

Ammonium removal from solution using ion exchange on to MesoLite, an equilibrium study

A. Thornton^{a,*}, P. Pearce^b, S.A. Parsons^a

^a Centre for Water Sciences, Cranfield University, Cranfield, Bedfordshire MK43 0AL, UK

^b Thames Water, Spencer House, Manor Farm Road, Reading RG2 0JN, UK

Received 28 November 2006; received in revised form 22 January 2007; accepted 24 January 2007

Available online 30 January 2007

Abstract

This paper investigates the potential of MesoLite ion exchange media for ammonium (NH_4^+) removal from solution in the presence of competing cations. Batch tests were performed under a range of conditions to assess the effect of contact time, solution pH and solution concentration on the performance and capacity of the media for this application. The data obtained was fitted to the Langmuir and Freundlich isotherm models with the Langmuir model providing the better description of the process. Results indicate a maximum equilibrium capacity of $49 \text{ g NH}_4^+ - \text{N kg}^{-1}$ of media is achievable under the experimental conditions studied. A detailed examination of the data shows that increasing solution concentration and increased contact time provide the best performance at an optimum pH of between 6 and 7.

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Keywords: Ammonium; Ion exchange; Nutrient removal; Wastewater; Zeolite

1. Introduction

Ammoniacal nitrogen present in effluents arising from the treatment of municipal wastewater can promote eutrophication in receiving waters and increased toxicity to aquatic life [1–4]. Hence, the removal of ammonium from wastewater is of great importance in the control of nitrogen pollution [2]. Traditional methods of ammonium removal focus mainly on biological nitrification/denitrification processes [6–10]. These processes are extremely effective at nitrogen removal but are less responsive to shock loads in which case they can fall short of achieving the required effluent quality [3,11]. This can be compounded by the ever decreasing nitrogen discharge consent levels [3,12,13] imposed by regulatory bodies on wastewater treatment companies. In addition to this, rapid economic development and the improvement of the standard of living in developing nations will result in the production of much more treated wastewater [14].

A possible solution to the resulting problems is the use of ion exchange for ammonium removal as a complementary treatment option. Wastewater treatment plants could be upgraded for the direct treatment of high concentration problematic recycle streams or for the polishing of final effluent to meet the stringent consent levels imposed [11]. In the last 30 years many authors [15–25] have investigated the use of the naturally occurring mineral, zeolite, as an ion exchanger for the removal of ammonium from municipal wastewater and other waste streams. Zeolites are hydrated aluminosilicates [1] comprising silica and aluminium tetrahedra which are mutually bound by chemical covalent bonds with common oxygen atoms [12]. This gives rise to a three dimensional framework which is generally very open, containing channels and cavities, which are filled with cations and water molecules [26]. The cations are bound by weaker electrostatic bonds, increasing their mobility and the capability of being exchanged with cations present in solution [12]. The exchange capacity of zeolites is governed by the extent of aluminium substitution for silicon in the framework. Each aluminium generates a net negative charge which needs to be balanced by a cation to achieve overall electroneutrality. Therefore, the higher the aluminium substitution, the greater the ion exchange potential [1].

Organic resins are generally preferred to zeolites as ion exchangers due to their higher cation exchange capacity (CEC),

* Corresponding authors.

E-mail addresses: a.thornton@cranfield.ac.uk (A. Thornton), Pete.Pearce@ThamesWater.co.uk (P. Pearce), s.a.parsons@cranfield.ac.uk (S.A. Parsons).

higher reaction rates and chemical resistivity [12]. However, zeolites are reported to possess a higher cation exchange selectivity [12,21,27]. A number of zeolites have been investigated for the potential to remove ammonium from solution and it is almost universally accepted that clinoptilolite is the most suitable for this application. Clinoptilolite is a naturally occurring zeolite, which has a silica rich framework and therefore a lower CEC but displays a high affinity for ammonium with capacities in the range 0.94–21.52 g NH₄⁺–N kg⁻¹. However, initial work by Mackinnon et al. [28] indicates that MesoLite has an increased ammonium exchange capacity (45–55 g NH₄⁺–N kg⁻¹) compared to that of naturally occurring materials used by previous authors. MesoLite ion exchange media is produced by the modification of clay and other aluminium bearing minerals, resulting in the formation of the synthetic zeolite, zeolite N [29]. This results in an increase in the amount of exchange sites available, giving the media a higher exchange capacity than would be seen in the parent mineral and an increased surface area. This study investigates the performance of MesoLite under equilibrium conditions to assess the potential of the media to be used as an ammonium ion exchanger.

