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Enhanced ion exchange capacity of polyampholytic resins

N.P.G.N. Chandrasekara, R.M. Pashley *

School of Physical, Environmental and Mathematical Sciences, University of New South Wales Canberra, ACT 2610, Australia

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ABSTRACT

Ion exchange (IEX) resins are commonly available as cationic or anionic resins but not as polyampholytic resins. This is probably because sequential acid and base washing cannot produce complete regeneration of polyampholytic resins with chemically attached anionic and cationic groups in close proximity. However, it has recently been shown that these resins can be completely regenerated by washing with concentrated ammonium bicarbonate (AB) solution followed by heating. Even so, the low IEX capacities of polyampholytic resins restrict their commercial applications. Here we report a novel process for increasing the IEX capacity of a typical polyampholytic resin by exposing Ni^{2+} and Ca^{2+} saturated resins to concentrated ammonium bicarbonate solutions followed by heating. This process was found to increase the IEX capacity by 4–5 times with a corresponding increase in observable pore size and BET surface area.

1. Introduction

Regeneration of ion exchange (IEX) resins is an important component in many applications, such as in water treatment, industrial wastewater treatment, metal ion recovery and heavy metal separation [1,2]. Cationic and anionic resins are commonly used in mixed bed IEX resins; although the ion exchangers need large volumes of acid and base solutions for their regeneration [3]. Because of this, several new methods of IEX resin regeneration have been studied, for example, using thermal energy (the Sirotherm process), electrical energy (electrodialysis) and mechanical energy (piezodialysis) [4–8]. A physical mixture of weak acid and weak base ion exchange resin beads were utilised primarily in the “Sirotherm process” [4]; developed by the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Melbourne, Australia and more recently in resins comprising both weak acid and weak base groups within the same bead, in the so-called ‘plum pudding’ structure [5,6]. These resins were regenerated thermally and they were capable of removing salts from an aqueous solution at higher temperatures compared to the salt sorbed at ambient temperatures, with a significant reduction of the sorption capacity with increasing temperature [9].

Different types of mixed bead resins were studied together with the Sirotherm process over the last 40 years [5,10–13]. Chanda et al. recently used a thermally regenerable composite resin, synthesised with crosslinked polyacrylic acid and ethoxylated polyethyleneimine, for water desalination [14,15]. A new process for the efficient regeneration of mixed bead resins was studied recently and it was reported that a chemical/thermal regeneration technique was capable of completely regenerating such composite mixed bead resins [16]. Moreover, the regenerant, concentrated ammonium bicarbonate solution, could be decomposed into ammonia and carbon dioxide gases and then collected and re-used, with the potential of substantially reducing chemical waste [16]. These results suggest that these types of resins could be used more widely. However, these composite polyampholytic resin beads have lower IEX capacities than the two kinds of strong acid and strong base, individual IEX resins.

Generally, mixed beds composed of weak acid (WA) and weak base (WB) resin beads have different ion adsorption equilibrium conditions with changes in temperature, pH and ionic strength of the solution [9,17]. Also, the IEX capacity of such resins depend on many other factors for instance the polymeric structure of the resins, the acidity and the basicity of functional groups, the ratio of acid/base groups and the resin affinities for counter ions [9]. Consequently numerous studies [4,9,17–20] have been carried out to synthesise resins with enhanced IEX capacity.

All of these factors could affect the IEX capacities of the polyampholytic resins, as well as the methods used during the chemical synthesis of these resins. Chanda et al. [21,22] have performed studies to enhance the polyampholytic resin capacity by introducing ethoxylated polyethyleneimine (EPEI) which is considered as a good source of tertiary amine groups. The presence of both acid and base groups in close proximity in the same bead enhance rapid absorption of ions by shortening the diffusion path for the transfer

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* Corresponding author.
E-mail address: r.pashley@adfa.edu.au (R.M. Pashley).

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of protons [23]. Bolto et al. has discussed the disadvantage of the presence of inert polymeric matrix material in a particular resin which limits the IEX capacity and a few studies have been carried out to overcome this issue [6,14,24].

The IEX capacity of a resin can be enhanced by the affinity of counter ions and the presence of carboxylic groups, which also help to coordinate directly with divalent metal ions other than its normal behaviour which is the exchange of protons with cations [25]. In general, divalent cations have a stronger affinity for carboxylic groups than monovalent cations.

Synthesis of polyampholytes were reported in the 1950s using free radical polymerization [26–32] and a study has been carried out on their zwitterionic properties [33]. In the present work a typical polyampholytic resin was synthesised and studied for its monovalent and divalent cation sorption capacity, both before and after regeneration using a combination of concentrated ammonium bicarbonate solution washing and heat regeneration. The use of AB solutions removes the need for consumption of acid and base chemicals and, in addition, the AB solution can be re-formed on collecting the decomposition gases, NH_3 and CO_2 [34,35]. The general term ‘sorption’ was used in this paper to describe the ion exchange process, which can occur within the resin beads by both adsorption and absorption.

