Equilibrium studies of ammonium exchange with Australian natural zeolites

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ARTICLE INFO

ABSTRACT

This paper is concerned with the study of the equilibrium exchange of ammonium ions with two natural zeolite samples sourced in Australia from Castle Mountain Zeolites and Zeolite Australia. A range of sorption models including Langmuir Vageler, Competitive Langmuir, Freundlich, Temkin, Dubinin Astakhov and Brouers–Sotolongo were applied in order to gain an insight as to the exchange process. In contrast to most previous studies, non-linear regression was used in all instances to determine the best fit of the experimental data. Castle Mountain natural zeolite was found to exhibit higher ammonium capacity than Zeolite Australia material when in the freshly received state, and this behavior was related to the greater amount of sodium ions present relative to calcium ions on the zeolite exchange sites. The zeolite capacity for ammonium ions was also found to be dependent on the solution normality, with 35–60% increase in uptake noted when increasing the ammonium concentration from 250 to 1000 mg/L. The optimal fit of the equilibrium data was achieved by the Freundlich expression as confirmed by use of Akaikes Information Criteria. It was emphasized that the bottle-point method chosen influenced the isotherm profile in several ways, and could lead to misleading interpretation of experiments, especially if the constant zeolite mass approach was followed. Pre-treatment of natural zeolite with acid and subsequently sodium hydroxide promoted the uptake of ammonium species by at least 90%. This paper highlighted the factors which should be taken into account when investigating ammonium ion exchange with natural zeolites.

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1. Introduction

Despite intensive research the problem of excessive ammoniacal nitrogen discharge to aqueous environments still remains [1–3]. Ammoniacal nitrogen is defined as the sum of ammonium and ammonia species present in a wastewater, with the distribution of each moiety dependent upon parameters such as total ammonia/ammonium concentration, solution pH, temperature, and water salinity. Ion exchange technologies for ammonium removal from aqueous solution are attractive in that they are not only potentially very efficient but also the ammonium species can be recovered, and as such the process can be sustainable [4]. Alternate ammonia removal processes such as biological methods are destructive and have limitations in terms of resistance to system shocks; the capability to treat a wide and varying range of ammonium concentrations; and requirement for larger construction footprints than ion exchange [5–7].

In terms of ion exchange materials, zeolites [8] and synthetic resins [9] are the most obvious choices due to their abundance and availability. Synthetic resins have not been studied extensively in the open literature and this is presumably due to issues with selec-

tivity of the resins for ammonium ions in the presence of common competing ions in wastewater such as calcium, magnesium and sodium [9–11]. Zeolites can either be synthetic or naturally occurring. Synthetic zeolites display the advantages of high ammonium capacity and repeatable material quality but are invariably more costly on a per ton basis compared to natural zeolites [12–15]. Natural zeolites in contrast have lower cation exchange capacity, exhibit significant differences in quality, and possibly result in larger water treatment plant designs which can lead to increased capital and operational expenditure relative to synthetic zeolites.

Consequently, a technological solution of interest is to discover means to increase the efficiency of natural zeolites for ammonium exchange. To achieve this latter objective, it is initially of importance to understand the fundamentals of natural zeolite ammonium exchange processes such as the equilibrium uptake. Many studies have been reported wherein batch studies have been conducted in order to generate sorption isotherms [16–29]. Isotherms can either be interpreted by means of qualitative sorption models [30] or thermodynamic methods based upon the law of mass action [31,32]. With regards to ammonium exchange with natural zeolites, application of sorption models in the literature is prevalent. For example, Widiastuti et al. [16] deduced from their investigation of ammonium exchange with an Australian natural zeolite that the maximum loading was 6.3 g/kg zeolite and that the Freundlich model was the best fit. Malekian et al. [17] similarly looked at ammonium uptake on Iranian natural zeolite but reported that the three parameter Redlich–Peterson model was the most appropriate expression to represent the experimental data. Saltali et al. [28] applied linearized forms of the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich expressions to the removal of ammonium ions using Turkish natural zeolite. The Langmuir model suggested that the maximum loading of ammonium ions was 9.64 g/kg zeolite and from the r^2 values the Dubinin–Radushkevich equation optimally fitted the equilibrium data. Guo et al. [27] reported that both the Toth and Langmuir–Freundlich models exhibited higher values of the coefficient of determination, r^2, compared to either of the Langmuir or Freundlich expressions. However, it is not appropriate to compare three-parameter models with two parameter versions without further statistical analysis such as application of Akaikes Information Criterion (AIC) [33]. Tosun [23] applied a range of sorption models to the uptake of ammonium by clinoptilolite and concluded that the ammonium ions did not exchange with the zeolite surface but instead were physisorbed. Lin et al. [34] completed a detailed study of the exchange of ammonium and ammonia species with natural zeolite as a function of pH. Notably, they measured the ions released from the zeolite surface during the ammonium exchange process and showed that the ion exchange mechanism was solely involved at a solution pH less than 8. When the pH was raised above a value of 8, the overall uptake of ammoniacal nitrogen decreased due to reduced availability of ammonium ions and some evidence for molecular sorption of ammonia was apparent.

