

Ammonium removal from digested sludge liquors using ion exchange

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ABSTRACT

Liquors arising from the dewatering of digested sludge typically contain ammonium levels in the range 200–700 mg l⁻¹ NH₄⁺-N. These liquors are frequently recycled to the head of the wastewater treatment works (WwTW) untreated and can constitute >25% of the total nitrogen load entering the works at inlet. This paper investigates the use of a clay-based material, Mesolite, as an ion exchange medium for ammonium removal from recycle streams. Pilot-scale studies performed at Didcot WwTW, part of the Thames Water wastewater treatment network, indicate that Mesolite is highly selective for the ammonium ion. Results show that >95% of ammonium was removed from belt press liquors with an initial ammonium nitrogen concentration >600 mg l⁻¹, with an overall ion exchange capacity >51 g NH₄⁺-N kg⁻¹ medium and this resulted in an operating capacity in the range 27–36 g NH₄⁺-N kg⁻¹.

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1. Introduction

Domestic wastewaters comprise, amongst other constituents, organic nitrogen compounds derived from urine and faeces (Hedstrom, 2001), which during transport to wastewater treatment works (WwTWs), can be decomposed to form ammonium. In many developed countries, consent levels for the amount of ammonium contained in the final effluent invariably dictates the need for a nitrogen treatment step to be included as part of the wastewater treatment process. It is not uncommon for consent levels for NH₄⁺-N to be as low as 1 mg l⁻¹ (Pearce et al., 2000). Nitrogen removal is commonly achieved using a biological, nitrification–denitrification process, where ammonium is transformed firstly to nitrite and then to nitrate and finally to nitrogen gas (Hedstrom, 2001).

In addition to incoming wastewaters, recycle streams within the WwTW may also contribute to the nitrogen load applied to the biological nitrogen removal process. Liquors arising from dewatering of digested sludge by belt presses,

centrifuges or alternative dewatering measures are referred to as sidestreams. These are recycled back to the head of the works and, depending on their source, can markedly increase the ammonium loading on the WwTW (Siegrist, 1996; Pearce et al., 2000; Mackinnon et al., 2003). Although forming only a small proportion of the overall volumetric flow, the high concentration of recycled liquors (typically 200–700 mg l⁻¹ NH₄⁺-N) results in a disproportionate impact. Janus and van der Roest (1997) noted that sidestreams in Dutch WwTWs contributed up to 25% of the total nitrogen load, yet the contribution to the total influent flow was only 2%.

Due to urban expansion, ever-decreasing discharge consent levels and centralisation of selected sites as sludge handling centres (Belser Baykal et al., 1994; Kamarowski and Yu, 1997; Pearce et al., 2000), many treatment plants find themselves in the position where the design capacity for ammonium removal is being approached or even exceeded. It is not unreasonable to assume that in the future some treatment processes may not be able to sustain the level of treatment

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Table 1 – Summary of ammonium exchange capacities for materials used in various studies

Author	Adsorbent	Capacity (g NH ₄ ⁺ -N kg ⁻¹)	Scale of work
Sprynskyy et al. (2005)	Clinoptilolite	13.56–21.52	Lab
Du et al. (2005)	Clinoptilolite	5.81–7.74	Lab
Farkas et al. (2005)	Croatian clinoptilolite	6.0–13.65	Lab
Jung et al. (2004)	Zeolite	6.0–7.4	Lab
Mackinnon et al. (2003)	MesoLite	45–55	Pilot
Nguyen and Tanner (1998)	Mordenite/c clinoptilolite	3.7–6.5	Lab
Weatherly and McVeigh (2000)	Clinoptilolite	6.58–13.3	Lab
Belér Baykal and Guven (1997)	Bulgarian Clinoptilolite	2.0–3.6	Lab
Booker et al. (1996)	Australian zeolite	4.5	Lab
Hlavay et al. (1982)	Clinoptilolite	1.37–9.15	Lab
Semmens and Porter (1979)	Clinoptilolite	3.9	Pilot
Jorgensen et al. (1976)	Clinoptilolite	0.94–2.41	Lab

required to meet the effluent discharge consent values imposed. In some cases an option may be to modify the operation of, or enlarge, the mainstream processes already on site and this may be the most cost-effective option. However, some works may not have this option available and on sites, where sidestreams comprise a significant proportion of the total ammonium loading on the mainstream processes, a possible option is to directly treat the sidestream liquors.

