BDST modelling of sodium ion exchange column behaviour with strong acid cation resin in relation to coal seam water treatment

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ABSTRACT

Reverse osmosis is the dominant technology utilized for desalination of saline water produced during the extraction of coal seam gas. Alternatively, ion exchange is of interest due to potential cost advantages. However, there is limited information regarding the column performance of strong acid cation resin for removal of sodium ions from both model and actual coal seam water samples. In particular, the impact of bed depth, flow rate, and regeneration was not clear. Consequently, this study applied Bed Depth Service Time (BDST) models to reveal that increasing sodium ion concentration and flow rates diminished the time required for breakthrough to occur. The loading of sodium ions on fresh resin was calculated to be *ca.* 71.1 g Na/kg resin. Difficulties in regeneration of the resin using hydrochloric acid solutions were discovered, with 86% recovery of exchange sites observed. The maximum concentration of sodium ions in the regenerant brine was found to be 47,400 mg/L under the conditions employed. The volume of regenerant waste formed was 6.2% of the total volume of water treated. A coal seam water sample was found to load the resin with only 53.5 g Na/kg resin, which was consistent with not only the co-presence of more favoured ions such as calcium, magnesium, barium and strontium, but also inefficient regeneration of the resin prior to the coal seam water test.

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1. Introduction

Queensland has experienced a nearly exponential growth in coal seam gas (CSG) production and exploration in recent times [1,2]. During production of CSG, it is common for a significant amount of water to be produced when the coal seam is depressurized [3]. The large volume of water extracted presents a challenge to the industry as it is typically saline in character and usually not in a state which facilitates beneficial reuse [4,5]. Coal seam (CS) water has a distinct geochemical signature with total dissolved solids majorly ranging from 500 to 10,000 mg/L. The water mainly contains sodium chloride and sodium bicarbonate with the exact composition depending upon location of the wells [4]. In areas where marine derived deposits make up the coal formation calcium, magnesium and sulphate are also found [6]. In a study conducted in the USA of over 3000 wells, almost all the wells were outside of the allowable ranges for drinking water, irrigation and livestock consumption [7–9]. Therefore, treatment of CS water is of importance to the industry in relation to protection of the environment.

Previously, a method for water treatment in the CSG industry was the use of evaporation ponds [5]. However, this latter approach had drawbacks in terms of the potential for shallow groundwater damage, inherent inefficiency and the need for synthetic linings to prevent contamination of the local environment [10]. Therefore, evaporation ponds are not recommended and are being phased out [5]. One solution which has been reported by Tuwati et al. [11] involved addition of sulphuric acid to sodium bicarbonate rich solutions typical of those found in the CSG industry. However, this latter approach mainly decomposed bicarbonate species by reducing solution pH with the resultant evolution of carbon dioxide, and did not remove other contaminants such as sodium ions. Build-up of sodium and salts in soil has been noted when CS water was used for irrigation, and limitations in terms of allowable

Nomenclature

a	Modified BDST rate parameter ($h^{-1/2}$)
BV	Bed volume
C	Solute concentration at time t (mg/L)
C_0	Initial solute concentration (mg/L)
C_b	Breakthrough concentration (mg/L)
CS	Coal seam
CSG	Coal seam gas
k	Adsorption rate constant (L/mg h)
k_{Th}	Thomas rate constant (L/mg h)
m	Mass of resin (g)
N_o	Adsorptive capacity of the resin (mg/g or mg/L)
N_t	Bed capacity at service time t
q_{max}	Maximum loading of the ions on the resin (mg/g)
Q	Flow rate (L/h)
t_s	Service time (h)
u	Linear flow rate (cm/min)
V	Volume of water treated (L)
Z	Bed height (m)
Z_o	Critical bed depth (m)

electrical conductivity and sodium adsorption ratio of the solutions evaluated [12]. Growing of salt tolerant plants can be used to remove base cations from the water and soil, such as calcium, magnesium, sodium, and potassium. This process is known as bioremediation, with the absorbed salts being removed through animal consumption or harvesting [7]. An alternative to this latter approach is to grow micro-algae as a base for bio-fuel production [13]. Currently, reverse osmosis (RO) is the dominant technology for the treatment of large quantities of CS water [14,15]. It is effective when using high pressures to remove monovalent salts and other impurities through a semi-permeable membrane. This has the resultant effect of being relatively expensive due to the high pressures involved and the extensive pre-treatment operations required before the reverse osmosis stage [11,16].

