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Nutrient removal from wastewaters using high performance materials

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Abstract Return side streams from anaerobic digesters and dewatering facilities at wastewater treatment plants (WWTPs) contribute a significant proportion of the total nitrogen load on a mainstream process. Similarly, significant phosphate loads are also recirculated in biological nutrient removal (BNR) wastewater treatment plants. Ion exchange using a new material, known by the name MesoLite, shows strong potential for the removal of ammonia from these side streams and an opportunity to concurrently reduce phosphate levels. A pilot plant was designed and operated for several months on an ammonia rich centrate from a dewatering centrifuge at the Oxley Creek WWTP, Brisbane, Australia. The system operated with a detention time in the order of one hour and was operated for between 12 and 24 hours prior to regeneration with a sodium rich solution. The same pilot plant was used to demonstrate removal of phosphate from an abattoir wastewater stream at similar flow rates. Using MesoLite materials, >90% reduction of ammonia was achieved in the centrate side stream. A full-scale process would reduce the total nitrogen load at the Oxley Creek WWTP by at least 18%. This reduction in nitrogen load consequently improves the TKN/COD ratio of the influent and enhances the nitrogen removal performance of the biological nutrient removal process.

Keywords Ammonia; anaerobic digestion; ion exchange; MesoLite; nutrient removal; sludge water

Introduction

In anaerobic digesters, active bacteria release large amounts of ammonia through break down of organic nitrogen-containing compounds. Depending on operating conditions, high concentrations of ammonia (between 500 mg/L and 1,500 mg/L) can be found in digester supernatant or the liquid return streams of sludge dewatering facilities such as centrifuges and belt filter presses. Generally, these return liquors or side streams are returned directly to the head of the wastewater treatment plant as shown in the schematic in Figure 1.

In many cases, this practice contributes significantly to the total nitrogen load of the influent flow. For example, the nitrogen load contributed by the centrate return from the dewatering centrifuge at Oxley Creek WWTP is approximately 20% of the total nitrogen load on the treatment plant when the centrifuge is operating. For plants with anaerobic digesters, treatment of sidestreams to remove nitrogen is emerging as a viable option for overall nitrogen reduction from wastewater treatment plants (Janus and van der Roost, 1997).

This paper evaluates pilot plant trials of side stream treatment using a novel ion exchange process for the removal of ammonia and describes basic attributes of regeneration and re-use of the ion exchange material. Objectives for these pilot scale trials at Oxley Creek WWTP included the determination of regeneration capacity, effective loading rate and rates of ammonia removal from sidestream.

Methods

Ion exchange material, MesoLite was produced by methods described in Mackinnon *et al.* (1997a,b) using Kingwhite 65 kaolin or a Ca-rich bentonite as stock raw materials.

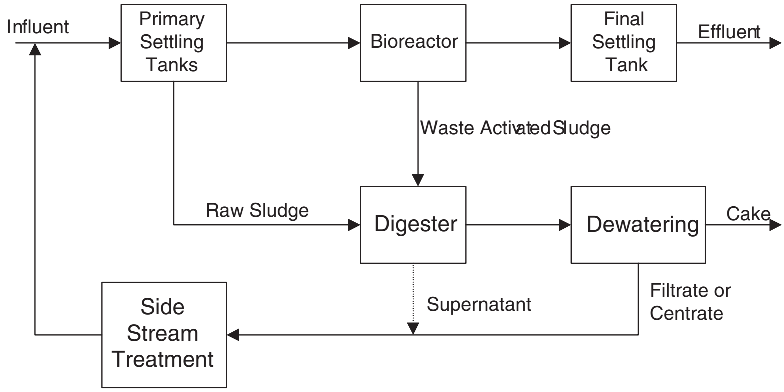

Figure 1 Typical process flow sheet showing side stream treatment and return to mainstream process

The average CEC (cation exchange capacity) value for this MesoLite powder was 490 meq/100g. The powdered material was aggregated into variable shaped blocks ranging in size between 3 mm and 9 mm using Lignox as a binder. In this form, MesoLite has potassium as the dominant exchange ion.

