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Sustainable waste water deammonification by vacuum membrane distillation without pH adjustment: Role of water chemistry

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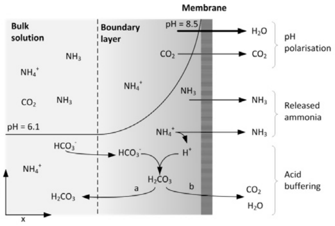
HIGHLIGHTS

- A new perspective to sustainable processes for waste water deammonification.
- Role of water chemistry for ammonia removal by VMD under no pH adjustment.
- A novel ‘pH polarisation and buffering’ mechanism was proposed.
- Up to 99.6% ammonia was removed from industrial effluents at pH as low as 6.1.

GRAPHICAL ABSTRACT

Conceptual diagram of ‘pH polarisation buffering’ effect at the liquid boundary layer of VMD deammonification process.



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ABSTRACT

Traditional aerobic processes used for deammonification in waste water treatment plants consume the majority of electrical energy. Ammonia can instead be recovered by membrane distillation but research to date proposes chemically intensive pH adjustment to release free ammonia from bulk solutions. Here we propose the novel application of membrane distillation to deammonify waste water without any pH adjustment. To demonstrate the concept, it was first shown that simple synthetic ammonia solutions strictly follow the classic ammonia-ammonium relationship with pH which shows little release as free ammonia until at least pH 9. However vacuum membrane distillation removed essentially all ammonium in solution as low as pH 6.1 due to carbonate that is often found in waste waters. Via a novel ‘pH polarisation and buffering’ mechanism, the functional effect was established due to CO2 released from the liquid-vapour membrane boundary layer causing a pH rise that released ammonia to the permeate. Via this mechanism, high depletions, up to 99.6%, occurred consistently on solutions containing carbonate and volatile acids at low pH, including two ‘as received’ industrial waste waters such as anaerobic digester effluent. Future work can consider effects including membrane fouling and cleaning for longer term waste water deammonification by ammonia capture.

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1. Introduction

Nitrogen is a key nutrient in fertilizers which produces food that sustains the world's population. However its use causes it to end up in effluent, and if not treated correctly, can lead to algal blooms or eutrophication of waterways which are harmful to the environment and our health [1–3]. A major form of nitrogen in effluent is ammonia with a concentration varying from 5 to 1000 mg-N/L. Besides the impact to the environment, release of volatile ammonia in sewer headspaces also presents a safety issue for sewer workers. Thus, the removal of ammonia from waste water is mandatory before environmental disposal.

The current treatment practice of ammonia containing waste water is commonly by biological processes such as deammonification by the aerobic and anoxic operations, which require aeration and consumes a significant amount of energy accounting for 80% of the overall electrical energy use in a typical waste water treatment plant [4]. A more sustainable approach of nitrogen removal that significantly reduces energy consumption include alternative biological deammonification such as anammox [5–7]. The ammonia capture concept appears more sustainable because the ammonia has to be synthesized by the energy intensive Haber Bosch process, consuming around 4% of all the world's energy [8]. Closing the nitrogen cycle is therefore part of a bigger picture potential for energy saving and greenhouse gas emissions reduction. Ammonia capture may be an effective alternative to waste water deammonification where a suitable reuse of the captured ammonia is identified, as indicated by a recent STOWA (Foundation for Applied Water Research, the Netherlands) report [9]. For example, a new thermal stripping process coupled with acid adsorption was shown effective in recovery ammonia nitrogen as ammonium sulphate from manure [10]. However, improvements are required to lower capital & energy costs and chemical consumption by introducing sustainable solutions. Membrane processes have been considered as a means to facilitate these cost reductions.

