Factors influencing kinetic and equilibrium behaviour of sodium ion exchange with strong acid cation resin

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ABSTRACT

This study reports an investigation of the ion exchange treatment of sodium chloride solutions in relation to use of resin technology for applications such as desalination of brackish water. In particular, a strong acid cation (SAC) resin (DOW Marathon C) was studied to determine its capacity for sodium uptake and to evaluate the fundamentals of the ion exchange process involved. Key questions to answer included: impact of resin identity; best models to simulate the kinetics and equilibrium exchange behaviour of sodium ions; difference between using linear least squares (LLS) and non-linear least squares (NLLS) methods for data interpretation; and, effect of changing the type of anion in solution which accompanied the sodium species. Kinetic studies suggested that the exchange process was best described by a pseudo first order rate expression based upon non-linear least squares analysis of the test data. Application of the Langmuir Vageler isotherm model was recommended as it allowed confirmation that experimental conditions were sufficient for maximum loading of sodium ions to occur. The Freundlich expression best fitted the equilibrium data when analysing the information by a NLLS approach. In contrast, LLS methods suggested that the Langmuir model was optimal for describing the equilibrium process. The Competitive Langmuir model which considered the stoichiometric nature of ion exchange process, estimated the maximum loading of sodium ions to be 64.7 g Na/kg resin. This latter value was comparable to sodium ion capacities for SAC resin published previously. Inherent discrepancies involved when using linearized versions of kinetic and isotherm equations were illustrated, and despite their widespread use, the value of this latter approach was questionable. The equilibrium behaviour of sodium ions form sodium fluoride solution revealed that the sodium ions were now more preferred by the resin compared to the situation with sodium chloride. The solution chemistry of hydrofluoric acid was suggested as promoting the affinity of the sodium ions to the resin.

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1. Introduction

Ion exchange remains a key technology, especially in the area of water and wastewater treatment. Of particular interest at present is the rapid growth of the coal seam gas (CSG) industry worldwide [1] especially in countries such as USA, India, China and Australia [2]. Extraction of the coal seam gas is achieved by reduction in water pressure which holds the gas in the coal cleats. As such, inevitably significant volumes of associated water are collected which contains salt concentrations that may require to be reduced to allow the water to be allocated for beneficial reuse options [3]. The primary contaminant is sodium ions which mainly arise from dissolution of sodium chloride and sodium bicarbonate species. Reverse osmosis has been predominantly installed in Australia for the desalination of coal seam water [4] whereas in the USA ion exchange processes have been successfully used [5]. The composition of coal seam water in the USA is typically different from that in Australia in terms of the relative quantities of sodium chloride and sodium bicarbonate present [5–7].

Ion exchange is attractive for coal seam water treatment because it may produce relatively small volumes of waste; is able to remove dissolved ions to very low levels (<1 mg/L); requires low energy input; and, is comparatively simple to operate. However, at present insufficient information exists regarding the performance of synthetic resins for coal seam water demineralization. Recently our research group has reported a study regarding the equilibrium and column behaviour of sodium ions with a strong acid cation resin supplied by Lanxess (S108H) [8]. Often, a strong acid cation

is placed in a fixed bed with either a weak or strong base anion resin located in a second column downstream to ensure major removal of both cations and anions from solution [9]. Millar et al. [8] found that the exchange of sodium ions from sodium chloride solutions and actual coal seam water was dependent upon several variables including solution normality and the presence of competing cations in solution. Drake has studied the kinetics of sodium ion exchange from contact of sodium bicarbonate solution with a strong acid cation resin [10]. It was reported that increasing sodium ion concentration or resin present in the kinetic tests accelerated the rate of sodium removal from solution with a pseudo first order relationship determined.