An available method of treatment is ion exchange on to materials selective to the ammonium ion. In recent years, many authors (Jorgensen et al., 1976; Semmens and Porter, 1979; Hlavay et al., 1982; Liberti et al., 1986; Booker et al., 1996; Balér Baykal and Guven, 1997; Nguyen and Tanner, 1998; Weatherly and McVeigh, 2000; Mackinnon et al., 2003; Farkas et al., 2005; Du et al., 2005; Sprynskyy et al., 2005) have investigated the ion exchange potential of various materials with respect to ammonium removal, including treatment of sludge dewatering liquors. Most of the research undertaken has studied the effectiveness of naturally occurring materials, mainly zeolites. To date the most suitable zeolite for this process has been clinoptilolite, a selective aluminosilicate of volcanic provenance, which shows an ammonium exchange capacity in the range 0.94–21.52 g NH₄⁺-N kg⁻¹ (Table 1). Initial studies by Mackinnon et al. (2003) indicate that MesoLite has a greater ammonium exchange capacity than naturally occurring materials used in previous studies (Table 1).

MesoLite ion exchange medium is produced by the chemical modification of clay minerals and other aluminium-bearing minerals. The resulting material is characterised by a predominance of tetrahedrally coordinated Al³⁺, which has resulted from the chemical modification of octahedrally coordinated Al³⁺ in the parent mineral (Mackinnon et al., 1997a, b). This modification results in the availability of more exchange sites than would be in the parent mineral, giving the material a high ion exchange capacity.

This paper outlines a study undertaken to evaluate the potential of MesoLite as an ion exchange medium for the treatment of high ammonium concentration sludge dewatering liquors. Experimental work has been undertaken on a pilot plant installed at Didcot WwTW, part of the Thames

Water network of wastewater treatment facilities. The works treats an average flow of 9000 m³ d⁻¹ and treats a population equivalent of 31,000. Sludge dewatering is undertaken using a single belt press fed by two anaerobic digesters.

2. Materials and methods

Particle size analysis of the MesoLite, supplied by NanoChem Pty Ltd., Australia, was performed using sieve sizes, 0.6, 1.18, 1.4, 1.7, 2.0, 2.36, 2.5, 2.8, 3.35 and 5.0 mm. Results show that the medium falls within a narrow size range, with >99% of the medium falling between 1.4 and 2.5 mm in diameter.

A proportion of the liquors arising from the dewatering process were collected for treatment. Due to the discontinuous operation of the belt press, it was necessary to store the amount of liquor required to operate the pilot plant. Prior to storage, liquors were pre-treated using a ceramic medium filter to remove any excess solids. This prevented excess fouling of the ion exchange medium, keeping head loss to a minimum and eradicating the need for backwashing of the ion exchange medium.

The stored filtered sludge liquor was pumped at a selected flow rate through two columns containing MesoLite medium. Each column was 1.8 m high with an operating bed height of approximately 1.2 m and internal diameter of 0.6 m resulting in an operating bed volume of 0.35 m³ with 100 l intergranular pore space. This equates to each column containing 290 kg of MesoLite medium. The columns were exhausted in a down-flow direction and the final effluent drained to the head of the works. A series of valves was incorporated to allow the column order to be reversed and also enable upflow feed for regeneration purposes. The plant was also designed to allow single column operation. A schematic of the pilot plant process operated at Didcot WwTW is presented in Fig. 1.

The columns were exhausted in series, with column A as the primary column, at a flow rate 500 l h⁻¹, which corresponds to 5 bed volumes per hour (BV h⁻¹) per column, giving a hydraulic retention time (HRT) of 12 min in each column. At the end of the cycle, the primary column was regenerated. The columns were again exhausted in series, with column B