Membrane processes are proven effective to strip ammonia from synthetic ammonium solutions and real waste waters [11–17], including membrane contactors [11,17,18], membrane distillation (MD) [12–16,19] and pervaporation [13,14]. The pH of the investigated solutions was purposely chosen to be in the range of 9–14. For example, hydrophobic membrane contactors using sulphuric acid to recover ammonia have been commercialised and trialled on waste water [11,17] but performance is recommended at pH above 9. In recent years membrane distillation (MD), which is a thermal process for water production that is driven by a vapour pressure difference across hydrophobic porous membranes [20], has been proposed for ammonia removal [12,14,21] in either direct contact mode (DCMD) or vacuum assisted mode (VMD). EI-Bourawi et al. [15] reported that up to 90% ammonia was removed from ammonium synthetic solutions with pH of 12–14 using polytetrafluoroethylene (PTFE) flat sheet membranes in vacuum MD mode. The concentration of ammonia in the permeate was up to 8-fold more concentrated than in the feed, (depending on the operating conditions) which is the key mechanism for the deammonification function. Similarly, a 10-fold ammonia concentration of the permeate was obtained in another vacuum membrane distillation (VMD) study using polypropylene (PP) hollow fibre membranes at pH 11 [14]. Compared to direct contact MD (DCMD) mode, a modified DCMD method with sulphuric acid as receiving solution was employed to remove up to 99.5% ammonia at optimum pH of 12.2. In the above mentioned membrane studies, the initial ammonia concentration of the synthetic solutions was found to have a negligible effect on ammonia removal efficiency; while both pH and feed temperature were identified as the key parameters influencing the intrinsic ammonia-ammonium equilibrium, with pH above 10 reported to be effective in liberating ammonia from aqueous solutions [22]. However, most industrial effluents containing ammonia nitrogen exist at, or are adjusted to, neutral or even lower pH [23], e.g., effluents from anaerobic digestion process (pH of 6–8) have little volatile ammonia available for MD removal. Raising pH to above 9 would require prohibitively expensive chemical dosing to the full waste water flow. Recently, Dow et al. reported that ammonia removal could be achieved by MD at unadjusted pH. A DCMD bench-scale tests demonstrated that more than 75% of ammonia was captured from the ion exchange regeneration effluent with pH of 7.7 from a electricity generator [24]. This effect was again observed in a 3-month pilot scale study with the same effluent. Similarly, another MD trial on a biologically treated textile waste water of similar pH [25] found that the transport of volatile ammonia through the membrane was due to the concentration effect by MD, which raised the feed pH as fresh water being extracted. While focussed on water recovery, these examples showed the possibility of ammonia capture from real industry effluent using MD technology without the costly need for chemicals to adjust pH. However a specific study on the chemistry responsible for this benefice feature would be of interest to further the potential for chemical-free ammonia capture. Work to demonstrate ammonia removal and capture from waste waters at real industry pH ranges of around 7 would be highly desired by industry.

Hence, this study explores the feasibility of deammonification from industry effluents under unadjusted pH conditions by vacuum MD. The role of water chemistries determining the recovery efficiency of ammonia is examined through a series of synthetic solutions with various compositions, mimicking real industry effluents from identified sites such as electricity generator and anaerobic digester of municipal waste water treatment plant. The findings will then be confirmed on real industry waste waters to demonstrate the viability of the novel MD ammonia capture process.

2. Experimental

2.1. Membrane and material

The hydrophobic polypropylene (PP) hollow fibre membranes with a nominal pore size of 0.1 μm were provided by Zena, the Czech Republic. Ammonium hydroxide with purity of 28–30 wt% NH_3 (Sigma-Aldrich) was used to prepare synthetic solutions. 1.0 wt% sulphuric acid (H_2SO_4) solution was used for nitrogen analysis. Analytical grade salts from Sigma Aldrich including NaCl, $MgSO_4$, $CaCO_3$, K_2SO_4 were used for preparing synthetic water samples.

2.2. Membrane performance tests

VMD experiments were performed using a bench-top setup, as shown in Fig. 1. In the present work, a submerged hollow fibre module containing 38 fibres was used. For each VMD test, the hollow fibres with a length of 150 mm and inner surface area of 0.0048 m^2 were potted into a dead-end membrane module, with opening to the capillary side on the top of module. The module was submerged into the feed solution; the permeate was collected at the lumen side with a vacuum pressure P_v (100–400 Pa) applied by an oil pump. Feed solution mixing was controlled by vigorous mixing at 500 rpm and heated to the desired operating temperature of 45 °C, which represents the grade of commonly available waste heat from industry [26]. Two cold traps containing liquid nitrogen were placed along the vacuum line to capture the vapour generated. The product was collected and measured at 60 min