As alluded to above, the core criteria evaluated for ion exchange processes are typically kinetics [11,12], equilibria [13,14] and column behaviour [15,16]. However, concern has been expressed by several authors regarding the robustness of the approaches used. For example, Tien [17] lamented the significant number of manuscripts concerning sorption studies which are rejected for publication due to a range of outlined deficiencies. A lack of understanding of the subject matter, limited data interpretation, and formulaic approach to experimental design were all cited as problems. Chu [18] has similarly emphasised issues associated with a lack of rigour concerning the often quoted Thomas model which is used to analyse sorption column data. The realization of the challenges faced in sorption studies has also been elegantly explained by Lehto and Harjula [19] who illustrated factors which may interfere with the collection of valid equilibrium isotherm data. Literature evaluation reveals that Langmuir [20,21] and Freundlich [22,23] equations are routinely applied to equilibrium isotherm interpretation along with a random assortment of other models including Temkin [24], Redlich Peterson [25], Toth [26], Sips [27], Dubinin Astakhov [28], Dubinin Radushkevich [29], Khan [30] and Brouers Sotolongo [31]. Indeed, the papers by Hadi et al. [32], Rangabhashiyam et al. [33] and Hamdaoui and Naffrechoux [13,14] describe numerous two, three and four parameter isotherm expressions which can be applied to interpret sorption equilibria. Recent publications by our research group have focussed on the impact of factors such as the bottle-point method used for equilibrium isotherm generation [34], influence of the initial ratio of sorbate ions in solution to the resin mass and equilibrium loading of sorbate species [35] and impact of solution pH upon sorbate uptake [36]. Overall, it is apparent that collection of equilibrium isotherm data is not a trivial exercise.

Ion exchange kinetic studies typically accompany investigations of equilibrium performance [37]. Similar to the case with equilibrium isotherm investigations, the methodology employed for analysis of exchange kinetics in solution appears not to have a standard approach [38–40]. Nevertheless, the pseudo first order and pseudo second order models invariably are found in many ion exchange publications [37,41,42].

Notably, both adsorption and ion exchange methods tend to use common approaches for data interpretation despite the fact that ion exchange is inherently limited by stoichiometric considerations. Consequently, ion exchange isotherms for example are often represented in stoichiometric plots, albeit care must be taken to ensure that interpretations of the exchange process take into account the possibility of super-equivalent ion exchange [43,44], non-structural ion exchange [35], and accompanying adsorption processes [45]. The use of solution concentrations instead of activities is also a factor which can make the analysis of sorption behaviour challenging, as the use of molarities is only applicable when the solutions involved are highly dilute. Hence, it is perhaps understandable why confusion may exist as to the merits of each model and validity of information which it provides. Compounding this

latter situation, is the fact that many studies have focussed on use of linearized equations when fitting experimental data and also limited assessment of the statistical validity of this approach [46–48]. Several authors have reported the inherent flaws in linearizing equations such as El-Khaiary and Malash [49], Bolster and Hornberger [50] and Bolster [51], yet this practice is still commonplace [52,53].

The object of this paper was to answer the following problems: (1) what is the impact upon ion exchange behaviour by using different strong acid cation resins; this issue relates to reported studies that resins of the same class can exhibit different exchange behaviour [54]: (2) does the identity of the anion the uptake of sodium ions from solution; this problem relates to the fact that coal seam water samples contain other ions apart from chloride species: (3) what is the impact upon data interpretation of both kinetic and equilibrium sorption information when using linearized and non-linearized equations; this target is based upon the previous discussion of problems with data management in the literature.

2. Background theory

2.1. Kinetics

2.1.1. Pseudo first order
Lagergren [55] first described the application of a pseudo first order kinetic expression pertinent to sorption studies wherein the rate limiting step is usually a diffusion controlled process (Eq. (1)).

$$dq_t/dt = k_1(q_e - q_t) \tag{1}$$

Integration of Eq. (1) using appropriate boundary conditions results in Eq. (2).

$$q_t = q_e(1 - \exp(-k_1 t)) \tag{2}$$

Many authors have used a linearized version of Eq. (2) which can be represented by Eq. (3).

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{3}$$

2.1.2. Pseudo second order
The pseudo second order equation has been described in detail by Ho [56] and is represented as shown in Eq. (4).

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{4}$$

Or in a linear form more convenient for analysis of kinetic data as illustrated in Eq. (5).

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{1}{q_e}t \tag{5}$$

Eq. (5) is actually one of four expressions which have been reported as linearized versions of the pseudo second order kinetic model. In the notation of Ho [57], Eq. (5) is termed Type 1, with the remaining three forms displayed in Eqs. (6)–(8):

$$\text{Type 2}: \quad \frac{1}{q_t} = \left(\frac{1}{kq_e^2}\right)\frac{1}{t} + \frac{1}{q_e} \tag{6}$$

$$\text{Type 3}: \quad q_t = q_e - \left(\frac{1}{kq_e}\right)\frac{q_t}{t} \tag{7}$$

$$\text{Type 4}: \quad \frac{q_t}{t} = kq_e^2 - kq_e q_t \tag{8}$$