



An examination of isotherm generation: Impact of bottle-point method upon potassium ion exchange with strong acid cation resin



Graeme J. Millar*, Sara J. Couperthwaite, Chun Wing Leung

Science and Engineering Faculty, Queensland University of Technology, Brisbane, Queensland, Australia

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ABSTRACT

This paper relates to the importance of impact of the chosen bottle-point method when conducting ion exchange equilibria experiments. As an illustration, potassium ion exchange with strong acid cation resin was investigated due to its relevance to the treatment of various industrial effluents and groundwater. The “constant mass” bottle-point method was shown to be problematic in that depending upon the resin mass used the equilibrium isotherm profiles were different. Indeed, application of common equilibrium isotherm models revealed that the optimal fit could be with either the Freundlich or Temkin equations, depending upon the conditions employed. It could be inferred that the resin surface was heterogeneous in character, but precise conclusions regarding the variation in the heat of sorption were not possible. Estimation of the maximum potassium loading was also inconsistent when employing the “constant mass” method. The “constant concentration” bottle-point method illustrated that the Freundlich model was a good representation of the exchange process. The isotherms recorded were relatively consistent when compared to the “constant mass” approach. Unification of all the equilibrium isotherm data acquired was achieved by use of the Langmuir Vageler expression. The maximum loading of potassium ions was predicted to be at least 116.5 g/kg resin.

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1. Introduction

Ion exchange has been the subject of numerous books and literally thousands of publications [1–6]. At the heart of the study of ion exchange materials are typically three fundamental areas of investigation: kinetics [4], equilibrium tests [7,8] and column trials [9–11]. It is evident from inspection of the sorption literature that there exists considerable confusion regarding the models to apply to these latter areas of study and the information which can be reliably extracted from the experimental data [12]. Indeed, there are several examples of common mistakes made in terms of misunderstanding of equations [13], deficiencies in content [14] and errors in analysis [15]. In relation to equilibrium studies wherein the objective is to generate exchange isotherms, the most common experimental procedure is the so called “bottle-point” method [16]. Inspection of ion exchange publications reveals that there are actually at least two bottle-point methods commonly described. The first variant involves the dosing of equal masses of sorbent material to vessels which contain constant volumes of

* Corresponding author at: Science and Engineering Faculty, Queensland University of Technology, P Block, 7th Floor, Room 706, Gardens Point Campus, Brisbane, Qld 4000, Australia. Tel.: +61 07 3138 2377, mobile: +61 425 815 148.

E-mail address: graeme.millar@qut.edu.au (G.J. Millar).

solution comprising of various concentrations of the solute of interest [17–19]. For simplicity, we can term this method “constant mass” bottle-point test. The second bottle-point variant involves the addition of various masses of sorbent material to vessels which hold constant volumes of solution comprising a constant concentration of solute [20–22]. This method we call the “constant concentration” bottle-point test. Ayoob and Gupta [23] have argued that the “constant concentration” bottle-point approach is more realistic than the alternative “constant mass” method. Certainly, when examining complex wastewater solutions from industry for example, it is difficult to conceive how it is possible to conduct the “constant mass” approach as the only means to vary the solution concentration would be to dilute it and this procedure may introduce errors. Surprisingly, to the best of our knowledge there exists minimal comparison of the two outlined “bottle-point” methods and the factors which are important in terms of analysis of the resultant isotherm profiles. Of particular relevance is the determination of accurate values of the maximum loading of sorbates on the sorbent surface (q_{max}), as this value is commonly used to decide which material is optimal for treating various water contamination problems [24]. Confirmation of whether or not the equilibrium isotherm tests conditions employed, generates a profile which shows maximum loading of sorbate is also essential with respect to the latter statement.

Conclusions concerning which isotherm model fits the data best and what this information implies in terms of mechanism or the nature of the sorption process (homogeneous or heterogeneous) are also pertinent questions. All too often, authors have been content to determine the model which best fits their data without further discussion as to what this implies [25].

The ion exchange of potassium ions from solution is of interest in relation to various problems such as the purification of molasses wastewater [26], and treatment of produced water, for example from the coal seam gas (CSG) industry [27–29]. These latter brackish waters are typically comprised of sodium chloride, sodium bicarbonate mixtures with lesser amounts of potassium, calcium, magnesium, barium, strontium, sulfate and ammonium ions [28,29]. Potassium ion exchange behavior with cation exchange resins has not been studied in great detail. De Lucas et al. [30] reported kinetic studies relating to the removal of potassium ions from polyols using strong acid cation resins. Similarly, De Lucas et al. [31] evaluated the potential for strong acid cation resins to remove potassium ions from water–methanol–polyol mixtures and demonstrated excellent selectivity. Equilibrium studies of potassium loading on acid cation resins have indicated an endothermic exchange process occurred [32], which is highly favorable [33].