Table 2 – Characteristics of liquors used in various trials

NH ₄ ⁺ -N (mg l ⁻¹)	pH	Ca ²⁺ (mg l ⁻¹)	Mg ²⁺ (mg l ⁻¹)	Na ⁺ (mg l ⁻¹)	K ⁺ (mg l ⁻¹)	Reference
520–690	7.8–8.1	160–180	15–20	60–80	100–110	Liquors at Didcot WwTW
640	7.77	128	196	1085	801	Farkas et al. (2005) (waste dump leakage)
100	—	—	—	—	—	Sprynskyy et al. (2005) (synthetic solution)
25	—	—	—	—	—	Du et al. (2005) (synthetic solution)
160	7–8	170	—	3232	160	Hankins et al. (2004) (synthetic solution)
500–800	—	—	—	—	—	Mackinnon et al. (2003) (sludge centrate)
400	7.87	46	30	73	278	Nguyen and Tanner (1998) (piggery waste)
180	7.41	38	11	33	215	Nguyen and Tanner (1998) (dairy waste)
29	7.8	20	9	25	107	Nguyen and Tanner (1998) (domestic waste)
14	7.5	29	7	57	21	Nguyen and Tanner (1998) (synthetic solution)
40	—	60	30	220	20	Lahav and Green (1998) (synthetic solution)
20	—	—	—	—	—	Beler Baykal and Guven (1997) (domestic wastewater)
30–51	—	—	—	—	—	Booker et al. (1996) (synthetic and real)
12–45	7.1	82.32	43.9	41.3	29.8	Hlavay et al. (1982) (synthetic wastewater)
10–18	8.2	105.6	41.7	39.8	30.8	Hlavay et al. (1982) (municipal wastewater)
10.88	7.45	34	8	58	12	Klieve and Semmens (1979) (synthetic solution)
20	—	14	12	62	4	Semmens and Porter (1979) (synthetic solution)
75	—	—	—	—	—	Jorgensen et al. (1976) (synthetic solution)
16.4–19.4	6.0–8.0	26–140	3–53	13–175	1–35.4	Koon and Kaufmann (1975) (synthetic and real)

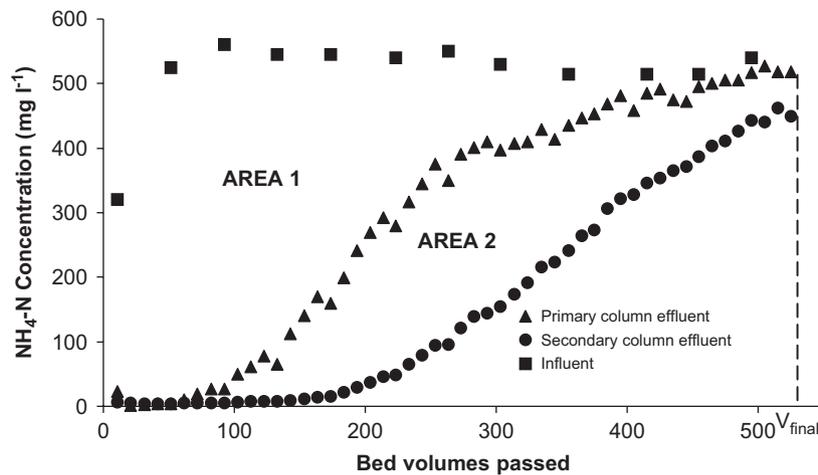


Fig. 2 – Primary and secondary breakthrough curves for loading 4.

An approximation of Eq. (1) can be used to calculate the ammonium removed from solution between any two sampling intervals as follows:

$$q = (C_0 - C_2)(V_2 - V_1), \quad (2)$$

where V_1 and V_2 are the respective volumes of liquid treated at the time the samples are taken, and C_2 is the effluent concentration. Therefore, the amount of NH_4^+ -N removed after n samples is given by

$$q = (C_0 - C_1)(V_1 - V_0) + (C_0 - C_2)(V_2 - V_1) + \dots + (C_0 - C_n)(V_n - V_{(n-1)}). \quad (3)$$

This can be used to keep a cumulative record of the amount of NH_4^+ -N removed throughout any loading cycle (Fig. 3) along with the amount of NH_4^+ -N removed per kg of medium (Q).

When effluent concentration in the primary column is equal to the influent concentration (i.e., $C_n = C_0$), the medium is fully exhausted, $q = q_{\text{max}}$, which is the maximum amount of NH_4^+ -N that can be removed under the specific loading conditions, and Q_{max} = the materials capacity, which in the present case is $47 \text{ gNH}_4^+\text{-N kg}^{-1}$ medium.