Industrial grade Na_2CO_3 sourced from a local chemical supplier was used for regenerant solutions. Earlier bench-scale trials indicated that a number of basic solutions and/or brine solutions are suitable for ammonium removal from loaded MesoLite. However, for this work Na_2CO_3 was selected for all regeneration cycles. At pilot plant scale, 0.5 mol l^{-1} and 1.0 mol l^{-1} regenerant solutions were used. At bench scale, regenerant solution concentrations ranging between 0.5 mol l^{-1} and 2.0 mol l^{-1} have been used at flow rates ranging from 0.5 BV/hour to 5 BV/hour (BV = bed volume).

Cation exchange capacity values are determined by standard equilibrium methods described by Ming and Dixon (1987) and using standardised measurements on the Clay Minerals Society Source Clay SAz-1 (Borden and Giese, 2001) for quality control. Measurements of ammonia concentrations for CEC values and for determinations of inlet and outlet flows are determined by standard Kjeldahl analysis. Surface area values are determined by conventional BET methods using a Gemini 2000 surface area analyser.

The pilot plant is designed to accommodate a maximum flow rate of 15kL/day (i.e. 10.4 L/min) using a simple pump system to control loading and regeneration. Loading cycles are generally gravity fed under ambient pressure conditions. Columns are constructed from industry standard PVC pipe and connected using conventional plastic plumbing components.

Operation of the pilot plant occurred during centrifuge processing periods on a continuous twenty-four hour basis. Ambient temperatures during this test period ranged between 28°C and 4°C. The average suspended solids concentration in the centrate is 1,500 mg/L. A sand filter was added to the pilot plant to remove these solids in order to reduce the potential for backpressure build-up. Filtered water is then pumped through four columns in series. Each column with a total volume 72 L is filled with MesoLite. Typical operating conditions for the pilot plant are listed in Table 1.

Results

Since the MesoLite material is mesoporous – compared with zeolites that are microporous – conventional ion exchange methods (e.g. Klieve and Semmens, 1980) are not a good guide to the performance of these materials. Accordingly, general operating conditions were established by a series of trials at bench-scale. A summary of data from the pilot plant trials that occurred over an eight-week period and which included a wide range of operating

Table 1 Typical operating conditions for pilot plant

System volume (L)	288
Column dimensions (mm)	$\phi \sim 200 \times 2{,}000$
Flow rate (L/hr)	290
Detention time (hrs)	1
Bed volume (L)	107
Flow rate (BV/hr)	2.7

conditions (e.g. variations in flow rate; backwashing and regenerant chemical concentrations) is reported in this document.

Ammonia loading

The target outlet ammonia concentration of the treated wastewater – or "breakthrough value" – was set at <50 mg/L so that the return centrate to the head of the plant would not significantly exceed the nitrogen concentration of raw sewage. With achievement of breakthrough for this system, the loading cycle was stopped and a regeneration cycle was initiated.

A breakthrough curve for the four columns of MesoLite material with wastewater flow rate of ~3 BV/hour is shown in Figure 2. Note that the wide range in ammonia inlet concentration is a result of discontinuous use of the centrifuge at the Oxley Creek WWTP. In this plant, the centrifuge is operated between 3 and 4 days per week on a twenty-four hour cycle. Thus, for the first stages of the breakthrough curve shown in Figure 2, ammonia inlet values range between 500 mg/L and 800 mg/L. With continued operation, inlet concentrations reached 1,000 mg/L over a full test cycle. The vertical lines in Figure 2 show the stage at which a regeneration sequence is initiated.

The data in Figure 2 show that MesoLite materials can maintain a very low breakthrough value with up to two times variation in inlet ammonia concentration. Better performance can also be achieved with improved process design and optimisation of MesoLite loading characteristics.

For example, data for a consistent inlet ammonia concentration and at a wastewater flow rate of 1 BV/hour (or approximately 3 hours detention) are shown in Figure 3. In this plot, which shows data for the fifth loading/regeneration cycle for the same material described in Figure 2, the outlet ammonia concentration is maintained well below breakthrough (i.e. ~5 to 15 mg/L) for the complete cycle.