There are two approaches to interpretation of equilibrium isotherm data, those which are thermodynamic based [34,35] and those which are based upon descriptive sorption models [36,37]. As the goal of this publication was to discuss the mechanics of isotherm generation, focus was made upon the simpler sorption based equations such as the Langmuir [38], Freundlich [1] and Temkin [39] models as well as the lesser applied Langmuir Vageler [40,41] expression which provided valuable insight when comparing bottle-point methods. An exhaustive overview of the outlined sorption models is not provided here and the reader is referred to other sources such as Limousin et al. [42], Hamdaoui and Naffrechoux [43,44] and Petrus and Warchol [8]. A critical aspect of this paper was to also emphasize the need to analyse equilibrium isotherm data using non-linear least squares (NLLS) methods [45,46] and not just the more commonly applied linear least squares approach [47].

2. Experimental

2.1. Resin

A strong acid cation resin was purchased from Lanxess, termed “Monoplus S108 H” [48]. This resin is a gel type resin supplied in the hydrogen form with an ion exchange capacity of >2 eq/L. The mean bead size is 0.65 mm, the bulk density 790 g/L and water retention is 47–53 wt%. The resin was used as supplied in the “wet form” in order to avoid adverse effects to the resin structure induced by drying at elevated temperatures.

2.2. Chemicals

Synthetic water solutions were prepared using triply distilled water to which appropriate amounts of salt were added. Analytical reagent grade potassium chloride was supplied by Rowe Scientific.

2.3. Solution analysis

Samples were analyzed using an Agilent 7500CE Inductively Coupled Plasma Mass Spectrometer (ICP-MS) for integration times of 0.15 s with 10 replications. Samples were diluted to a concentration between 10 and 50 mg/L using a Hamilton auto-dilutor with 10 mL and 1 mL syringes. A certified standard from Australian Chemical Reagents (ACR) was diluted to form multi-level calibra-

tion curves. An external reference was used to monitor instrument drift and accuracy of the results.

2.4. Equilibrium studies – methodology

Briefly, resin was precisely weighed and placed in a series of 250 mL Nalgene flasks. In “bottle-point method 1” the concentration of the exchanging potassium ions in solution was varied and the mass of resin maintained at a constant value. For “bottle-point method 2” the concentration of the potassium ions in solution was kept at a constant concentration and the mass of resin was varied. Stock solutions were prepared by dissolving potassium chloride in triply distilled water. The equilibrium time was previously derived from kinetic trials that showed equilibrium was reached within 1 h for resin samples using a temperature controlled incubator (Innova 42R, New Brunswick Scientific). Exchange times ranged from two to 24 h for each resin test. The exchange temperature was 30 ± 0.1 °C with samples were agitated at 200 rpm. The supernatant was decanted from the Nalgene bottle then transferred to a centrifuge to further separate solid from liquid. Concentrations of the target ion remaining after the equilibration period C_e (mg/L) were then recorded and the equilibrium sorbate concentration in the resin phase q_e (mg/g) deduced from Eq. (1);

$$q_e = \frac{V}{m} (C_o - C_e) \quad (1)$$

where V is the solution volume (L), m is the mass of resin (g) and C_o is the initial concentration of the target ion (mg/L). To ensure experimental accuracy, experiments were normally repeated under identical conditions. Solution pH and conductivity were also monitored for each sample in order to provide deeper understanding of the exchange processes occurring.

3. Sorption theory

3.1. Langmuir Vageler

The Langmuir Vageler equation can be represented as in Eq. (2) [40,41].

$$q_e = \frac{(VC_o/m)q_{\max}}{((VC_o/m) + K)} \quad (2)$$

where V = volume of solution, C_o = the initial concentration of potassium ions in solution, m = mass of the resin, q_e = loading of potassium on the resin at equilibrium (mg/g), q_{\max} = maximum capacity of potassium ions on the resin (mg/g) and K is a constant called the “half value”.

3.2. Competitive Langmuir

The Competitive Langmuir expression which relates to ion exchange processes can be described as shown in Eq. (3) [49].

$$q_{eK} = \frac{kq_t C_{eK}}{C_o + (k-1)C_{eK}} \quad (3)$$

where q_{eK} represents the loading of potassium ions on the resin at equilibrium and C_{eK} is the concentration of potassium ions in solution at equilibrium. The system is described by a mass balance wherein $q_t = q_{eNa} + q_{eH}$ and $C_o = C_{eH} + C_{eNa}$.

3.3. Freundlich

The common representation of the Freundlich isotherm equation is revealed in Eq. (4) [50].

$$q_e = K_F C_e^{1/n} \quad (4)$$

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