Chemical Engineering Journal 302 (2016) 641–649

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Valorization of ammonia concentrates from treated urban wastewater using liquid–liquid membrane contactors

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HIGHLIGHTS

- Hollow fibre liquid–liquid membrane contactors were used to produce liquid fertilizers.
- The influence of operational parameters was evaluated in a closed-loop configuration.
- A mass transport algorithm to predict the pH on the stripping stream was developed.
- The closed-loop configuration allowed recovery ratios of ammonia higher that 98%.
- High quality products were obtained as pollutants transport on the HFMC is restricted.

ARTICLE INFO

Article history:
Received 24 March 2016
Received in revised form 20 May 2016
Accepted 21 May 2016
Available online 21 May 2016

Keywords:
Ammonium valorization
Membrane contactor
Hollow fibre
Nitrate
Phosphate
Liquid fertilizers

ABSTRACT

The removal of ammonium from tertiary effluents by zeolites generates basic ammonia concentrates (up to 1–3 gNH_3/L in 1–2 g NaOH/L). This study evaluates the use of hollow fibre liquid–liquid membrane contactors (HFMCs) as a concentration and purification step for ammonia effluents to produce NH_4NO_3 and $(NH_4)_2(HPO_4)$ solutions for potential use as liquid fertilizers. The influence of various operational parameters (i.e., flow rate, initial ammonia concentration and stripping acid concentration) was investigated using a closed-loop setup. Due to the high basicity of the ammonia feed streams (pH > 12), the mass transport process was primarily controlled by the free acid concentration in the stripping phase (e.g., HNO_3 and H_3PO_4). A mass transport algorithm to predict the pH of the stripping stream was developed to describe the contactor performance, predict the requirements of the free acid concentration in the stripping phase and optimize the ammonia recovery. Therefore, the closed-loop configuration allowed for ammonia recovery ratios higher than 98% when the required free acid concentration of the stripping phase was maintained. The exhausted $NH_3/NaOH$ streams after NH_3 removal can be re-used for regeneration of the ammonium-exhausted zeolite filters.

1. Introduction

Free ammonia/ammonium that occurs in industrial, farming and domestic wastewater is a major environmental issue because its accumulation in water bodies leads to eutrophication and depletion of oxygen–harming waterborne organisms [1]. Several methods to remove ammonia have been proposed for rich ammonium streams (0.5–2 g/L NH_4) (e.g., supernatant liquor of anaerobic digesters (ADs)), ammonia stripping with air at high pH [2], ion exchange [3], magnesium ammonium phosphate precipitation [4] or biological nitrogen elimination [5]. Recently, membrane distillation (MD) and liquid–liquid membrane contactors (LLMCs) have been investigated as an alternative for ammonia removal from AD effluents with a high suspended solid content [6] or directly from a digestion process that treats slaughterhouse waste [7] to reduce the ammonia inhibition during the use of an AD. Although MD possess significant potential for improving NH_3 removal [8,9], the main obstacle in their use with an AD is membrane fouling caused by undegraded organic matter (e.g., proteins and complexes with cations) [10,11]. Fouling reduces membrane hydrophobicity, which hinders ammonia transport and limits scale up of the process [12,13].

For dilute ammonium streams (0.05–0.1 gN-NH_4/L) (e.g., effluents from conventional activated sludge reactors or tertiary treatments), the challenges are related to new legislation

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http://dx.doi.org/10.1016/j.cej.2016.05.094
1385-8947/

requirements to reduce the ammonium discharge levels from regulated values of 15 $mgNH_4/L$ to new recommended values of 1 $mgNH_4/L$ [14]. Ammonium removal treatment processes, such as air stripping and biological nitrification–denitrification [15], are not economically feasible, and a specific adsorption step is required. Typically, the reduction of ammonium levels below 1 mg/L involves the integration of ion exchange (IX) processes using zeolites [16] where the regeneration step involves generating rich ammonium/ammonia concentrates up to 1–3 g/L in NaCl, NaOH or NaOH/NaCl brines. Because the IX concentration step involves pre-treatment steps including particulate matter removal using sand filters or ultrafiltration processes, the quality of these effluents is more suitable for successful implementation of LLMCs.

MD and hollow fibre membrane contactors (HFMCs) have been proposed as a polishing step to remove low levels of ammonia/ammonium (up to 100 $mg\text{-}NH_4/L$) from industrial effluents [17,18]. HFMCs in PVDF exhibit high ammonia removal efficiencies that are dependent on the feed pH and independent of the ammonia concentration in the feed [19–23]. In comparison to conventional scrubbers, membrane contactors have a much larger specific surface area, and therefore, the space requirements and capital costs are less. In comparison to conventional air stripping processes, LLMCs provide independent control of gas and liquid flow rates without any flooding or foaming and do not require operation at a high-pressure drop [22,24].

