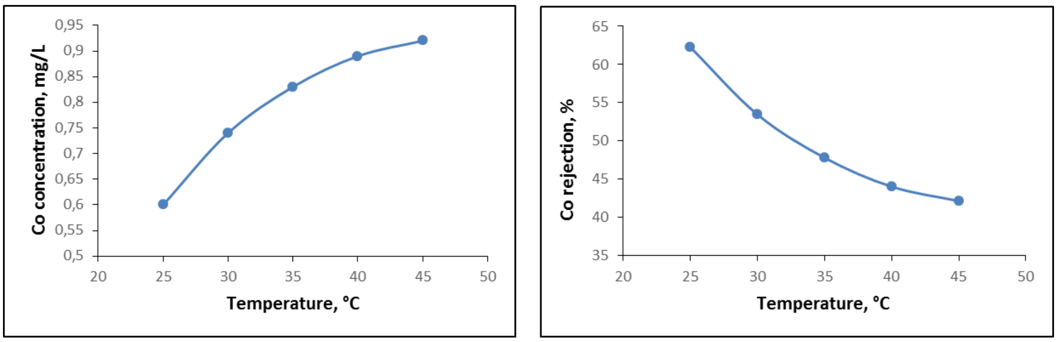


Fig. 13. Effect of feed waste temperature on Co concentration in permeate/Co rejection

It can be observed from Figs. 11-13 that as feed waste temperature increased, the flux, conductivity and Co concentration in permeate increased (salt rejection decreased). As temperature increases, viscosity decreases and water permeation rate through the membrane increases, but, also, the solubility of solute increases and higher diffusion rate of solute through the membrane is possible.

4. Conclusions

Practical experience in the development and operation of pilot and full-scale facilities utilizing RO process for treatment of liquid radioactive waste is considered to be of particular importance and interest. This research, but also the development and application of different new materials for treatment of liquid radioactive waste, aimed at improving the treatment efficiency.

Hydranautics SWC1-4040 RO membrane was tested for ARW treatment. The membrane was found to be sensitive to various operating parameters such as feed ARW pressure, pH and temperature. RO membranes have shown to be effective in rejecting dissolved species while maintaining higher flux, but the feed ARW requires pretreatment like ultrafiltration and pH adjustment.

Based on membrane performance, during these experiments has been gathered the key technical information and have been determined the acceptable limits for parameters variability for which treatment process meets a good performance. Long-term experiments should be conducted to study the fouling effects on the performance and economy of the process.

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