2. Materials and methods

MesoLite media supplied by Nanochem Pty Ltd., Australia was ground down to a grain size range of 0.1–0.6 mm and samples of 0.5 g were equilibrated with 100 ml of NH₄⁺–N solution (i.e. 5 g l⁻¹) of various concentration (0–2000 mg l⁻¹ NH₄⁺–N) at 20 °C for 24 h. The media as supplied contains approximately 15% sodium silicate which acts as a binding agent and it is probable that the same proportion of binding agent is present in the crushed sample. The solutions were prepared by the addition of ammonium chloride powder (NH₄Cl), supplied by Fisher Scientific, Loughborough, UK to domestic tap water. The method of using tap water in solution preparation was adopted to ensure the presence of competing cations (sodium, calcium, potassium and magnesium) in solution (Table 1). A number of tests were also performed by adding NH₄Cl to distilled water. Kinetic experiments to study the effect of contact time on equilibrium capacity were performed under the same experimental conditions but samples were extracted at certain time intervals (5, 10, 15, 30, 45, 60, 120, 180 and 240 min) to assess the uptake characteristics of the material.

Equilibrium data for ammonium uptake on to MesoLite was compared to both the Freundlich and Langmuir isotherm models, which relate the amount of ammonium exchanged per gram of media, to the equilibrium ammonium concentration remaining in solution. The ammonium concentration remaining in solution was determined using a Lasa 100 spectrometer supplied by Hach Lange GMBH, Düsseldorf, Germany. Prior to

testing, solution samples were filtered using a 45 µm microporous membrane filter to separate the solution and solid phases. The ammonium concentration in the solid phase was calculated using the following mass balance equation [3,12,16,30].

$$Q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where Q_e is the amount of ammonium in the solid phase (mg/g); C_0 is the initial ammonium concentration in solution (mg/l); C_e is the ammonium remaining in solution at equilibrium (mg/l); V is the solution volume (l); M is the mass of MesoLite introduced (g).

3. Results and discussion

3.1. Isotherm models

The Langmuir model is represented by:

$$Q_e = \frac{KbC_e}{1 + Kc_e} \quad (2)$$

where K is the maximum exchange capacity of 1 kg of exchanger (g NH₄⁺–N kg⁻¹) and b is the Langmuir energy constant or binding index (m³ g⁻¹) [1]. These constants can be determined by rearranging to Eq. (3) and plotting $1/C_e$ versus $1/Q_e$. The resulting plot forms a straight line with an intercept of $1/b$ and a gradient of $1/Kb$ [13,30].

$$\frac{1}{Q_e} = \frac{1}{KbC_e} + \frac{1}{b} \quad (3)$$

Experimental results give the Langmuir equation for MesoLite with respect to ammonium uptake as

$$Q_e = \frac{1.828C_e}{(1 + 0.0658C_e)} \quad (4)$$

The Freundlich model is represented by

$$Q_e = KC_e^{1/n} \quad (5)$$

where K and n are the Freundlich constants for any given exchanger in a given system. These constants can be determined by rearranging to Eq. (6) and plotting $\log C_e$ versus $\log Q_e$. The resulting plot is a straight line with an intercept of $\log K$ and a gradient of $1/n$ [4,13,30].

$$\log Q_e = \log K + \frac{1}{n} \log C_e \quad (6)$$

From experimental results the Freundlich equation for MesoLite with respect to ammonium uptake is given by

$$Q_e = 2.196C_e^{0.534} \quad (7)$$

A comparison of experimental data with that of the models can be made by plotting liquid ammonium concentration (C_e) versus solids concentration (Q_e) to produce isotherms (Fig. 1). The Langmuir and Freundlich isotherms are generated using Eqs. (4) and (7) and experimental data for C_e to calculate theoretical Q_e values. For the case of MesoLite, the Langmuir model displays a much more consistent fit to experimental data than that

