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Moving towards sustainable resources: Recovery and fractionation of nutrients from dairy manure digestate using membranes

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ABSTRACT

The fractionation of nitrogen (as ammonia/ammonium) and phosphorus (as phosphate ions) present in the dairy manure digestate was investigated using a nanofiltration membrane NF270. The filtration and separation efficiencies were correlated to pH across the range $3 < pH < 11$. Filtration at pH 11 enabled higher permeate flux of 125–150 LMH at 20 bar, however rejection of ammonia was high at 30–36% and phosphate was 96.4–97.2%. At pH 3 and pH 7, electrostatic charge effects led to higher permeation of ammonium and thus more efficient separation of nitrogen. The rejection of phosphorus was relatively constant at any given pH and determined as 83% at pH 3, 97% at pH 7 and 95% at pH 11. The fractionation of nitrogen and phosphorus from complex aqueous solutions was demonstrated to be highly dependent on the charge of the membrane and ionic speciation. Solutions rich in nitrogen (as ammonia/ammonium) were obtained with almost no phosphorus present (<1 ppm) whilst the purification of the PO_4–P was achieved by series of diafiltration (DF) operations which further separated the nitrogen. The separation of nutrients benefited from an advantageous membrane process with potential added value for a wide range of industries. The analysis of the process economics for a membrane based plant illustrates that the recovery of nutrients, particularly NH_3–N, may be commercially feasible when compared to manufactured anhydrous NH_3.

1. Introduction

Fertilizers, including nitrogen and phosphorus, *i.e.* nutrients, have had a pivotal role in sustaining the food supply to an increasing world population. However, the manufacture and use of fertilisers is causing continuous environmental problems, such as the emission of nitrous oxide, a potent greenhouse gas (Janson, 2012; Vanthoor-Koopmans et al., 2013). In addition, the production of nitrogen (as ammonia/ammonium, nitrite/nitrate and urea) and phosphorus (as phosphate) also carries a significant carbon footprint. Indeed, 1.5–2.6 tonnes of $CO_2$are produced per tonne of N (van Straaten 2008; Wood and Cowie 2004)and up to 1.0 tonnes of CO_2 per kg of P_2O_5 fertilizer (Oh-Ishi and Maeda, 2002). The runoff of fertilisers into watercourses also has a direct impact on human health, as well as the depletion of oxygen supplies in the water leading to "dead zones".

In recent times, agro-industrial wastes are being seen as a source of both energy and resources. One particular example is that of manure waste being transformed into methane by anaerobic digestion, whilst the nutrient-rich digestate is used as a replacement to conventional fertilisers (Cornejo and Wilkie, 2010; Desloover et al. 2012; Klavon et al. 2013). Nonetheless, there is only so much that can be applied to the soil without causing nutrient excess and consequent damage to the environment. Also, nutrient run-offs owing to rainfall and excess load may lead to the eutrophication of water courses (Smith and Schindler, 2009; Smith et al. 1999). Indeed, the nitrate –directive (91/676/EEC nitrate) was created with the purpose to protect ground water and lakes. According to the directive, the maximum application of manure corresponds to 170 kg N/ha/year. However, during a transient period up to 210 kg N/ha/year can be allowed (Commission, 1991).

Abbreviations: P, phosphorus; N, nitrogen; MF, microfiltration; DMDL, dairy manure digestate leachate; NF, nanofiltration; DF, diafiltration.

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Therefore, one of the greatest engineering challenges of the 21st century is to develop strategies that help to control the impact of agriculture on the environment.

Previous work has demonstrated the possibility of recovering nutrients in particle and bacteria-free solutions from dairy manure digestate (Gerardo et al. 2013), trout farm wastewater (Gerardo et al., 2015) and municipal wastewater (Lovitt et at., 2012). Strategies such as diafiltration (DF, i.e. addition of equal amounts of water for effective dialysis of solutes) and acidification of the digestate showed to critically influence the leaching of soluble nitrogen (NH_3–N), phosphorus (PO_4–P) and metals. When the digestate was acidified at pH 3, a nearly 3-fold increase of PO_4–P was possible with no effect on NH_3–N.However, such process does not lead to the effective separation of NH_3–N from PO_4–P in aqueous solution. Undeniably, separate streams of NH_3–N and PO_4–P are desirable and would potentially have a much higher range of applications and market value. Fertilizer, textile, chemical and biotechnology industries are heavily reliant on NH_3–N.Also, PO_4–P is an essential element to all living cells and has a crucial role in maintaining high crop yields (Beardsley, 2011; Gaterell et al. 2000; Tonini et al. 2013). In our recent work we have also suggested that separate streams of waste derived NH_3–N and PO_4–P could allow optimal microalgae growing strategies associated to biofuel production (Gerardo et al. 2014).

