Long-term performance of a gas-permeable membrane for nitrogen recovery of acidogenic fermentation effluents

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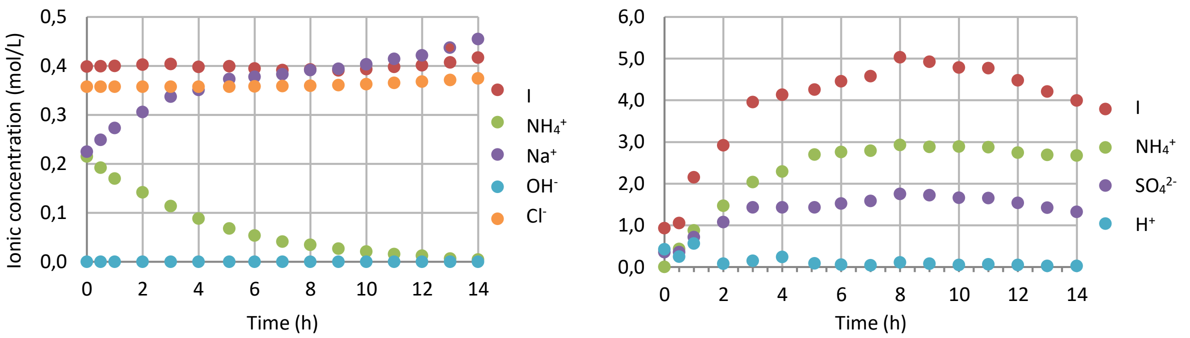
Abstract: Ammoniacal nitrogen recovery from residual effluents by means of hydrophobic gas-permeable membranes (GPM) is a well-proven technology capable of producing a highly rich nitrogen solution with potential use as fertiliser (Dube et al., 2016; Rongwong and Goh, 2020). To optimise the process, previous studies have focused on the effect of several operating factors, such as pH, temperature or the feed-to-trapping volume ratio, among others (Serra-Toro et al., 2024). However, there is a lack of knowledge regarding the membrane sensitivity at long-term conditions to fouling and wetting, two crucial aspects that affect the membrane performance and life span. Membrane fouling causes pores clogging and has a direct impact on the nitrogen transfer (Guangze et al., 2022). On the other hand, wetting occurs when water fills the membrane nanopores allowing water permeation through the membrane together with small organic and inorganic molecules (Wenting et al., 2023). The aim of this study is to determine the long-term resistance to fouling and wetting of a commercial GPM contactor while obtaining a $(NH_4)_2SO_4$ rich solution from fermented Organic Fraction of Municipal Solid Waste (OFMSW).

The experimental set-up consisted of a 5.0 L tank for the feed stream and a 0.5 L tank for the trapping solution (diluted H_2SO_4). This implies a feed-to-trapping volume ratio of 10 and, therefore, a potential TAN concentration in the trapping solution of 10 times the initial feed concentration. Agitation was provided in both tanks with magnetic stirrers and temperature was controlled in the feed tank. The GPM consisted of a hollow fibre membrane contactor of nanoperforated polypropylene. Two feed solutions were used: (i) a synthetic feed solution and (ii) a fermentation liquid of OFMSW collected in a mechanical-biological treatment plant. The feed stream was circulated in a closed loop in the shell side of the contactor while the acidic trapping solution circulated in the lumen side to strip the NH_3 and produce $(NH_4)_2SO_4$. The pH was set at 9.0 and 1.0 in the feed and trapping solution, respectively, by using a pH control system connected to peristaltic pumps to supply NaOH 10M and H_2SO_4 75% w/w, respectively. Analyses were performed according to the Standard Methods (APHA, 2005).

Figure 1 shows the ionic concentration in the synthetic feed and the trapping solutions for the 3 replicates of the experiment carried out at 25 ºC using synthetic wastewater with 6.5 g TAN/L. The ionic strength was calculated by $I=0.5\Sigma[i]\cdot z_i^2$ where $[i]$ is the molarity of each ion present in the solution and z_i is its ionic charge. The ionic strength in the feed solution remained nearly constant since the gain by the sodium ion (NaOH addition to control the pH) was compensated by the loss of NH_3 that diffused through the membrane. However, the trapping solution suffered a sharp increase in the ionic strength during the first 3 hours due to the high TAN transfer and, correspondingly, the addition of H_2SO_4 to maintain the pH at 1.0. The 68% of the TAN was recovered within the first 3 hours and this value increased to 99% after 8 hours of operation, when water diffusion through the membrane was also promoted. From this point on, the feed solution volume decreased until 4.77 L while the trapping volume increased to 0.71 L at the end of the experiment. The change in the trapping solution volume represented an increase of 42%, a value high enough to cause the ionic strength to decrease during the last 6 operation hours.