The first four loading cycles were conducted to establish the operational parameters for the pilot plant. In loadings 2 and 4 the medium in the primary column was run to exhaustion (i.e., the medium's full capacity was used), and in subsequent loadings (5–11) a final effluent breakthrough concentration of $50 \text{ mg l}^{-1} \text{ NH}_4^+\text{-N}$ was established. When run to exhaustion the medium displayed a total capacity of $47\text{--}51 \text{ gNH}_4^+\text{-N kg}^{-1}$, with later loading cycles delivering an operational capacity in the range $27\text{--}32 \text{ gNH}_4^+\text{-N kg}^{-1}$ (Table 3).

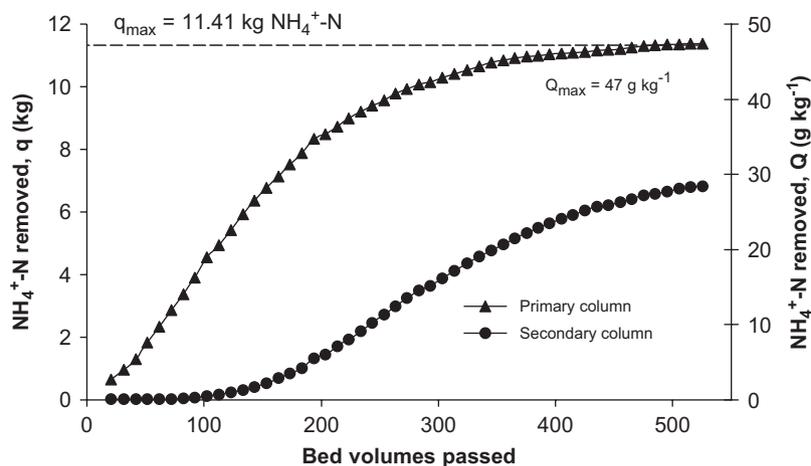


Fig. 3 – Cumulative ammonium exchange for loading 4.

Table 3 – Loading conditions for pilot trials performed

Run	Feed concentration (mg l ⁻¹ NH ₄ ⁺ -N)	Flow rate (l h ⁻¹)	Run time (h)	Volume treated (l)	Ammonium removed (kg)	Capacity (g NH ₄ ⁺ -N kg ⁻¹)
1	440–580	520	15	7800	3.71	N/A
2	500–605	515	77	40,000	12.73	51
3	570–620	520	56	29,000	6.17	25
4	525–540	510	98.5	51,000	11.41	47
Effluent breakthrough selected at 50 mg l ⁻¹ NH ₄ ⁺ -N						
5	625–650	405	46.5	18,300	9.75	39
6	625–680	405	27.5	10,800	7.1 (2.9,4.2)	29
7	630–680	400	27	10,050	6.8 (3.9,2.9)	27
8	625–650	390	35	14,000	8.4 (2.5,5.9)	29
9	660–685	390	34.5	13,750	8.1 (5.2,5.9)	32
10	630–715	395	35.5	14,000	10.7 (4.0,6.7)	36
11	640–715	405	29	11,900	6.7 (2.4,4.3)	27

This reduced operational capacity has been reported for a number of other zeolite trials. Farkas et al. (2005) conducted experiments on Croatian clinoptilolite, and the results indicated a total capacity of 6.9 g NH₄⁺-N kg⁻¹ but an operational capacity at breakthrough of 3.98 g NH₄⁺-N kg⁻¹. Semmens and Porter (1979) reported clinoptilolite capacities at pilot scale when the effluent concentration reached a breakthrough value equal to 10% of the influent concentration, returning an operational capacity of 3.9 g NH₄⁺-N kg⁻¹. Here, loadings 5 and 10 did deliver apparently higher operational capacities of 39 and 37 g NH₄⁺-N kg⁻¹, respectively but these inflated figures can be attributed to distinct factors. Loading 5 was conducted with the primary column containing freshly regenerated medium, i.e. it had not been reduced in capacity by being used previously as a secondary column and therefore the cycle time was considerably longer. In loading 10, the breakthrough value was exceeded (i.e., the final effluent concentration reached 100 mg l⁻¹) resulting in extra removal by the primary column.

When a breakthrough concentration was in place, the pilot plant delivered consistent results with a high degree of repeatability (Fig. 4). With influent concentrations consistently above 600 mg l⁻¹ NH₄⁺-N, final effluent concentration was maintained below breakthrough concentration for an average of 33.5 h. Regeneration occurred each time breakthrough was reached but had no detrimental effect on the ammonium removal performance of the medium.