2. Materials and methods

2.1. Materials

Acrylic acid (AA), ethylene glycol dimethacrylate (EGDMA) (crosslinking agent) and 1,1′-azobis(cyclohexanecarbonitrile) (ABCN) (initiator) were used for making crosslinked polyacrylic acid (XPAA). 80% ethoxylated polyethyleneimine (EPEI) in 37% aqueous solution and 25% glutaraldehyde (crosslinking agent) were used during this synthesis. All the chemicals were purchased from Sigma–Aldrich, Australia as reagent grade.

Ammonium bicarbonate (99%) was obtained from May & Baker LTD, Dagenham, England, 98% nickel(II) chloride and 99% calcium chloride dihydrate were obtained from Sigma–Aldrich, Australia. These salts were used as purchased.

2.2. Resin synthesis

The composite resin designated as (XPAA-EPEI-XG) was synthesised by free radical copolymerisation according to previously published procedures [16,14] as outlined schematically in Fig.1.

2.3. Resin analysis

Partially dried samples of the wet resin solid product (XPAA-EPEI-XG), were obtained using filter paper to remove excess water followed by 10 min air drying in a filtered air laminar flow cabinet. These samples were used for the sorption studies. The synthesised polyampholytic resin beads typically had a particle diameter in the range of 0.3–1.2 mm and a moisture content of about 40%. The moisture content of the resin samples were measured according to a previously published procedure [16] using an air oven at 104 °C for 18 h.

The concentrations of nickel, calcium and sodium ions in solution were analysed through atomic absorption spectroscopy (AAS) using a Varian, SpectrAA-400 (Test methods followed were ASTM D1886-03, D511-03 and D4191-03). The concentration of nickel and calcium retained in the resin were analysed by energy dispersive X-ray fluorescence spectroscopy (XRF) using a Shimadzu, EDX-800HS.

Resin morphology was studied using a scanning electron microscope (SEM) made by Hitachi, model number TM3000, using the bulk sample analysis technique. The pore volume of the resin was monitored by measuring the Brunauer–Emmett–Teller (BET) surface area using a Micrometrics, TriStar 3000. The carboxylic acid content and the amine content of the resin were determined by acid/base titrations and pH measurements as shown in Table 1.

2.3.1. Ion exchange properties

Equilibrium studies for the mixed bead resins was carried out by immersion in a series of $NiCl_2$ and $CaCl_2$ solutions (in the range 0.0001 M to 0.05 M, at pH 5.6) within tightly stoppered tubes at 20 °C, with continuous mechanical shaking for 15 h. 1.0 g of the wet resin was used in each sorption study. Here the resin samples were immersed in 25 ml of the $NiCl_2$/$CaCl_2$ solutions to determine the sorption levels. The extent of sorption was calculated using the initial and final concentrations of nickel and calcium for each sample. These equilibrium studies were performed twice for the mixed bead resins with the metal ion solutions at each concentration to ensure the accuracy of the results.

2.3.2. Resin regeneration

The synthesised mixed bead resin was used in regeneration studies, following the previously published procedure [16]. In this study the mixed bead resin in State 1, in Fig. 2, was exposed to 0.01 M $NiCl_2$/0.01 M $CaCl_2$ solutions and equilibrated for 15 h at 20 °C. After this time the resin was converted into State 2 (see Fig. 2). The resulting ‘exhausted’ resin was then repeatedly washed in distilled water at room temperature (20 °C) until the rinse water had an electrical conductivity close to that of distilled water.

The distilled water washed resin was then partially dried on filter paper and stored as a wet solid (with a determined moisture content, MC, of about 40 w/w%).

These washed resin samples were then re-equilibrated with 0.01 M $NiCl_2$/0.01 M $CaCl_2$ for 15 h at 20 °C and the extent of sorption was obtained. The percentage of regeneration was calculated by measuring the residual nickel/calcium concentrations in the equilibrated solutions.

Samples (each of about 1 g) of the exhausted and distilled water washed resin, in State 2, were heated to 80 ± 1 °C for an hour in 1 L of distilled water, with continuous stirring. Then the resin samples were repeatedly washed in distilled water at room temperature, partially dried in a filter paper and stored as a wet solid (MC about 40 w/w%). This resin was equilibrated again with a solution of 0.01 M $NiCl_2$/0.01 M $CaCl_2$ for 15 h at 20 °C. Then the residual nickel/calcium concentrations of the sorbate in the equilibrated solution was analysed to determine the extent of sorption and the percentage of regeneration.

Samples of the washed, exhausted resin in State 2 were immersed in 2 M ammonium bicarbonate solution for 15 h at 20 °C and then repeatedly rinsed with distilled water until the rinse water conductivity approached that of distilled water. The samples were then heated for an hour with continuous stirring at 80 ± 1 °C, followed by washing several times in distilled water and partially dried in filter paper and stored as a wet solid. The regenerated samples were used again for equilibrium studies with a range of $NiCl_2$/$CaCl_2$ solutions for 15 h at 20 °C. Then the residual nickel/calcium concentrations of the sorbate in the equilibrated solution was analysed to determine the extent of sorption and the percentage of regeneration.

In addition, samples exhausted by exposure to $NiCl_2$ solutions were regenerated using AB solutions followed by heating and were then equilibrated with a range of NaCl solutions for 15 h at 20 °C. The residual sodium concentrations of the sorbate in the equilibrated solutions was then analysed to determine the extent of sorption and the percentage of regeneration.