Membrane technology for the recovery and fractionation of nutrients from digestate is preferential over alternative technologies such as precipitation, absorption and thermal treatments. Ease of scaling up, chemical-free separations, low operating and maintenance costs, compact and modular design and highly selective separations are some of the advantages over their counter parts (Cheryan, 1998; Strathmann, 2011). Nanofiltration (NF) membranes have been widely reported to selectively allow the passage or retention of solutes based on both steric and electrostatic effects. Several NF membranes have been associated with the retention of phosphorus, chloride, micropollutants and ammonia. Pronk et al. (2006) compared three NF membranes (NF270, DS5 and N-30-F) and concluded that PO_4–P and NH_4 could be retained from synthetic urine at around 95% and 45%, respectively, using an NF270 (polyamide) membrane (Pronk et al. 2006). Rejection of up to 98% of PO_4 was reported using a tailored made multilayer polyelectrolyte NF membrane (Hong et al. 2009). Phosphate anions, $H_2PO_4^-$ and HPO_4^{2-}, were also demonstrated to be retained by NF200 at 85% and at 96%, respectively (Ballet et al. 2007). Other authors have reported that polyethersulphone membranes rejected up to nearly 70% of NH_3–N in solution (Ali et al., 2010). NF membranes have a potential role in the recovery of valuable resources from aqueous solution. Nonetheless, much of the results reported to date and associated phenomena are based on lab-grade synthetic solutions which do not mimic real separation conditions.

The objective of this work was to investigate the fractionation of NH_3–N and PO_4–P derived from dairy manure digestate using an NF270 membrane. Upon leaching nutrients by MF, the influence of pH on the effective rejection of both NH_3–N and PO_4–P was discussed. Filtration of up to 42% of the feed volume allowed evaluating the dynamics of such process in relation to the variation of the concentration of nutrients in the permeate stream. Diafiltration strategies were investigated to enhance the separation and purification of nutrients. Finally, capital expenditure and operational costs of a membrane filtration plant were determined.

2. Materials and methods

2.1. Preparation of the dairy manure digestate leachate (DMDL)

Dairy manure digestates were obtained from Fre-Energy dairy farm (Wrexham, Wales, UK). Initial conditioning treatment consisted of adjustment to pH 3 with concentrated HCl (Fisher Scientific, UK) and sedimentation for at least 1 h. The supernatant was then collected and screened through a 500 μm mesh. Nutrient rich leachates were produced by permeation through a bench-top cross-flow filtration unit. The crossflow membrane filtration unit consisted of an AGT Quix Stand benchtop system. This system featured a 1 L graduated polysulfone reservoir, peristaltic pump and a polysulphone hollow fiber cartridge with 0.2 μm pore size and 0.042 m^2 surface area, all from AGT (now part of GE Healthcare). The DMDL was analysed for nitrogen (as NH_3–N), phosphorus (as PO_4–P), metals and conductivity. pH 3 was chosen because of the high recovery of phosphorus and metals, with no influence on the recovery of nitrogen (Gerardo et al. 2013).

2.2. Characterisation of the NF270 – electrokinetic study

Zeta potential measurements were performed using Electro Kinetic Analyser (EKA, Anton Paar GmbH -Austria) for pH range of 3–10. The dimension of the streaming channel were 74 mm × 10 mm × 0.3 mm (Oo and Ong, 2010). An electrolyte solution was pumped through the cell and the pressure drop was measured by two pressure probes located up- and downstream of the cell. The potential difference resulting from the accumulation of charge at one end, i.e. streaming potential, was detected by two Ag/AgCl electrodes which provide information on the electrostatic charge at the shear plane36N.Streaming potential can be determined experimentally by plotting the voltage difference (ΔE) against various pressure drop (ΔP). A linear relation was obtained and the gradient (streaming potential coefficient) was used to calculate the zeta potential using Helmholtz–Smoluchowski equation (Ariza et al., 2001; Chapman Wilbert et al., 1999; Huisman et al., 1998)

$$\xi = \frac{dU}{dp}\frac{\eta}{\varepsilon_r \varepsilon_0}K_B \tag{1}$$

where ξ is the zeta potential in mV, dU/dp is the slope of streaming potential versus pressure (streaming coefficient) in mV/Pa, η the electrolyte viscosity in Pa.s, ε_r the relative liquid permittivity (dielectric constant, dimensionless), ε_0 the vacuum permittivity (8.854×10^{-12} C^2 J^{-1} m^{-1} or s m^{-1} Ω^{-1}), and K_B the specific conductivity of the bulk electrolyte solution (Ohm). When ξ is zero the membrane is said to isoelectric also known as isoelectric point (IEP).

The membrane was characterised using KCl salt solutions at different concentrations (0.001 M, 0.01 M and 0.025 M KCl) and three diluted solutions of the DMDL. The dilution factors are 100(10 mL of wastewater in 1000 mL water), 50(20 mL of wastewater in 1000 mL) and 33.33 (30 mL wastewater in 1000 mL water). All chemicals used in the experiments are analytical grade (Fisher Scientific, UK). The physical properties of the NF270 membrane used in this study are summarised in Table 1.

2.3. Fractionation of nutrients – NF and DF

The high-pressure stirred cell was sourced from Membranology® (Membranology Ltd, Swansea, UK) with a total volume capacity of 400 mL, maximum operational pressure allowance of 100 bar and a membrane area of 32.17 cm^2. The system was pressurized with nitrogen gas and controlled via valves and digital pressure gauges. The permeate line was connected to a collecting vessel placed on a digital scale and the automated weight was recorded via the RS232 (serial) port. A diagram of the NF setup is given in Fig. 1. The filtration was operated at 20 bar and 300 rpm (1.2 m/s) using a new and clean membrane for every DMDL sample.