Few studies of the removal of ammonia using HFMCs in alkaline solutions have been reported, and in general, these studies are devoted to enhancing the ammonium extraction efficiency in slightly alkaline solutions using sulfuric solutions. The aim of this study was to experimentally study the use of hydrophobic hollow fibre LLMCs as an ammonia separation and concentration step for the production and valorization of ammonium nitrate and diammonium phosphate solutions. A closed-loop experimental configuration was employed using nitric and phosphoric solutions as the stripping solution. The ammonia removal was evaluated from aqueous concentrated streams that were generated during the regeneration step for zeolites used to recover ammonium from a tertiary treatment effluent on a domestic wastewater treatment plant (WWTP). A factorial experimental design was used to determine the influence of the flow rate as well as the initial ammonia concentration on the overall ammonia mass transport coefficient. In addition, numerical modelling was developed based on the mass transport of ammonia through the membrane contactor, and this model also accounted for pH changes in the stripping solution (details provided in Appendix B). For nitric and phosphoric acid, the effects of the concentration and the nature of the stripping solution on ammonia removal were evaluated.

2. Materials and methods

2.1. Experimental set-up

The experimental set-up is schematically shown in Fig. 1. This set-up consisted of a hollow fibre membrane contactor (HFMC) module mounted in a horizontal position, two peristaltic pumps and two tanks of polypropylene (i.e., one for the $NH_3/NaOH$ feed solution and the other one for the nitric or phosphoric acid solution). Clear PVC flexible tubes were employed to connect all of the components. The propylene HFMC module consisted of a Liquid-Cel 2.5 × 8" Extra Flow X30HF from Membrane–Charlotte (Celgard, USA). The properties of the HFMC are summarized in Table S1 (Supplementary Information) [25].

The hydrophobic polypropylene (PP) hollow fibre separates both the feed and the stripping circulating phases, and the system works in a closed loop. The ammonia aqueous phase is fed on the

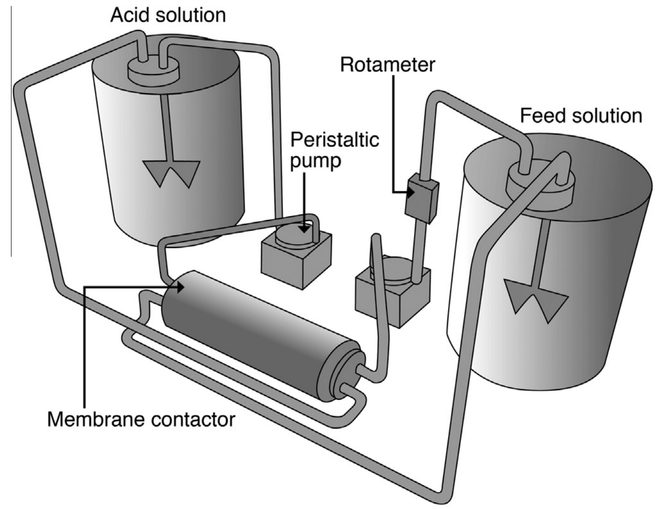

Fig. 1. Experimental set-up of the hollow fiber LLMC including a polypropylene tank containing the feed stream ($NH_3/NaOH$ solution) and polypropylene tank containing the nitric/phosphoric acid solution.

lumen side, and the strong acid stripping solution (nitric or phosphoric) is fed on the shell side. An air gap fills the pore of the hydrophobic polypropylene membrane, which is not wetted by the aqueous solutions. In the first step of the removal process, the ammonia gas forms ($NH_{3(g)}$) and diffuses from the bulk of the feed stream to the feed–membrane interface. Then, $NH_{3(g)}$ volatilizes through the feed–membrane interface and diffuses across the air-filled pore of the membrane. Finally, the gas reacts immediately with the nitric or phosphoric acid at the membrane interface of the shell side.

Initially, deionized water was passed through the module to flush out any trace of the compounds from the previous experiments. The $NH_3/NaOH$ feed solutions were pumped through the lumen side of the hollow fibre membrane contactor at different flow rates, and the stripping acid solution was circulated into the shell side in a countercurrent mode using two peristaltic pumps. Both solutions were recirculated to their respective reservoirs. The volumes of the feed and stripping solutions were 10 and 2 or 3 L, respectively, depending on the experiment requirements. At regular time intervals (10 min), samples (20 mL) were removed from the feed tank to measure the pH and total ammonia concentration. The pH (for solutions between 2 and 12) and acid (nitric or phosphoric) concentration of the receiving tank were monitored by taking samples at specific times. At the end of the experiment, the shell and lumen flows were stopped. The system was cleaned by passing deionized water through both sides to remove the remaining solution. All of the tests were carried out at room temperature

Table 1
Details of the factorial experimental design for the ammonia concentration using the HFMC with a 1.2 g/L NaOH background feed composition and a 0.5 M HNO_3 stripping stream.

Experiment	Feed stream C_0 (mg NH_3/L)	Stripping stream C_0 (HNO_3) (M)	Q (cm^3/s)	X^*_{C0}	X^*_Q
1	500	0.5	8.05	−1	−1
2	1500	0.5	8.05	1	−1
3	500	0.5	10.5	−1	1
4	1500	0.5	10.5	1	1
5	292.9	0.5	9.16	−1.414	0
6	1707.1	0.5	9.16	1.414	0
7	1000	0.5	7.59	0	−1.414
8	1000	0.5	11.055	0	1.414
9	1000	0.5	9.16	0	0