Regarding accuracy of fitting of experimental isotherm data, Karadag et al. [26] compared the use of both linear and non-linear regression methods to model data for ammonium exchange with a Turkish natural zeolite mineral. Not only did these latter authors conclude that non-linear regression procedures were more appropriate but also they noted that the Freundlich equation was the best experimental fit. Notably, only one error function was employed, yet it is important to recognize that a range of error functions can be used when performing non-linear fitting methods. For example, in the publication by Ho et al. [35] multiple error analysis techniques were reported: correlation coefficient; sum of errors squared (ERRSQ); hybrid fractional error function (HYBRID); Marquardt's percent standard deviation (MPSD); average relative error (ARE) and sum of the absolute errors (EABS). Gunay [29] has fol-

lowed the precise approach recommended by Ho et al. [35] in the study of ammonium exchange with Turkish natural zeolites. Six isotherm models were evaluated and the three parameter models were reported to be a better fit than the two parameter expressions, albeit, again a proper statistical interpretation was not performed.

Inspection of existing literature has revealed that a systematic examination of the application of sorption models to ammonium exchange with natural zeolites has not been completed. Indeed, there is a discrepancy in the optimum sorption model to apply and the relationship to zeolite identity. In addition, the use of non-linear fitting methods has not been widely used nor has a comprehensive investigation of error functions been performed. Another aspect which has received minimal attention is the methodology used to generate equilibrium isotherms for ammonium ion exchange with natural zeolites. Millar et al. [36–38] have demonstrated when using resins, the importance of not only choice of the correct bottle-point method but also the need to carefully select appropriate experimental parameters. A gap in our knowledge also exists as to the impact of modifying the exchanging ion on the natural zeolite, as often papers present results only for freshly received zeolite which is not representative of the practical situation after regeneration. Consequently, this paper presents a study of ammonium exchange with two natural Australian zeolites, and highlights the influence of bottle-point methods, the suitability of sorption models and impact of chemical modification of natural zeolites to improve ammonium uptake.

2. Material and methods

2.1. Zeolites

Zeolite mineral samples were obtained from both Zeolite Australia (ZA) and Castle Mountain Zeolites (CMZ). Each material was sieved to 0.5–1 mm, washed, and then dried at 110 °C to remove dust and excessive moisture prior to use. Both sorbents were supplied predominantly in the calcium form. Zeolite Australia also supplied acid modified zeolite which was then then treated with a solution of sodium hydroxide before ion exchange with ammonium solutions. A glass column of 0.052 m diameter was filled with an appropriate quantity of acid modified zeolite and a 1 M solution of sodium hydroxide was flowed at a rate of 3.70 L/h (1.74 m/h or 2.47 BV/h) until the exchange was deemed complete. Ion exchange capacities of zeolites as supplied are difficult to determine unambiguously. If one just looks at the compositional analysis and estimates a cation capacity this is invariably wrong due to factors such as: (1) pores which are too small to allow access of the exchanging cations; (2) impurities in natural zeolite which are not part of the structural framework, such as excess quartz which may distort the real value of Si:Al ratio in the zeolite structure. Hence, this study used only ammonium equilibrium exchange to estimate the capacity of the natural zeolites studied.

2.2. Chemicals

Aqueous solutions were prepared using triply distilled water to which appropriate amounts of salt were added. Analytical reagent grade ammonium chloride (99%, Rowe Scientific) and sodium chloride (min 99%, Rowe Scientific) were used.

2.3. Analysis

Total ammoniacal nitrogen concentrations in water were analysed using a Kjeldahl-type distillation process, where the sample of ammonium was distilled (Velp Scientifica UDK 149) to an indicating solution, which was then back-titrated to the end point using sulphuric acid. The mixed indicator solution contained 0.034 g