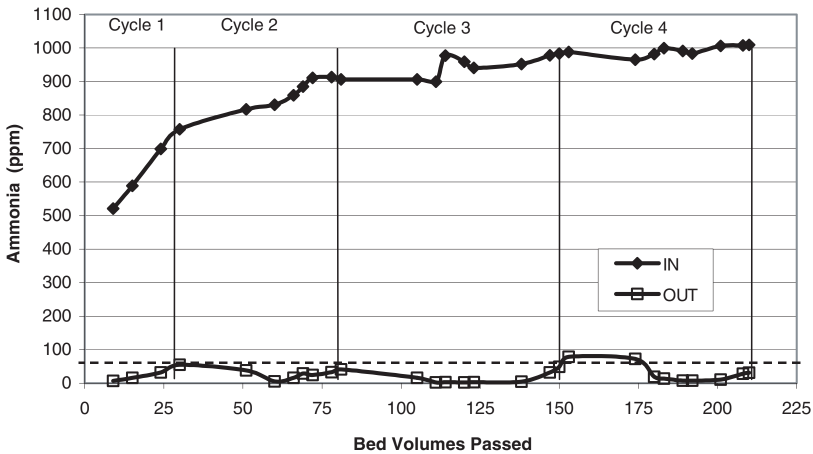

Figure 2 Typical MesoLite breakthrough curve

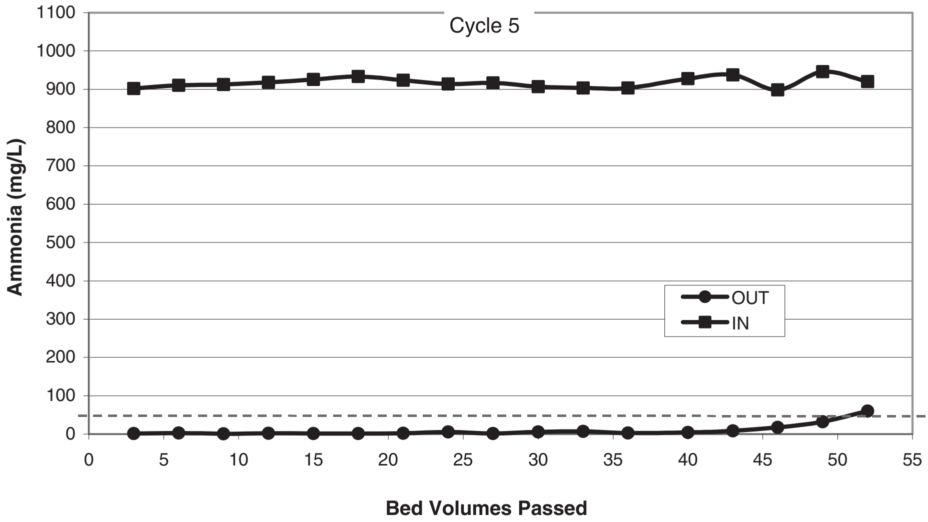

Figure 3 Breakthrough curve at 1 BV/hour flow rate

MesoLite regeneration

Bench-scale trials of regeneration were carried out over a range of flow rates and regenerant concentrations. A summary plot of typical de-loading curves showing the percentage of ammonia removed from a fully loaded MesoLite is shown in Figure 4. In these cases, Na_2CO_3 concentration ranges from 0.5 mol l^{-1} to 2.0 mol l^{-1}.

An evaluation of the regeneration capacity after a first cycle of regeneration was also undertaken at bench-scale for fully loaded MesoLite. Typical data obtained for two uses of Na_2CO_3 for successive regenerations at different flow rates are shown in Figure 5. These data show that lower ammonia removal rates are achieved with higher flow rate and that at low flow rates similar amounts of ammonia can be removed in successive cycles.

At pilot plant scale, Na_2CO_3 regeneration was undertaken at 0.5 BV/hour and 1.5 BV/hour. Higher concentrations of ammonia were achieved in the lower flow rate regenerations.

Values of up to 10,000 mg/L ammonia were obtained at low flow rate compared with average concentrations of 4,000 mg/L to 5,000 mg/L at higher flow rates.

