



Determination of an engineering model for exchange kinetics of strong acid cation resin for the ion exchange of sodium chloride & sodium bicarbonate solutions



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ABSTRACT

This study identified an appropriate engineering model which described the exchange kinetics of sodium ions with a strong acid cation resin. Synthetic resins have potential application for the demineralization of coal seam (CS) water prior to beneficial reuse. However, there is limited data regarding the kinetic behaviour of strong acid cation (SAC) resin for the removal of sodium ions, the most prevalent ions in the water collected from coal seams (produced water) during natural gas extraction. In particular, exchange kinetics need to be understood in relation to estimating how full scale columns of resin may perform. Kinetic analysis revealed that the exchange of sodium ions from both sodium chloride and sodium bicarbonate solutions with SAC resin reached equilibrium within minutes at ambient temperature. Optimal simulation of the kinetic data for both chloride and bicarbonate containing solutions was achieved by application of the Brouers, Weron and Sotolongo (BWS) fractal equation; and this should be used as the basis for development of an engineering model. The model parameters varied depending upon the ratio of resin to liquid employed in the tests, with rates showing substantial enhancement once an excess of resin exchange sites were present. The exchange process was apparently controlled in part by intraparticle diffusion, with three phases inferred for sodium chloride solutions and two for sodium bicarbonate solutions. Other rate limiting phenomena such as film diffusion appeared to play a role under certain conditions.

1. Introduction

The Queensland coal seam gas industry is producing liquefied natural gas (LNG) primarily for the export market [1,2]. The gas which is mainly composed of methane is usually trapped on the surface of the coal deposits by means of water pressure [3,4]. Consequently, in order to allow the gas to flow out of the coal seams the water pressure must be released by drilling of wells [5]. Upon reaching the surface the water is separated from the gas and this resource is usually termed “produced water” or coal seam (CS) water. Coal seam water typically contains dissolved salts in the concentration range of 200–10,000 mg/L [6–8]. Since Queensland routinely suffers drought conditions and a general lack of water availability, CS water can represent a significant and valuable resource for applications such as agricultural irrigation assuming issues associated with soil salinity and sodicity are addressed [9,10]. Analysis of CS water reveals that it is predominantly composed of sodium cations and chloride and bicarbonate anions [11]. Also commonly present are alkaline earth ions, dissolved silicate, iron, aluminium, sulphate, dissolved organics and algae [12,13]. Options

currently available commercially for treatment of the CS water (where required) prior to beneficial use include reverse osmosis [14,15] and ion exchange [16,17].

Ion exchange processes using resins has been employed to treat CS water in the Powder River Basin region of the USA as part of the Higgins Loop process [18,19]. Relatively little published literature exists regarding the performance of resins for treating CS water. The key issues to address for ion exchange processes are the kinetics, equilibrium and column behaviour of the system. Our research group has presented data relating to equilibrium and column behaviour of sodium ions from sodium chloride solutions and actual CS water samples [20]. Strong acid cation (SAC) resin was demonstrated to be very efficient at loading sodium ions (up to 67.5 g Na/kg resin) and reducing the concentration of sodium ions in column effluent to less than 5 mg/L. Equilibrium data has also been presented in relation to the exchange of sodium ions from mixtures of sodium chloride and sodium bicarbonate [21], which showed that sodium ions associated with bicarbonate ions were preferentially loaded on the resin. Corresponding kinetic studies which would complement previous studies have however been scarce.

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Drake [22] reported a kinetic investigation of sodium ion exchange from sodium bicarbonate solutions with a SAC resin, in relation to CS water applications in the USA. However, modelling of the kinetic data was limited and no studies of sodium chloride exchange were presented.

A knowledge of exchange kinetics is particularly valuable in the CSG industry context as models are required to determine the feasibility of ion exchange resin application. Hoffman et al. [23] described the importance of understanding the exchange kinetics of resins in a mixed bed system for drinking water purification, especially in relation to process limits introduced due to diffusional resistances. McKeivitt and Dreisinger [24–26] elegantly illustrated the development of an engineering model relating to the uptake of nickel ions by an imino-diacetate chelating resin. Engineering models focus on modelling system performance in a manner which facilitates process design and optimization of parameters. Engineering models are simpler in construction than detailed fundamental models and are more functional as they do not attempt to interpret the complexities and uncertainties involved in ion exchange units.

There exist many published papers referring to approaches to modelling kinetics of sorption processes such as the publications of Febrianto et al. [27], Plazinski et al. [28], Sen Gupta and Bhattacharyya [29] and Ho et al. [30] which provide excellent background information. More specifically, Dizge et al. [31] applied pseudo first and second order, Elovich and Weber-Morris models to interpret kinetic data from the exchange of nickel ions with a SAC resin. In this instance, the pseudo second order model was proposed to optimally simulate the experimental data and the exchange kinetics were determined to be significantly influenced by intraparticle diffusion. Chabani et al. [32] employed a similar suite of kinetic models as outlined by Dizge et al. [31] to evaluate the exchange of nitrate ions with an anionic resin. Again the second order kinetic expression was deemed to best fit the exchange data, with pore diffusion proposed to control the exchange process. Alternate models based upon various pore diffusion equations and un-reacted core expressions can also be used to analyse kinetic mechanisms in ion exchange processes [33], however the previously highlighted models are normally sufficient to initially differentiate variances between sorption systems.

