Innovative Hybrid Ion Exchange-Nanofiltration Membrane Process for Water Desalination

Dr. Hasan Al Abdulgader

OUTLINE

Introduction and background

Evaluation of sulfate/chloride ion exchange performance.

Membrane filtration of IX treated feed water.

Conclusion Remarks.

Future research.

INTRODUCTION

- Word population > 7,000,000,000 and increasing.
- Rapidly diminishing recourses of clean and potable water.
- Higher rate of water consumption in developing countries.
- Desalination is the one of the most important solutions for the water crises.
- Desalination accounts for >55% of potable water consumption in the country.
- Current desalination technologies is hampered by high energy consumption.

OVERALL IDEA

- Chloride ions are the prime monovalent anion in saline water (>87%).
- CI^{-} in feed water is exchanged with SO_4^{-2} using ion exchange resin (IXR).
- NaCl salt in the feed is converted to Na_2SO_4 .
- NF membranes is used desalinate IX treated water.
- NF concentrate used to regenerate IXR.



CHANGING WATER CHEMISTRY

Various commercial anion exchange resins have been tested for their exchange performance under different water salinities.

Tested parameters include:

 SO_4^{-2}/Cl^{-} exchange equilibrium.

Effect of resin dosage.

Effect of operating conditions (e.g. feed concentration and flowrate).

Physical and chemical characteristics of IXRs used in this investigation

Resin name	Ambersep 900SO₄	A500TLSO ₄	A400TLSO ₄	A850	Purolite A109	Purolite A149S	Purolite A111
Manufacturer	Dow Chemical	Purolite international	Purolite international	Purolite international	Purolite international	Purolite international	Purolite international
Physical form	Spherical beads	Spherical beads	Spherical beads	Spherical beads	Spherical beads	Spherical beads	Spherical beads
Matrix	Styrene divinylbenzene copolymer	Polyacrylic crosslinked with divinylbenzene	Gel polyacrylic crosslinked with divinylbenzene	Polyacrylic crosslinked with divinylbenzene	Polyacrylic crosslinked with divinylbenzene	Polystrene Crosslinked with Divinylbenzene	Polyacrylic crosslinked with divinylbenzene
Structure	Macroporous	Macroporous	Gel	Gel	Macroporous	Macroporous	Macroporous
Functional groups	Trimethyl ammonium	Quaternary Ammonium	Quaternary Ammonium	Quaternary Ammonium	Primary Amine	Secondary Amine	Tertiary Amine
lonic form as shipped	SO4=	SO4=	SO4=	CI [.]	Free Base	Free Base	Free Base
Total exchange capacity	1.00 eq/L (Cl ⁻ form)	1.15 eq/L (Cl ⁻ form)	1.3 eq/L (Cl ⁻ form)	1.25 eq/L (Cl ⁻ form)	1.0 eq/L (Free Base form)	1.7 eq/L (Free Base form)	1.7 eq/L (Free Base form)
Moisture holding capacity	60- 68% (Cl ⁻ form)	53- 58% (Cl ⁻ form)	48-54% (Cl ⁻ form)	57- 62% (Cl ⁻ form)	58 - 65 % (Free Base form)	30 - 35 % (Free Base form)	56 - 62% (Cl ⁻ form)
Shipping weight	690g/L (approx)	665 - 695g/L (approx)	680 – 705 g/L (approx)	680 – 730 g/L (approx)	660 - 685 g/ L (approx)	645 - 675 g/ L (approx)	640 - 680 g/ L (approx)
Particle size	-	425 - 850 µm	425 - 850 µm	300 - 1200 µm	425 - 1000 µm	425- 1200 µm	300 - 1200 µm
Uniformity coefficient	1.45	1.35	1.35	1.7	1.6	1.6	1.7
Maximum reversible swelling	Cl ⁻ -OH ⁻ : 25%	Cl ⁻ - OH ⁻ : 1 <i>5</i> %	Cl ⁻ - OH ⁻ : 20%	Cl ⁻ - OH ⁻ : 1 <i>5</i> %	Free form - CI ⁻ : 25%	Free form - CI ⁻ : 15%	Free form - Cl ⁻ : 40%

CI⁻/SO₄⁻² IX EQUILIBRIUM



Fig. 1 Concentration of Cl⁻ over time during IX treatment of 10,000 mg/L NaCl solution using 5 g resin Fig. 2 Removal of chloride ions from 32.0 g/L NaCl solution after IX treatment with Ambersep 900SO4 resin at various resin dosages. Contact time is 1 h and 42 h.

CI^{-}/SO_{4}^{-2} IX KINETICS



Fig. 3 Removal of Cl⁻ in (a) 1 g/L (b) 5 g/L (c) 10 g/L (d) 32 g/L NaCl solutions at various resin dosage using Purolite A500TLSO₄, Purolite A400TLSO₄ and Ambersep $900SO_4$ resins.

EFFECT OF AMINE FUNCTIONAL GROUP IN IXR



Fig. 4 $\alpha_{SO_4}^{Cl}$ separation factor for Purolite resins with different amino groups at various feed NaCl concentrations

Fig. 5 Chloride IX isotherms for Purolite AT500SO4 resin during treatment of NaCl solutions of different concentrations.

CI^{-}/SO_{4}^{-2} IX PERFORMANCE



Fig. 6 Breakthrough curves of chloride and sulphate ions during filtration of 5 g/L NaCl solution through a column with (1) Purolite A400TLSO₄, (2) Ambersep $900SO_4$ and (3) Purolite A500TLSO₄ resins.