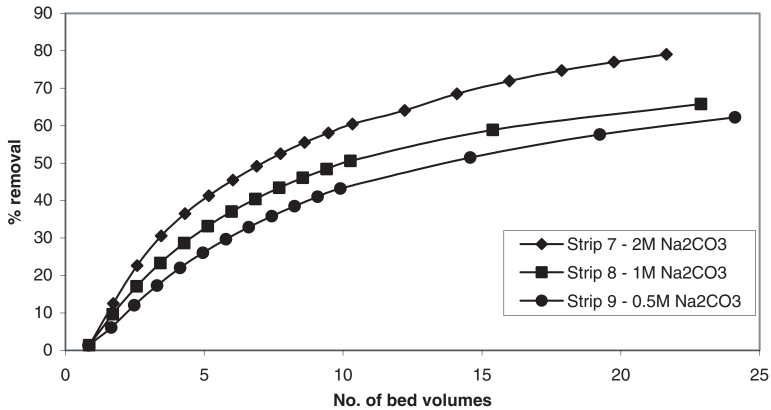

Figure 4 Summary plot of Na_2CO_3 regeneration trials on fully loaded MesoLite

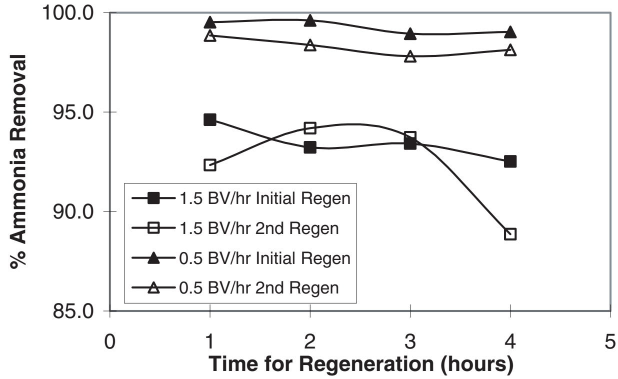

Figure 5 Efficiency of ammonia removal on successive re-use of Na_2CO_3 at different flow rates

Solution pH

Figure 6 shows the variation of pH between inlet wastewater and outlet water after treatment in the pilot plant with MesoLite. The inlet pH remains constant at about 7.6 over a twenty-four hour period while the pH of treated wastewater gradually decreases from a high of 8.8 to 7.9 as the loading cycle reaches breakthrough. During the complete series of pilot plant trials, pH values ranged between 7.1 and 10.2 for the inlet wastewater. Over this range of inlet pH values, the treated wastewater pH remained between 9.0 and 7.6.

Phosphate removal

Trials of orthophosphate removal using the same system configuration but with only one column of MesoLite media optimised for phosphate absorption (Mackinnon *et al.*, 1997a,b) were undertaken at an export-quality abattoir. The wastewater was pumped from final pond storage at the abattoir after conventional primary and secondary treatment stages. The abattoir wastewater also contained 200 mg/L ammonia and similar levels of fats and grease. Target breakthrough for phosphate removal at this site is 5 mg/L for a test flow rate of 10 kL/day. A breakthrough curve for phosphate removal using MesoLite material is shown in Figure 7.

Discussion

Data shown in Figures 2 and 3 demonstrate that MesoLite is an effective material for the capture of ammonia from anaerobic digester sidestreams. Reductions of more than 90% ammonia are achieved in the treated water and, depending on the design of the system and operating parameters, reductions of >95% are routinely achieved (e.g. Figure 3).

Pilot plant trials did not result in a fully loaded MesoLite column in which the outlet

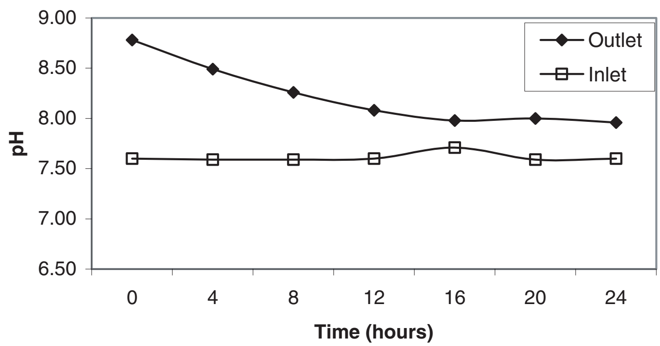

Figure 6 Typical range of pH values for inlet and outlet solutions during pilot plant operation

