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A combined ion exchange–nanofiltration process for water desalination: I. sulphate–chloride ion-exchange in saline solutions

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HIGHLIGHTS

- Sulphate/chloride ion exchange in saline water has been studied both on laboratory and pilot scales.
- Sulphate–chloride exchange depends on the feed salt concentration and the nature of the functional group of the resin.
- Exhausted anion exchange resins were successfully regenerated using 0.2 M Na_2SO_4 solution.
- The osmotic pressure of sea water was significantly reduced after SO_4/Cl ion exchange.

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ABSTRACT

Removal of chloride ions from saline water with seven different ion-exchange (IX) resins in sulphate form has been studied both on laboratory and pilot scales. It was found that sulphate–chloride exchange is very fast in aqueous solutions and that the feed salt concentration and the nature of the functional group of the resin play an important role in this process. It was shown that the chloride/sulphate separation factor depends on salt content in feed water and the higher the substitution of hydrogen atoms in amine functional group of anion exchange resin the higher chloride over sulphate selectivity. Exhausted IX resins were successfully regenerated using 0.2 M Na_2SO_4 solution and multiple regeneration/saturation cycles proved that this did not affect the resin's performance on chloride ion removal. It was shown that the osmotic pressure of sea water was significantly reduced after SO_4/Cl ion exchange. Due to the drop of osmotic pressure lower energy consuming nanofiltration membranes compared with reverse osmosis membranes might be used for salty water desalination after IX treatment.

1. Introduction

A sharp growth in the worlds' population coupled with urbanization has resulted in a rapidly increased demand for fresh water [1]. A lot of efforts are focused on suitable methods to obtain freshwater by sea water or brackish water desalination and various desalination technologies, including thermal multi-stage flash distillation and reverse osmosis, which have been increasingly used to enhance a fresh water supply around the world [2]. However, the cost-effectiveness of these technologies is still hampered by high energy consumption [3]. Therefore the development of a technology capable of producing fresh water by desalting brackish and/or seawater at the lowest possible cost is of crucial importance.

In this work we have studied the sulphate–chloride exchange in saline solutions. If monovalent chloride ions of salty water convert into divalent sulphate ions using ion-exchange (IX), that would reduce the osmotic pressure of the treated feed and in turn would essentially reduce the energy required for further membrane desalination, because nanofiltration (NF) membranes, which efficiently reject the sulphate ions and operate at significantly lower transmembrane pressures compared with reverse osmosis membranes, can be used for water desalination [4].

Many researchers have tested IX resins for the removal of chloride ions, but in exchange of anions other than sulphate [5–8]. For example, the removal of chloride, nitrate and sulphate ions from aqueous solutions with a macroporous resin Amberlite IRN 9766 in hydroxyl form was studied by Dron and Dodi [5]. It was shown that Langmuir adsorption

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isotherms provide a good estimation of the sorption capacity on the contrary to Freundlich and Dubinin–Radushkevitch models.

The strongly basic ion exchanger Amberlite IRA-420 resin in OH form has been used for chloride ion removal from chloride-polyethylenimine solution at different temperatures to evaluate the possibility to apply the IX technology to convert the polyethylenimine flocculant in chloride form into an adhesive product for printing applications [6]. The equilibrium isotherms of chloride ions in aqueous solution on Amberlite IRA-420 have been obtained and the kinetic studies indicated that the chloride ions are slowly removed when the polyethylenimine is in solution due to the ionic pair formation.

The layered double hydroxides such ZnAl–NO_3 containing nitrate as the interlayer anion has been studied as an anion exchanger material to remove chloride ions from aqueous solution [9]. The effect of dosage of IX material, solution pH and temperature on the removal efficiency have been investigated. It was found that the influence of solution pH was not very significant in the range 5.0–8.0, and the rate of anion-exchange increases upon raising the temperature of aqueous solution.

Chloride–sulphate exchange for sulphate removal from the sea water fed to an evaporation plant by means of anion exchange resins has been studied by Boari et al. [10,11]. It was shown that the selectivity for the bivalent ion depends strongly on the basicity of the resin and the affinity of every resin for the sulphate ion increases with the dilution of the aqueous phase and with the equilibrium temperature. The obtained results showed that in heterovalent exchange processes an important role is played by the phenomena connected with the electrostatic interactions.

Direct sulphate–chloride ion exchange for removal of chloride ions from water has been studied by few investigators. Sarkar and SenGupta [12] illustrated that sulphate/chloride selectivity depends on degree of the substitution of hydrogen atom in the amine functional group of the anion exchange resin. For most of their experiments Purolite A850 anion-exchange resin of a gel type with quaternary ammonium functional group was used.

