Desalination 357 (2015) 131–139

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Study of a new process for the efficient regeneration of ion exchange resins

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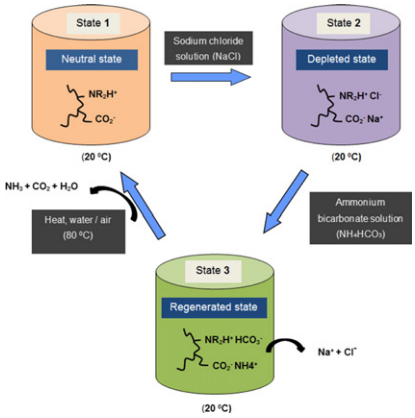
HIGHLIGHTS

- A novel process of ion exchange regeneration was developed and evaluated.
- Thermal regeneration may be linked to resin configurational changes.
- Ammonium bicarbonate solutions form the basis of reversible regeneration systems.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 July 2014
Received in revised form 17 October 2014
Accepted 21 November 2014
Available online 27 November 2014

Keywords:
Desalination
Ion exchange
Sirotherm resin
Sorption
Regeneration
Ammonium bicarbonate

ABSTRACT

Mixed bead resins comprising weakly acidic (carboxylic acid) and weakly basic (tertiary amine) groups were produced with properties similar to the thermally regenerable Sirotherm resin. This resin typically had a capacity of about 0.5 mmol NaCl per gram and the sorption isotherm was found to be consistent with the Langmuir equation. The resin could be partially regenerated by heat (80%) and water washing (40%) as the ion sorption capacity was much reduced on heating to 80 °C. However, the resin could be completely regenerated by a combination of heat and pre-washing with concentrated ammonium bicarbonate solution. On heating to 60 °C or more the bicarbonate salt completely decomposes and can be removed from the resin as carbon dioxide and ammonia gases. These initial results suggest that this type of ion exchange resin could be used in a continuous process where the regeneration salt (ammonium bicarbonate) is thermally decomposed, collected and re-used to improve the efficiency of regeneration.

1. Introduction

Most commercial desalination processes are currently achieved by two main methods: reverse osmosis (RO) membrane filtration and thermal evaporation/condensation. Both methods have considerable technical problems. Seawater reverse osmosis (SWRO) processes require high pressure pumping (up to 65 bar) and use expensive specialised membranes [1,2] which only last typically for about 5 years [3]. In addition the seawater feed has to be pre-treated to prevent fouling of the membranes. Thermal methods require the application of large quantities of thermal energy to overcome the large enthalpy of

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http://dx.doi.org/10.1016/j.desal.2014.11.024
0011-9164/

vaporisation of water and so are often dependent on waste heat from power stations and other industrial plants [4].

Mixed bed ion exchange (IEX) resins have been used for many years to remove scale-forming ions such as Ca^{2+} and Mg^{2+} from feed water and to produce distilled quality water from tap water. They can also be used for the desalination of fairly concentrated brackish water, without the need for high pumping pressures, extensive pre-treatment or high thermal energy input. However, the ion exchange process is limited by the depletion of the resin and the need for large volumes of acid and base solutions for their regeneration. In this work a novel combined process of thermal and chemical mixed bead ion exchange regeneration was developed and evaluated.

Desalting using ion exchangers requires the continuous removal of the adsorbed salt ions using large volumes of mineral acids and bases. For example, it has been found [5] that for the removal of one equivalent of salt, 1.2–3 equivalents of mineral acid and 1.3–2 equivalents of base have to be used. Because of this such desalting processes result in high operating costs and create substantial volumes of by-product saline waste and require high levels of acid and base consumption. To overcome these issues new methods to regenerate ion exchange resins by other means, such as heat energy (Sirotherm process), electrical energy (electrodialysis) or mechanical energy (piezodialysis) have been studied [6–10]. The "Sirotherm" process [6] was developed by the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Melbourne, Australia. This process was originally based on the use of a physical mixture of weakly basic and weakly acidic ion-exchange resin beads. It was later employed for resins containing both weak acid and weak base components within each bead in the so-called 'plum pudding' structure [7,8]. These resins are thermally regenerable, that is, they are capable of removing salts from an aqueous solution by sorption at ambient temperatures and at higher temperatures their sorption capacity is significantly reduced [11].

The Sirotherm process has been used and studied with many different types of mixed bead resins over the last 40 years [7,12–15]. A thermally regenerable composite resin of crosslinked polyacrylic acid and ethoxylated polyethyleneimine was used for water desalination more recently by Chanda et al. [16,17]. This type of resin, which is similar to that used in the present study, can be regenerated thermally with no apparent loss of capacity for up to 10 cycles of operation [16]. Sirotherm resins are composed of weak acid and weak base groups; thus during the exchange process a proportion of the Na^{+} and Cl^{-} ions remain in the solution, due to the hydrolysis of the weak resin salts. Therefore, high purity deionized water cannot be produced using these resins and they are suitable only for partial removal of salts. Sirotherm resins are typically usable only for partial removal of salts which have salinities in the range of 2000 and 3000 mg/l [16].