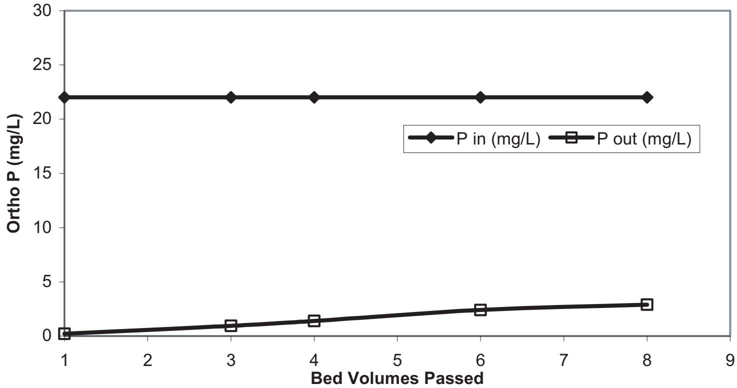

Figure 7 Breakthrough curve for orthophosphate removal from abattoir wastewater

ammonia concentration matched inlet value(s). Hence, the maximum loading capacity of this material was not determined for these trials. However, practical loading rates of between 45 and 55 gN-NH_4^+ per kg of MesoLite media have been determined from loading/regeneration cycles at bench-scale.

These results have been achieved with a one-hour detention time in the loading columns. When compared to alternative processes such as biological nitrification and denitrification, which requires between 8 and 24 hours detention time, the short detention time required by this novel process represents significant benefits in capital cost and footprint required for a full-scale system.

For Na_2CO_3 regeneration, removal efficiencies between 60% and 80% can be achieved depending on the concentration of caustic regenerant. This level of efficiency will result in a gradual reduction in loading capacity of the MesoLite material. However, data shown in Figures 2 and 3 suggest that the material is effective after five cycles of regeneration and reuse. This level of ammonia removal efficiency by the stripping solution is sufficient to concentrate ammonia to approximately 4,000 ppm in the regenerant solution. Further work is required on the regeneration process in order to achieve higher concentration factors for commercial implementation.

Higher stripping efficiencies can be achieved by use of an appropriate flow rate for the regeneration process. This effect is demonstrated in Figure 5 in which a lower flow rate shifts not only the initial stripping phase efficiency to >90% but also the second stripping phase efficiency. Optimum efficiency in regeneration will be achieved through an appropriate match of Na^+ concentration and flow rate for the level of ammonia loading.

For typical side stream wastewater configurations, dosing of the inlet stream to adjust pH for optimum ion exchange is unnecessary. In addition, data collected over the period of pilot plant operation suggests that MesoLite accommodates a variation of up to three pH units in a typical process plant system. Furthermore, treated wastewater shows pH values within an acceptable range for return to the head of the plant and may, in fact, be beneficial to some wastewater treatment processes.

Data in Figure 7 show that there is good potential to remove orthophosphates from wastewaters containing both ammonia and phosphate under typical plant operating conditions. In these trials, regeneration of the column used to remove orthophosphates was not as effective as regeneration of ammonia-loaded MesoLite. Further work is required to develop regeneration methods for orthophosphate recovery that are consistent with the ammonia recovery methods outlined above.

However, with successful removal and recovery of ammonia and phosphate from wastewaters using MesoLite materials, WWTP operators may achieve significant benefits through optimisation of the main process train to maximise removal of both nutrients. Conventional biological treatment methods may then operate at higher levels of efficiency.

For the Oxley Creek full-scale plant, the level of ammonia reduction achieved in the pilot plant is equivalent to an 18% reduction in the nitrogen load on the plant. This reduction in nitrogen load is highly beneficial to downstream processes in a treatment plant particularly if the WWTP is at maximum design capacity. For example, the 18% reduction in nitrogen is achieved in the main treatment process without consuming any carbon. This lower carbon consumption requirement per unit of mainstream process flow improves the TKN/COD ratio in the influent and reduces oxygen demand on downstream processes. Improvement in the TKN/COD ratio in influent wastewaters and control of dissolved oxygen are critical factors for enhanced performance of downstream biological nutrient removal processes (Ekama and Wentzel, 1999).

Conclusions

New ion exchange materials, MesoLite, show a strong capacity for removal of ammonia from WWTP sidestreams to reduce the total nitrogen load on the plant. Over 90% removal of ammonia is achieved in the sidestream using a simple fixed bed column arrangement in which the wastewater solution is passed over the exchange medium for an effective contact time of one hour. At full-scale, removal of > 90% ammonia from the sidestream results in a reduction of ~18% in the total nitrogen load of the WWTP. Further improvement in operating efficiency of a main process train can be achieved through simultaneous removal of orthophosphates using variations on the same MesoLite product. Efficiencies of the sidestream treatment process are dependant on typical ion exchange design parameters such as flow rate, bed volume, and inlet concentration and target breakthrough value for nutrient concentration in the treated water.

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