In relation to the Queensland CS water context, the water composition has been found to be significantly different from corresponding waters in the USA. In particular, CS water in the USA is predominantly composed of sodium bicarbonate species [11] whereas in Queensland sodium chloride is a major component along with sodium bicarbonate [3]. It was our hypothesis that ion exchange using strong acid cation resin may be able to cost effectively desalinate coal seam water. However, an engineering model has not yet been developed for the exchange of sodium ions from mixtures of dissolved sodium chloride and sodium bicarbonate which are representative of coal seam water samples. Therefore, the major aim of this study was to evaluate a SAC resin for treating solutions comprising of either sodium chloride or sodium bicarbonate in order to obtain fundamental data which can facilitate understanding of the treatment of CS water using resin technology. Specific research questions to answer included: (1) what is the impact of resin/liquid ratio upon sodium ion exchange kinetics; (2) which kinetic expression optimally simulates experimental data; (3) which factor controls the exchange kinetics. Consequently, we examined the exchange of sodium ions from solutions of ca. 1260 mg/L sodium ions (a value typical for CS water) with H^+ -SAC resin and fitted the experimental data with a range of models reported in literature.

2. Experimental

2.1. Resins

A SAC resin (Monoplus S108 H) was supplied by Lanxess [34]. This material was a gel type resin in the hydrogen form based upon styrene-

divinylbenzene co-polymer with a stated ion exchange capacity of > 2 eq/L. The mean bead size was 0.65 mm, the bulk density 790 g/L and quoted water retention in the range 47–53 wt%. Upon replacement of H^+ species with sodium ions the resin contracted by 10 vol%.

2.2. Chemicals

Solutions were prepared using triply distilled water to which appropriate amounts of salt were added. Analytical reagent grade sodium chloride, sodium bicarbonate and concentrated hydrochloric acid (35 wt/v%) were supplied by Rowe Scientific.

2.3. Analysis

Solutions were analysed using an Agilent ICP-MS 7500CE instrument. Samples were typically diluted to a concentration between 10 and 50 mg/L by use of a Hamilton auto-dilutor equipped with both 10 and 1 mL syringes. Certified standards from Australian Chemical Reagents containing 1000 mg/L sodium ions were diluted to create a multi-level calibration curve. An external reference was used to monitor instrument drift and ensure accuracy of the results. Data was acquired using an integration time of 0.15 s with 10 replications.

2.4. Kinetic tests

Kinetic tests were conducted in the following manner. A known mass of resin was carefully weighed and then introduced to a large volume syringe. Concomitantly, 200 mL of aqueous solution was prepared comprising of accurate concentrations of sodium chloride or sodium bicarbonate, introduced to a suitable container and placed on a magnetically stirred plate. Concentrations of sodium chloride and sodium bicarbonate were chosen on the basis typical values encountered with coal seam water samples [6,7]. Under vigorous agitation (400 rpm) the resin was added rapidly to the solution and the conductivity of the solution continuously monitored using a fast response conductivity meter (TPS Aqua-C). Typically, the exchange process was complete within 8 min as evidenced by stabilization of the conductivity values. Measurements were recorded every 20 s and converted to concentration of sodium ions in solution by comparison to calibration curves deduced from preparing appropriate mixtures of sodium chloride and hydrochloric acid. ICP-MS analysis was also used to confirm sodium concentrations in the starting solutions and for the solution after ion exchange had reached equilibrium. Experiments were duplicated to ensure experimental veracity and all data shown represent the average experimental values obtained. The errors in the data were less than 5% in all cases.

2.5. Background theory

A range of models commonly used for kinetic studies of adsorption and ion exchange systems will be described. To facilitate analysis of the data fits and model parameters we used commonly accepted terms such as “rate constant”, pseudo reaction order *etc.* It is however emphasised that although the following models are widely used there are caveats which must be heeded when interpreting their meaning. For example, Tien [35] has noted that the Lagergren equation which is used in the majority of published sorption kinetic studies is actually equivalent to the Vermeulen-Hiester model which demonstrated that the rate parameter could be described by either a rate constant, mass transfer coefficient or indeed a combination of both [36]. Consequently, using this equation simply to fit data in a manner which allows use as an engineering model is more valid as any mechanistic inference is inherently unreliable. Simonin [37] issued a similar warning in relation to inferring whether a pseudo first or second order expression was a better fit of sorption kinetic data. Application of linearized versions of the kinetic models was deemed to introduce bias towards the second

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