As the secondary column was not regenerated between loadings, a notable proportion of the medium capacity was utilised in keeping the final effluent concentration below breakthrough. In loading 8 (Fig. 5) the primary column removed a total of 8.36 kg NH₄⁺-N resulting in a capacity of 28.81 g NH₄⁺-N kg⁻¹. A breakdown of the data indicates that 2.45 kg NH₄⁺-N was removed by the primary column during loading 7 (when acting as the secondary column) with a further 5.91 kg NH₄⁺-N removed in loading 8. Figures in parentheses in Table 3 show this breakdown of the results for loadings 6–11.

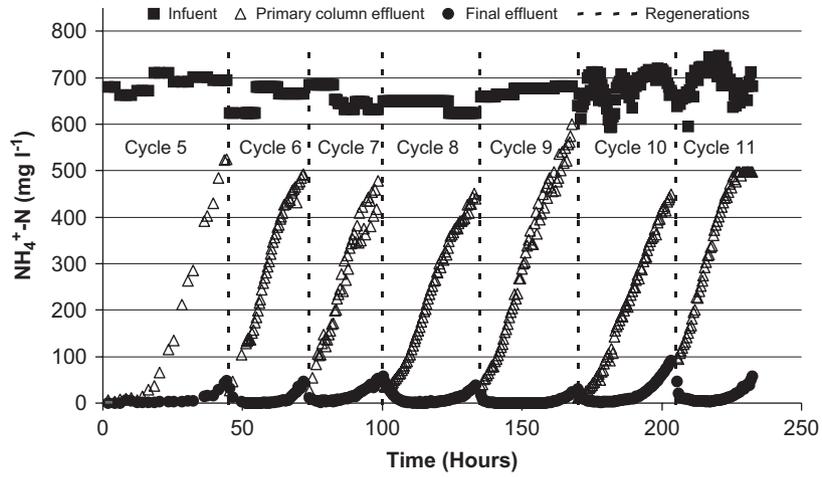


Fig. 4 – Breakthrough curves for all experiments performed at Didcot WwTW.

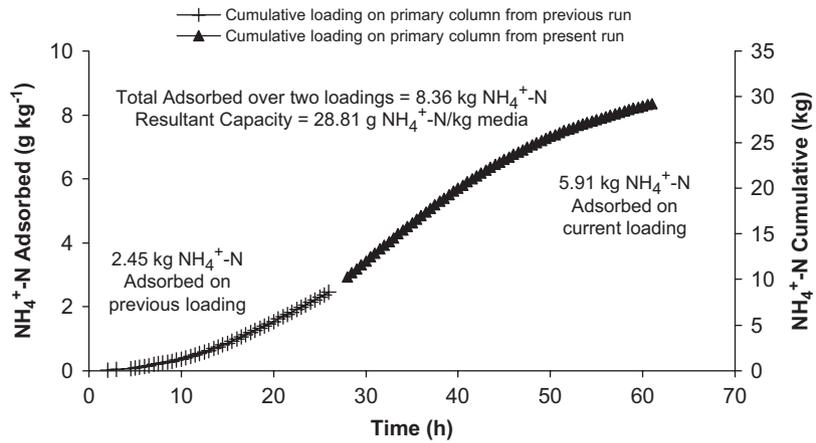


Fig. 5 – Cumulative ammonium uptake on primary column over two loading cycles.

concluded that for given operating conditions there would be an optimum loading rate.

4. Conclusions

Studies at Didcot WwTW give a total loading capacity of 47–51 gNH₄⁺-Nkg⁻¹ for MesoLite medium. This is consistent with values given by Mackinnon et al. (2003) who reported a capacity in the range 45–55 gNH₄⁺-Nkg⁻¹. When a breakthrough value is selected, this total capacity cannot be fully utilised and the resulting practical operational capacity is in the range 27–32 gNH₄⁺-Nkg⁻¹. However, this still compares favourably with other ion exchange media (Table 1). With a breakthrough value set at 50 mg l⁻¹ NH₄⁺-N, it was possible to treat 100–140 bed volumes of high-strength liquor before regeneration was required, and removal efficiencies >95% were observed.

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