The aim of this work is to use various commercial anion exchange resins and test their performance in exchange with chloride ions at different water salinities. The IX studies were carried out in batch and continuous modes to investigate the sulphate–chloride exchange equilibrium, effect of resin dosage and operating conditions on the IX process and on the shape of breakthrough curves of the resins. For the first time we have used two mutually interlinked routes to study sulphate–chloride exchange in aqueous solutions, which included both the experimental studies on a laboratory scale and further scaling up and optimization of a pilot scale IX system.

2. Materials and methods

2.1. IX resins

Seven IX resins, Purolite A500TLSO$_4$, Purolite A400TLSO$_4$, Purolite A850, Purolite A109, Purolite A149S, Purolite A111 and Ambersep 900SO$_4$ which contain quaternary, tertiary, secondary and primary aminogroups in the polymer matrix have been used in this work. The characteristics of the resins are presented in Table 1.

It should be mentioned that Purolite A500TLSO$_4$, Purolite A400TLSO$_4$ and Ambersep 900SO$_4$ resins are available in SO_4^{2-} form, while Purolite A850 resin was shipped in Cl^- form and it was transferred to SO_4^{2-} form by treatment with 2 M H_2SO_4.

Purolite A109, Purolite A149S and Purolite A111 resins were provided in free base form and according to a procedure suggested by the manufacture the resins were treated with 5 wt.%. Na_2SO_4 and washed with distilled water to convert the resin from free base to sulphate form.

Purolite A500TLSO$_4$, Purolite A850, Purolite A109, Purolite A149S, Purolite A111 and Ambersep 900SO$_4$ are macroporous resins, while Purolite A400TLSO$_4$ is in a gel form.

2.2. Batch studies with IX resins

The batch studies with IX resins were performed using NaCl solutions of various concentrations, considering that sodium chloride (i.e. Na^+ and Cl^- ions) is the primary constituent of brackish water or sea water. NaCl stock solution (32.0 g/L) was prepared by weighing and dissolving an appropriate amount of NaCl salt in Millipore-Q water. The testing solutions were prepared by an appropriate diluting of the stock NaCl solution. The pH values of the solutions were about 7, as was measured with a JenWay 3540 pH metre.

For batch IX studies, weighted amounts of air-dried sulphate-forms of the resins were added in NaCl solutions with concentrations of 30–550 meq/L. Then the samples were agitated with a shaker (Innova 44, New Brunswick Scientific) at a constant speed of 150 rpm for 0.1–24.0 h at room temperature. With time, 0.5–1.0 mL aliquots were periodically collected and analyzed to determine contents of Cl^- and SO_4^{2-} ions in the probes using an ion chromatograph (Dionex IC900) with AS14A (4 mm) anion-exchange column.

The removal efficiency of Cl^- ions with IX resins was calculated as:

$$\text{Removal efficiency} = [(c_0 - c)/c_0] \times 100\%,$$

where c_0 and c are chloride concentrations (mg/L) in the solution before and after IX treatment.

2.3. Column studies with IX resins

Column IX tests were performed to elucidate a shape of breakthrough curves of IX resins and to evaluate the effect of operating conditions for optimization of SO_4^{2-}/Cl^- exchange process. A glass chromatographic type column with an internal diameter of 2.0 cm and the column aspect ratio (height: width) of 20:1 was used for these experiments. The feed solution was delivered to the column using a peristaltic pump (Watson-Marlow 101 U/R) at a flow rate of 0.12–0.45 mL/s. From the outlet of the column, the effluent fractions of 20 mL each were collected and analyzed with IC.

2.4. Pilot scale IX system

To progress the experimental work to pilot scale trials a pilot scale IX system has been designed and built. The process and instrumentation diagram (P&ID) of the designed IX system is presented in Fig. 1. The system is constructed from polyvinylchloride pipe work and two 100 L

Table 1
Physical and chemical characteristics of IX resins used in the study.

IX resin	Polymer matrix	Functional group	Shipped form	Resin particle size
Purolite A500TLSO$_4$	Polyacrylic crosslinked with divinylbenzene	Quaternary ammonium	SO_4^{2-}	425–850 μm
Ambersep 900SO$_4$	Polystyrene crosslinked with divinylbenzene	Trimethyl ammonium	SO_4^{2-}	300–1200 μm
Purolite A400TLSO$_4$	Polystyrene crosslinked with divinylbenzene	Quaternary ammonium	SO_4^{2-}	425–850 μm
Purolite A109	Polystrene crosslinked with divinylbenzene	Primary amine	Free base	425–1000 μm
Purolite A149S	Polystrene crosslinked with divinylbenzene	Secondary amine	Free base	425–1200 μm
Purolite A111	Polystrene crosslinked with divinylbenzene	Tertiary amine	Free base	300–1200 μm
Purolite A850	Polyacrylic crosslinked with divinylbenzene	Quaternary ammonium	Cl^-	300–1200 μm

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