The ion adsorption equilibrium conditions in weak acid and weak base mixed bed resins vary greatly with changes in temperature, pH and the ionic strength of the solution in equilibrium with the resins [11,18]. In addition, the capacity of such resins to remove salts also depends on the polymeric structure of the resins, the acidity and basicity of functional groups, the ratio of acid to basic groups and the resin affinities for counter ions. Titration curve data was reported over a temperature range of 20 °C to 80 °C for carboxylic acid resins and weakly basic amine resins [11]. These studies showed that when the temperature is raised in the mixed bed system, which was in equilibrium with a salt solution, there is a transfer of protons from the base groups to the acid groups in the mixed bead resin to an extent determined by the titration curves of the resins [18].

That is, when amine resins are heated they become weaker bases; hence the amine resins have a plateau in the titration curves which are displaced to lower pH values with increasing temperature. Carboxylic acid resins have titration curves which demonstrate a reduced affect with temperature.

These composite resin beads also have a slightly greater adsorption capacity compared to other typical mixed bed systems but this capacity is lower than for chemically regenerated strong acid/strong base resin systems. Recent studies [16,17] on thermally regenerable composite (Sirotherm-type) resins showed that a weak acid/weak base mixed bead resin had a substantially reduced ion adsorption capacity at higher temperatures. Heating from 30 °C to 80 °C reduced the capacity by a factor of 8 [16].

Studies have been carried out employing ion exchange resins comprising both weakly acidic and weakly basic groups in the resin matrix, with chemical/thermal regeneration. While using weak acid and weak base groups, it was found that the desalting capacity of such resins was lower compared to when using two kinds of cation and anion individual ion exchange resins [19]. The same study found [19] that conversion of weakly basic ion exchange functional groups to the carbonate form would make it likely to maintain a higher level of desalting capacity.

Moreover, the presence of a weak base group in the mixed bed resin is known to enhance the ion adsorption properties of the mixed bed resin [20]. According to Weiss et al. [6], tertiary amines have a higher ability for salt sorption than primary and secondary amines in concurrence with carboxylic acid groups. Numerous studies have been carried out for the empirical determination of resin pair behaviour under different temperature, pH and ionic strengths [6,11,18,21]. In addition, the prediction of titration curve behaviour is also useful for resin synthesis design. Experimental studies have been carried out [11] on the behaviour of ion-exchange pairs.

Ethoxylated polyethyleneimine (EPEI) is considered a good source of tertiary amine groups, since it consists of large numbers of amine groups compared to polyethylene amine and studies have been carried out on this by Chanda et al. [22,23]. Further, the studies carried out by Weiss et al. [21] showed that variation of acid strength can be achieved by varying the cross linkage in the resin; by using either methacrylic acid or acrylic acid or their copolymers during the synthesis of carboxylic acid resins.

Bolto and Siudak [7] showed that resin bead sizes in the range 0.3–1.2 mm should be ideal for thermally regenerable ion exchange resins, which are composed of both acidic and basic groups together within the porous particles. Further, they showed that the presence of both acid and base groups within the same particle absorbed ions rapidly due to the close proximity of the groups, which shortens the diffusion path for the transfer of protons [24]. The "Plum pudding" resin structure, which is prepared by embedding microparticles of polyamines and microparticles of polyacids in a water and salt permeable matrix, has been discussed by Bolto and Jackson [8]; who also described the disadvantage of the presence of a high proportion of inert polymeric matrix material, which tends to limit the thermally regenerable capacity of a particular resin. Studies have been carried out by Hatch [25], Bolto and Jackson [8] and Chanda et al. [16] to overcome this issue.

Shimizu [19] stated that the particle diameter of the resin beads is a key point and it is desirable to be as small as possible, to enhance the rate of exchange capacity and suggested an optimum size of about 0.5 mm. Generally, the component particles are in the range 0.3–1.2 mm in particle diameter. The smaller sizes are used in fluidized beds but care has to be taken to prevent the dispersion and overflow of fine particles. The larger sizes are generally used in fixed bed systems, where the size distribution can determine the pressure loss across the bed [19]. Dissociation constants of weak acid/weak base groups also play a vital role in such desalting processes and these properties directly contribute to the elution capacity of a resin. The method discussed in Shimizu's work is generally effective at sodium chloride concentrations below 3000 mg/l.

Because of the need for large volumes of acid and base solution, the recovery of regeneration chemicals is an important aim, thus many groups have tried to develop suitable methods using a variety of techniques. Kadlec et al. [5] used weak acidic cation exchangers during the desalting process to recover ammonium ions using raised temperatures between 80 and 150 °C.

Concentrated solutions of ammonium bicarbonate have been used as a draw solution in Forward Osmosis (FO), which was developed [2] to