Ion exchange (IX) has been demonstrated by Couperthwaite et al. [17] to be effective for the desalination of CS water at pilot plant scale using a combination of weak acid cation (WAC), strong acid cation (SAC) and weak base anion (WBA) resins. The commercial use of ion exchange for coal seam water treatment has also been reported by Dennis [18] in relation to use of Higgins Loop technology. Natural zeolites have been proposed for the desalination of coal seam water [19] but doubt has been expressed in terms of economics [20] and performance limitations due to slow diffusion of cations through the zeolite structure [21]. Consequently, an understanding of the interaction of the most dominant components in the coal seam water (sodium chloride and sodium bicarbonate) with ion exchange beds is of interest in relation to optimization of the process. Millar et al. [22] studied the equilibrium behaviour of sodium chloride solutions and coal seam water with a strong acid cation (SAC) resin. The bottle point methodology used for obtaining the equilibrium isotherm data was shown to be important, with the constant concentration approach the recommended option. The maximum capacity for sodium ion uptake was estimated to be 61.7–67.5 g Na/kg resin depending upon the initial concentration of sodium ions in solution. Similar loading values for sodium ions on the SAC resin were recorded when the equilibrium exchange behaviour of coal seam water was evaluated. Column studies suggested that the capacity of the SAC resin was 62.9 g Na/kg resin.

There is a growing opportunity for ion exchange technology for desalination of coal seam water that is either found in fields where smaller volumes of water are produced or which is of relatively low concentration (less than *ca.* 4000 mg/L), where the economics may be more attractive compared to reverse osmosis [15]. Consequently, information is required to guide process engineers as to the performance of ion exchange resins. At present there is minimal information published regarding the impact of flow rate upon the performance of strong acid cations in relation to removal of sodium ions from either simulated or actual coal seam water samples. Moreover, investigation of the behaviour of sodium ion exchange within columns which mimic the depth of beds found in industrial practice has not been reported. An important question to be answered concerns the effectiveness of regeneration procedures as there is a critical requirement in terms of process economics that not only minimum volumes of regenerant are used but also that the regeneration efficiency is optimized [23]. In addition, the viability of ion exchange also relates to the ratio of the volume of water treated until the breakthrough point relative to the volume of waste produced during the regeneration process. For example, Maul et al. [24] discussed the issue of disposal of regenerant waste and the potential impact with regards to process costs and environmental liability.

In relation to understanding the behaviour of sorption columns, the semi-empirical BDST equation has been applied by many authors [25–27]. The benefits and limitations of the BDST model have been elegantly explained by Singha and Sarkar [28], and it is apparent that it is a useful approach to estimating performance of sorption columns when operational parameters are varied. Consequently, this study expanded upon previous preliminary column studies of sodium ion exchange with strong acid cation resin [22], by examining multiple columns in series and application of Bed Depth Service Time (BDST) model for a range of flow rates ranging from 40 to 70 bed volumes (BV)/h. The effectiveness of regeneration using dilute acids was also investigated as was the amount of regeneration waste produced compared to the quantity of water treated each cycle. Overall, the aim of this study was to provide information which could guide future designs of ion exchange units for coal seam water treatment.

2. Materials and methods

2.1. Ion exchange columns

The column experiments were carried out using a bench scale ion exchange column system supplied by Miontec GmbH. The clear PVC columns were 57 mm inner diameter, and the amount of resin packed in the bed was pre-weighed and the height of resin loaded in the column measured. At either end of the bed was located a porous, plastic frit to restrict the flow of the resin. Typically, four columns were prepared with approximately the same bed depth to create a total depth of *ca.* 1.56 m. Notably, the bed depth used was in excess of the minimum recommended bed depth by Lanxess of 0.8 m [29]. The flow rate was controlled by a Masterflex II peristaltic pump with the flow rate being manually verified. Effluent samples were collected at the exit of each column, with pH (TPS, Aqua-pH meter) and conductivity testing (TPS, Aqua CP/A conductivity meter) performed at the inlet of the first column and outlet of the fourth column. The system was pressurised by means of a control value at the exit point of the system to inhibit the formation of "holes" in the resin beds due to carbon dioxide evolution from the decomposition of dissolved bicarbonate species.

2.2. Resins

A strong acid cation (SAC) resin, Monoplus S108H supplied by Lanxess was used for these experiments. The gel type resin based on a styrene-divinylbenzene copolymer was in an "H$^+$" exchanged