Fig. 7 Breakthrough curves of the chloride and sulphate ions during filtration of NaCl solution through the column with Purolite A500TLSO₄ resin at various feed concentrations, g/L.

REGENERATION OF IXR 1 5000 0.8 4000 Relevent concentration Chloride (10 g/L) 0.6 Chloride (1 run) C, meq/l Sulphate (10 g/L) 3000 Sulphate (1 run) Chloride (28 g/L) Chloride (2 run) 0.4 2000 Sulphate (28 g/L) Sulphate (2 run) Chloride (3 run) Chloride (50 g/L) Sulphate (3 run) 0.2 1000 Sulphate (50 g/L) 0 0 5 10 15 20 25 30 0 0 8 10 12 2 6 Bed volume Bed volume

Fig. 8 Breakthrough curves of chloride and sulphate ions during filtration of 5 g/L NaCl solution through a column with (1) Purolite A400TLSO₄, (2) Ambersep 900SO₄ and (3) Purolite A500TLSO₄ resins.

Fig 9 Breakthrough curves of chloride and sulphate ions with regenerated Purolite A400TLSO4 resin during treatment of 10 g/L NaCl solution (three exhaustion runs).

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NF MEMBRANES CHARACTERISTICS

Fig. 10 Mean pore diameter of the studied membranes according to AFM data.

Fig. 11 Zeta potential as a function of the pH for NF270, NF90, BW30 and SW30 membranes.

NF270

NF90

BW30

FILTRATION OF SINGLE Na₂SO₄ Solutions

80

60

40

20

0

1000

Flux (L/m²h)



Fig. 12 Rejection of sulphate ions with NF270, NF90 and BW30 membranes at different concentrations of Na_2SO_4 solutions. Operating pressure is 6 bar. pH= 6.4. T= 22 °C.

Fig. 13 Membrane fluxes of NF270, NF90 and BW30 membranes at different concentrations of Na_2SO_4 solutions. Operating pressure is 6 bar. pH= 6.4.

 Na_2SO_4 concentration (mg/L)

5000

2500

10000

FILTRATION OF SINGLE Naci solutions



Fig. 14 Rejection of chloride ions with NF270, NF90 and BW30 membranes at different concentrations of NaCl solutions. Operating pressure is 6 bar. pH= 6.4. T= 22 °C.

Fig. 15 Membrane fluxes of NF270, NF90 and BW30 membranes at different concentrations of NaCl solutions. Operating pressure is 6 bar. pH= 6.4.

FILTRATION OF MIXED NaCL/Na₂SO₄ Solutions







Fig. 17 **Rejection of chloride ions** with membrane **NF270** during filtration of binary NaCl/Na₂SO₄ solutions at different total feed concentrations and NaCl/Na₂SO₄ concentration ratios. Operating pressure is 6 bar. pH= 6.4. T = 22 °C.

EFFECT OF pH

Table 3

Changes in permeate flux and anion rejection during the filtration of 2.5 g/L feed solution at different molar $Na_2SO_4/NaCl$ ratios through NF90 and NF270 membrane at various feed pHs. The flux and rejections are compared with ones at neutral pH = 6.3. Operating pressure is 6 bar.

Feed	рН	Changes in flux (%)	Changes in chloride rejection (%)	Changes in sulphate rejection (%)
2.5 g/L Na ₂ SO ₄ /NaCl	3	- 15.56	3.93	- 1.64
solution (50%– 50%)	4	-9.3	1.19	-0.15
	8	-2.19	6.38	0.5
	10	- 15.85	32.61	0.3
2.5 g/L Na ₂ SO ₄ /NaCl	3	-4.35	-56.07	-16.19
solution (90%–10%)	4	-2.27	-33.24	-1.98
	8	12.2	-0.26	0.41
	10	21.95	3.37	0.63
	Feed 2.5 g/L Na ₂ SO ₄ /NaCl solution (50%– 50%) 2.5 g/L Na ₂ SO ₄ /NaCl solution (90%–10%)	Feed pH 2.5 g/L Na2SO4/NaCl 3 solution (50%- 50%) 4 8 10 2.5 g/L Na2SO4/NaCl 3 solution (90%-10%) 4 8 10 10 3 10 3 10 10 10 10 10 10 10 10 10 10	FeedpHChanges in flux (%)2.5 g/L Na2SO4/NaCl3-15.56solution (50%- 50%)4-9.38-2.1910-15.852.5 g/L Na2SO4/NaCl3-4.35solution (90%-10%)4-2.27812.21021.95	FeedpHChanges in flux (%)Changes in chloride rejection (%)2.5 g/L Na2SO4/NaCl3-15.563.93solution (50%- 50%)4-9.31.198-2.196.3810-15.8532.612.5 g/L Na2SO4/NaCl3-4.35-56.07solution (90%-10%)4-2.27-33.24812.2-0.261021.953.37

CONCLUSION

- Fast kinetics of chloride-sulfate IX process.
- Higher solution concentration leads to higher separation factor ($\alpha_{SO_A}^{Cl}$).
- The higher the substitution of hydrogen atoms in amine functional group of AXR the higher chloride over sulfate selectivity.
- Exhausted AXRs were successfully regenerated using concentrated Na₂SO₄ solution.
- Both feed concentration and salt composition play a major role in rejection of ions by NF membranes.
- Electrostatic repulsion plays a main role in the rejection of Cl⁻ in NF270 membranes

RECOMMENDATIONS AND FUTURE WORK

- Detailed feasibility/economic study of the hybrid system.
- Evaluation of appropriate pretreatment.
- Study the effect of competing anions on the performance of chloride-sulfate exchange.
- Optimized and tailored IX and NF membrane materials.

THANK YOU