Table 1
Concentrations of competing cations in solution

Cation	Calcium	Magnesium	Sodium	Potassium
Concentration (mg l ⁻¹)	111 ± 6	3.1 ± 0.2	16.3 ± 0.8	3 ± 0.3

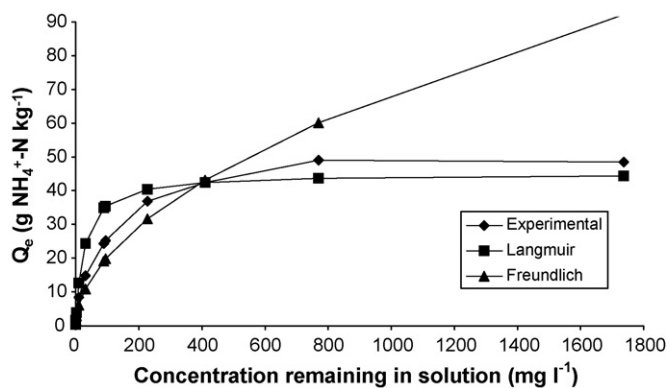


Fig. 1. Ammonium uptake equilibrium on to MesoLite.

of the Freundlich model, although at lower concentrations the fit is more consistent for both models. This concurs with previous authors [13,14,30] and where a comparison is made all conclude that the Langmuir model best describes the process of ammonium uptake onto zeolites.

It is important to note that both models have their limitations in accurately describing equilibrium exchange. Hankins et al. [23] argues that the Freundlich model imposes no intrinsic limit on the capacity of the zeolite although it is generally accepted that the capacity of any ion exchange material is limited to the number of exchange sites available and therefore, the single component Langmuir model is more applicable because a limit on adsorption is imposed. However, the authors further argue that the Langmuir model fails to account for the true nature of ion exchange as a binary, displacement adsorption process, which involves at least two species, whose relative proportions and hence concentrations alter. The comparison of isotherm coefficients to those stated by other authors for different materials is somewhat difficult as they are only true for specific experimental conditions [33]. Their values will be affected by the relative concentrations or absence of competing cations, pH, temperature and the media loading of the solution. Separate trials on MesoLite with a media loading of 1 g l⁻¹ (as opposed to 5 g l⁻¹) deliver the following Langmuir and Freundlich equations:

$$\text{Langmuir } Q_e = \frac{2.819C_e}{(1 + 0.0488C_e)} \quad (8)$$

$$\text{Freundlich } Q_e = 6.02C_e^{0.3917} \quad (9)$$

The experimental conditions adopted by different authors is by no means consistent (Table 2). For example, Wang et al. [14] employed a loading of 5 g/100 ml (i.e. 50 g l⁻¹) for the naturally occurring zeolite, clinoptilolite, and generated three different sets of equations for varying media grain size. Calculations using the derived equations at an equilibrium concentration of 100 mg NH₄⁺-N l⁻¹ result in maximum Q_e values of 2.33 g NH₄⁺-N kg⁻¹ (Langmuir) and 4.24 g NH₄⁺-N kg⁻¹ (Freundlich). Conversely, Weatherley and Miladinovic [13] used a significantly lower clinoptilolite loading of 10 g l⁻¹ over a similar range of concentrations. Calculations at the same equilibrium concentration, deliver

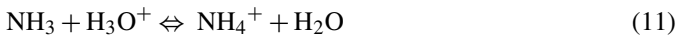
Table 2
Experimental conditions and isotherm equations generated by a selection of authors