(a) (b)

Figure 1. Evolution of the ionic concentration (mol/L) and the ionic strength (mol/L) in the feed synthetic solution (5.0 L) (a) and the trapping solution (0.5 L) (b) working at 25 ºC.

Figure 2 summarises the experiments carried out with OFMSW fermentation liquid, which contained a volatile fatty acids (VFA) concentration of 40 g COD/L and 7 g TAN/L. These experiments were carried out with a volume ratio of 10, pH control in the feed tank at 9.0 and 35 ºC. Each day a new load (or cycle) of feed and trapping solution was replaced while the membrane was not cleaned nor replaced between cycles. This experiment lasted 40 days, when the nitrogen recovery performance was worsened. The TAN removal and recovery percentages were always very similar, what means that almost no loss of TAN was recorded (Figure 2a). Their value remained above 95% until day 24, when this N recovery started to decrease. The same behaviour was observed in the ammonia mass transfer constant (K_m) that reached values of about $1.8 \cdot 10^{-7}$ m/s until day 24 when it started to decrease (Figure 2b). Within this period, the obtained trapping solution was highly concentrated in $(NH_4)_2SO_4$ but water diffusion was detected in the last hours of each cycle and, therefore, a volume increase of the trapping solution was recorded. The decrease in K_m was mainly caused by the fouling of the membrane, which was visible by looking through the transparent shell of the membrane. However, the membrane performance was not only affected by fouling but also wetting was detected at a certain extent. More concisely, acetic acid started to cross the membrane from day 10 on and propionic acid at day 25, with increasing amounts along new nitrogen recovery cycles. This observation is attributed to wetting, since it has been reported that only non-ionized forms of carboxylic acids could diffuse through the membrane (which could only be feasible for acidic pH values but not at pH 9).

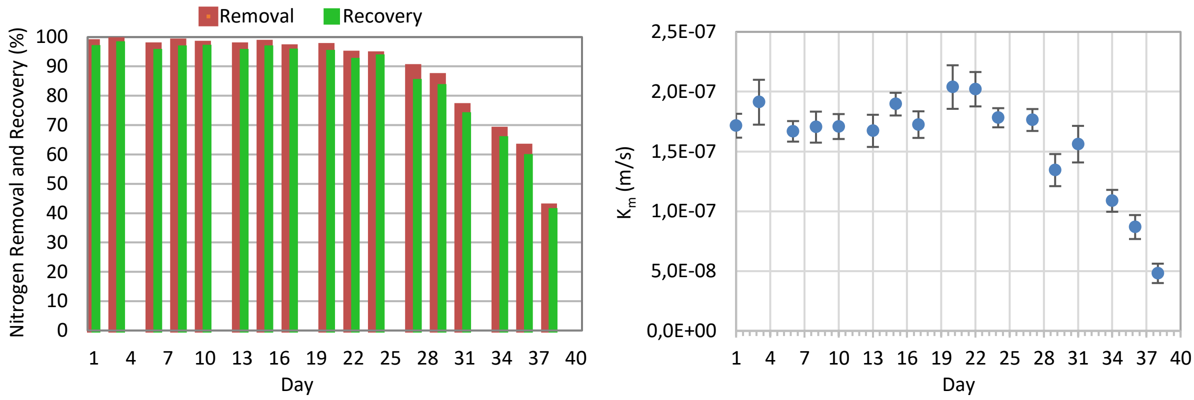


Figure 2. Evolution during 40 days of operation with a fermented OFMSW of the TAN removal and recovery (a) and the K_m (b).

This study demonstrates that an $(NH_4)_2SO_4$ solution at nearly 20% w/w could be obtained using a GPM contactor for the treatment of OFMSW fermentation liquid. However, water diffusion was promoted when high ionic strength differences exist at both sides of the membrane and limits the possibility of obtaining a trapping solution with higher $(NH_4)_2SO_4$ content.

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