Material	Experimental conditions	Langmuir equation		Freundlich equation		Ref.
		Langmuir	Freundlich	Langmuir	Freundlich	
Natural Chinese clinoptilolite	Media loading 50 g l ⁻¹	$Q_e = 0.387C_e / (1 + 0.182C_e)$	$Q_e = 0.428C_e^{0.458}$	2.02	3.53	[14]
	Temperature 20 °C, pH 6	$Q_e = 0.442C_e / (1 + 0.186C_e)$	$Q_e = 0.596C_e^{0.341}$	2.26	2.87	
	Concentration range 23–115 mg l ⁻¹ NH ₄ ⁺ -N	$Q_e = 0.412C_e / (1 + 0.167C_e)$	$Q_e = 0.432C_e^{0.496}$	2.33	4.24	
Natural Turkish clinoptilolite	Media loading 10 g l ⁻¹	$Q_e = 0.236C_e / (1 + 0.029C_e)$	$Q_e = 0.612C_e^{0.517}$	6.05 (25 °C)	6.62 (25 °C)	[3]
	Temperature 25, 40 and 55 °C	$Q_e = 0.209C_e / (1 + 0.034C_e)$	$Q_e = 0.437C_e^{0.550}$	4.75 (40 °C)	5.50 (40 °C)	
Sulfonated polystyrene silica gel	Concentration range 25–150 mg l ⁻¹ NH ₄ ⁺ -N	$Q_e = 0.139C_e / (1 + 0.027C_e)$	$Q_e = 0.405C_e^{0.498}$	3.76 (50 °C)	4.01 (50 °C)	[31]
	Temp 25 °C pH ≤ 7	$Q_e = 1.88 C_e / (1 + 0.213C_e)$	$Q_e = 2.79C_e^{0.261}$	8.43	9.28	
Bigadic zeolite (Turkey)	Concentration range 0.4–140 mg l ⁻¹ NH ₄ ⁺ -N	$Q_e = 0.440C_e / (1 + 0.085C_e)$	$Q_e = 0.608C_e^{0.537}$	4.6 (Raw)	7.21 (Raw)	[30]
	Media loading 1 g l ⁻¹	$Q_e = 0.770C_e / (1 + 0.069C_e)$	$Q_e = 0.806C_e^{0.727}$	9.7 (Conditioned)	22.9 (Conditioned)	
New Zealand mordenite and clinoptilolite	Concentration range 10–80 mg l ⁻¹ NH ₄ ⁺ -N	Clinoptilolite	Clinoptilolite	6.54	10.66	[13]
	Media loading 10 g l ⁻¹ pH < 7.5	Mordenite	Mordenite	12.01	15.09	
Natural Chinese clinoptilolite	Concentration range 0–200 mg l ⁻¹ NH ₄ ⁺ -N	$Q_e = 1.79 C_e / (1 + 0.139C_e)$	$Q_e = 1.255C_e^{0.540}$	–	4.9	[4]
	Media loading 5 g l ⁻¹ pH < 6	–	–	–	–	
Chabazite	Concentration range 2–94 mg l ⁻¹ NH ₄ ⁺ -N	$Q_e = 5.01 C_e / (1 + 1.690C_e)$	–	2.94	–	[19]

Q_e values of $6.54 \text{ g NH}_4^+-\text{N kg}^{-1}$ (Langmuir) and $10.66 \text{ g NH}_4^+-\text{N kg}^{-1}$ (Freundlich). Calculations for MesoLite using Eqs. (4) and (7) result in $24 \text{ g NH}_4^+-\text{N kg}^{-1}$ and $25.7 \text{ g NH}_4^+-\text{N kg}^{-1}$, respectively, whereas, Eqs. (8) and (9) return values of $47.92 \text{ g NH}_4^+-\text{N kg}^{-1}$ and $36.56 \text{ g NH}_4^+-\text{N kg}^{-1}$. It is generally true to say that Q_e increases (up to a maximum) for any given concentration as the media loading decreases. However, isotherms are specific to the system they describe [33] and to accurately compare two or more ion exchangers using these models requires the experiments to be performed under identical conditions.

3.2. The effect of pH

Ammoniacal nitrogen is present in aqueous solution in two forms non-ionised ammonia (NH_3) or ionised ammonium (NH_4^+), according to the following equations [13]:



Ammonia–ammonium equilibrium in solution is largely pH dependant [32] and it stands to reason that only the ionised form can be removed from solution by ion exchange. At pH 8 and below the substantial majority of ammoniacal nitrogen is present in the ionised form, therefore, it is reasonable to assume that these conditions would best favour the removal process. Above pH 8 the equilibrium shifts rapidly towards the non-ionised form and these conditions become increasingly less favourable. Solutions were prepared at pH values of 6, 7, 8 and 10 to establish the optimum pH range for ammonium removal using MesoLite. Results confirm that pH values of 8 and below are best suited to the ion exchange process with the optimum removal being achieved at pH 6–7. With an initial concentration of $1000 \text{ mg NH}_4^+-\text{N l}^{-1}$, an equilibrium capacity of $49 \text{ g NH}_4^+-\text{N kg}^{-1}$ is achieved at pH 6–7 in comparison to $37 \text{ g NH}_4^+-\text{N kg}^{-1}$ at pH 8.3. Removal efficiency decreases rapidly at pH values above 8 and at 10 the equilibrium capacity is reduced to $29 \text{ g NH}_4^+-\text{N kg}^{-1}$. This concurs with results reported by previous authors [4,18,23] and can be explained by the fact that under alkaline pH conditions, the ammonium ion becomes neutralised by the hydroxyl ion, rendering it uncharged [23]. Experiments for MesoLite did not investigate solutions below pH 6 because it is unlikely that these conditions would be experienced in the target application. However, literature indicates that performance is reduced below pH 6, attributing this to the fact that the increased number of hydrogen ions in solution provides added competition for exchange sites [18,23,32].

3.3. The effect of initial ammonium concentration

Results indicate that the initial ammonium concentration has an influence on both the equilibrium capacity and the rate of uptake of NH_4^+-N . At higher initial concentrations the initial rate of uptake is far greater than at lower concentrations (Fig. 2). This can be attributed to the fact that higher concentrations

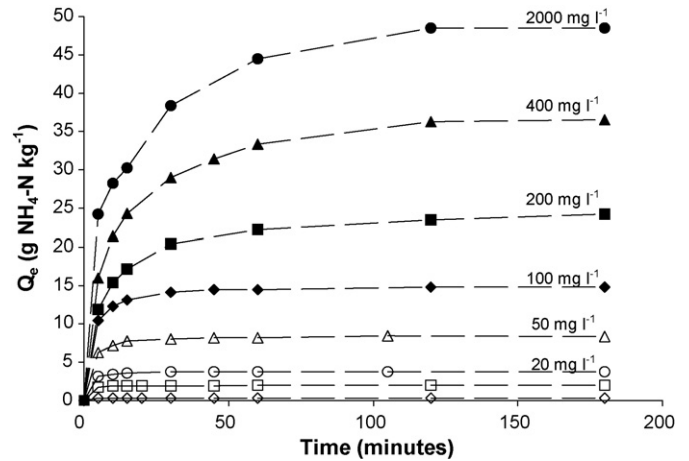


Fig. 2. Effect of initial solution concentration on the rate of NH_4^+ uptake.

result in a higher solute gradient, providing the necessary driving force for ammonium ions to replace cations in the media framework for a given contact time [4,14]. Increasing concentration also results in a higher equilibrium capacity being obtained for any given set of conditions. Initially a sharp increase in capacity can be observed with increasing concentration, reaching a maximum, in this case $49 \text{ g NH}_4^+-\text{N kg}^{-1}$ at a solution concentration of $1000 \text{ mg NH}_4^+-\text{N l}^{-1}$ (Fig. 3). This maximum value is indicative of the fact that the ion exchange surface is increasingly saturated with the ammonium ion [3] and is reflected by the accompanying reduction in removal efficiency [23]. This is the maximum amount of ammonium which can be exchanged on to the surface of the material under the experimental conditions and after this point further increases in solution concentration are ineffective in raising the media's capacity (Fig. 3). Experiments performed with distilled water at an initial concentration of $1000 \text{ mg NH}_4^+-\text{N l}^{-1}$ show that a capacity of $72 \text{ g NH}_4^+-\text{N kg}^{-1}$ is achievable. This is in agreement with Mackinnon et al. [28] who reports an average CEC for MesoLite of $69 \text{ g NH}_4^+-\text{N kg}^{-1}$. This indicates that the presence of competing cations in solution has a significant effect on the ammonium exchange capacity with only 70% of maximum removal being realised. Wang et al. [14] also reported a reduction in the capacity of clinoptilolite of 10–20% when competing cations were present in solution.

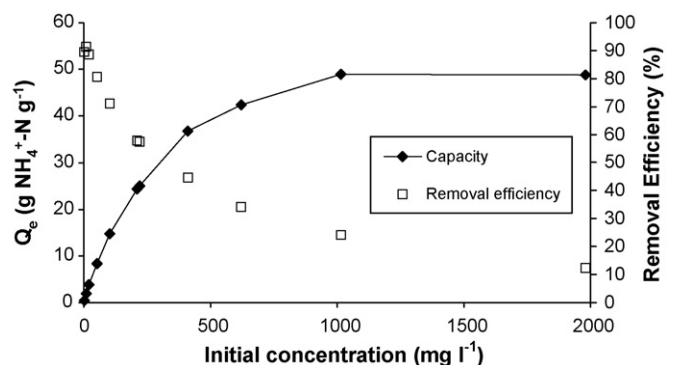


Fig. 3. Effect of initial concentration on capacity and removal efficiency.

3.4. The effect of contact time

Results from kinetic experiments indicate that the rate of uptake of ammonium by MesoLite is initially a fast process with over 90% of the equilibrium capacity reached within the first 60 min. After this time the rate of uptake slows dramatically and after 4 h is negligible, indicating a state of equilibrium. This

is consistent with results reported by previous authors, all of who observed the same behaviour. Hankins et al. [23] reported that 50% and 75% of uptake on to clinoptilolite was achieved in 15 and 60 min, respectively. Wang et al. [14] also reports a high rate of uptake within the first hour, which gradually decreases with increased contact time. Experiments by Booker et al. [22] and Du et al. [4] result in the majority of ammonium uptake being

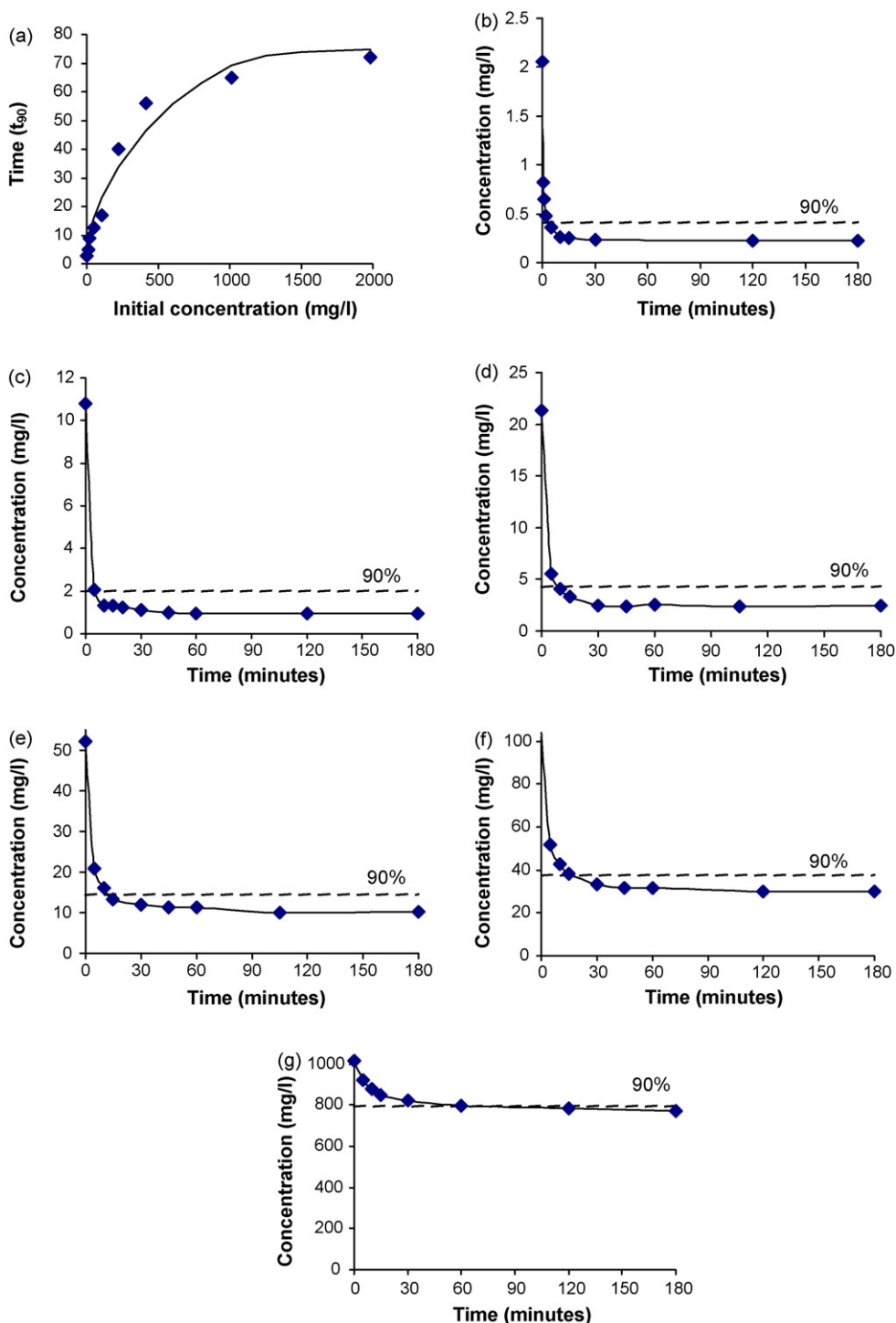


Fig. 4. (a) Time to reach 90% equilibrium against initial solution concentration. (b–g) Concentration remaining in solution against contact time for a range of initial solution concentrations.

achieved in even shorter time periods of 10 and 15 min, respectively. The reasons for these discrepancies may be specific to the materials used, the experimental conditions or a combination of the two. However, all authors are consistent in the fact that uptake is negligible after a period of 4 h has elapsed. This is by no means an indication that the exchange process has ceased it is just an indication that the rate of adsorption is equal to the rate of desorption and there is therefore no net alteration of the concentration of ions in the solution and solid phases.

A more detailed examination of results for MesoLite indicates that the effects of contact time vary with the solution concentration. The exact point in time at which equilibrium is achieved is difficult to assess but the time to reach 90% of equilibrium can be easily calculated. At low concentrations the time to reach 90% equilibrium is significantly less than that at higher concentrations (Fig. 4a). At an initial concentration of 2 mg l^{-1} , 90% is reached in less than 3 min (Fig. 4b) whereas at 1000 mg l^{-1} it takes 65 min to reach the same point (Fig. 4g). Fig. 4c–f show the relationship between contact time and equilibrium for a range of concentrations. Although the initial rate of uptake is less at lower concentrations (Section 3.3), most of the exchange process is completed in a shorter period of time. This can be attributed to the fact that at lower concentrations, the vast majority of exchange sites remain unused, even at equilibrium. At an initial concentration of 2 mg l^{-1} the loading on the media is $0.37 \text{ g NH}_4^+ \text{--N kg}^{-1}$ whereas at a concentration of 1000 mg l^{-1} the loading on the media is a maximum $49 \text{ g NH}_4^+ \text{--N kg}^{-1}$ (Fig. 2). Therefore, because the initial rate of uptake is initially high at 1000 mg l^{-1} , the majority of the exchange sites are used up in the early stages (i.e. saturation is approached), leaving the remaining ammonium in solution to “scavenge” for less accessible exchange sites. The opposite is true at lower concentrations where exchange sites are abundant throughout the process.

4. Conclusions

A range of batch tests were performed to assess the uptake of the ammonium ion by MesoLite media with the following conclusions:

- A comparison of the data with Langmuir and Freundlich isotherm models show a good correlation at low concentrations but over the whole range of experimental conditions the Langmuir model describes the process more accurately.
- The capacity of the material is affected by solution pH and optimum conditions for removal are between pH 6 and 7.
- The initial solution concentration has an effect on performance with both the rate of uptake and the capacity increasing with increased solution ammonium concentration.
- The capacity of the media is reduced when competing cations are present in solution and an approximate 30% reduction in ammonium uptake is observed from 72 to $49 \text{ g NH}_4^+ \text{--N kg}^{-1}$.
- Ion exchange occurs at a high rate with the majority of the process being complete within the first hour and after 4 h the rate of uptake becomes negligible for all solution concentrations studied.

Acknowledgements

The authors would like to express their appreciation to Thames Water Utilities Ltd. and the Engineering and Physical Sciences Research Council for the funding of this work and NanoChem Pty Ltd. for continued technical assistance with this project.

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