

Efficient nitrogen removal and recovery from reject water by combining electroconcentration and stripping

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Keywords: Nitrogen; reject water; electrochemistry

Summary of key findings

A 3-chamber electrochemical cell combining electroconcentration technology and NH₃ stripping at the cathode was found to be efficient in nitrogen removal from both synthetic and real reject water from an anaerobic digester treating sewage sludge, with nitrogen removal efficiencies up to >99 % with real reject water. Over 50 % was recovered as a liquid concentrate with both studied reject water types and the two tested cathode materials, nitrogen-doped activated carbon foam (NDACF) and ultra-high surface area stainless steel mesh (UHSASSM). The recovery efficiency was further increased by up to an additional 35 % with NH₃ stripping at the cathode, utilising *in situ* generated H₂ as carrier gas.

Background and relevance

Macronutrients nitrogen, phosphorus and potassium are extensively used in agricultural fertilisers. Issues related to fertiliser production include the use of finite resources, high energetic demand and environmental pollution (Sutton *et al.*, 2013). For example, nitrogen conversion from atmospheric N₂ gas into plant-available ammonium (NH₄⁺) via the Haber-Bosch process contributes to 1–2 % of the total global energy consumption annually (Smith, 2002; Sutton *et al.*, 2013). In order to reduce the energy need and emissions related to it, more efficient recycling and reuse of nitrogen fertilisers is needed. A potential source for recovering nitrogen for reuse are municipal wastewaters that contain 11–18 % of the nitrogen originally used as fertilisers (Mulder, 2003; Billen, Garnier and Lassaletta, 2013; Sutton *et al.*, 2013).

In a contemporary municipal wastewater treatment plant (WWTP), nitrogen is predominantly present in the reject water resulting from the dewatering of anaerobically-digested sewage sludge, whereas most of the phosphorus remains in the solid fraction of the sludge when chemical phosphorus removal is utilized (Ek *et al.*, 2006). The nitrogen-rich reject waters are typically recirculated back to the treatment process, adding to the nitrogen load and thus the energy demand of the process (Arnold, Böhm and Wilderer, 2000; Wu and Modin, 2013). Instead, reject waters could be used as sources for nitrogen recovery.

Nitrogen recovery via ammonia (NH₃) stripping at high pH is well-studied but often energy-intensive and requires the addition of chemicals (Siegrist, Laurenzi and Udert, 2013). In electrochemical systems, electrical energy is used to drive oxidation and reduction reactions, which leads to the formation of pH differences between the anode and cathode chambers, facilitating ammonia stripping at the cathode (Desloover *et al.*, 2012). Furthermore, the ionic nature of the key nutrients in wastewaters can be taken advantage of using a 3-chamber (bio)electroconcentration set-up for recovery as a liquid concentrate (Ledezma *et al.*, 2017).

Here, nitrogen recovery from synthetic (containing 1170 mg NH₄-N L⁻¹) and real reject water from Rahola WWTP in Finland (containing 570 mg NH₄-N L⁻¹) was studied in a continuously-operated 3-chamber electrochemical cell combining electroconcentration and NH₃ stripping (Fig. 1.1). NH₃ was stripped at the cathode using H₂ gas produced *in situ* by the electrochemical (electrolysis) process then captured as ammonium sulfate using 2 M sulfuric acid solution. The performance of two different cathode materials, nitrogen-doped activated carbon foam (NDACF) and ultra-high surface area stainless steel mesh (UHSASSM) was compared.

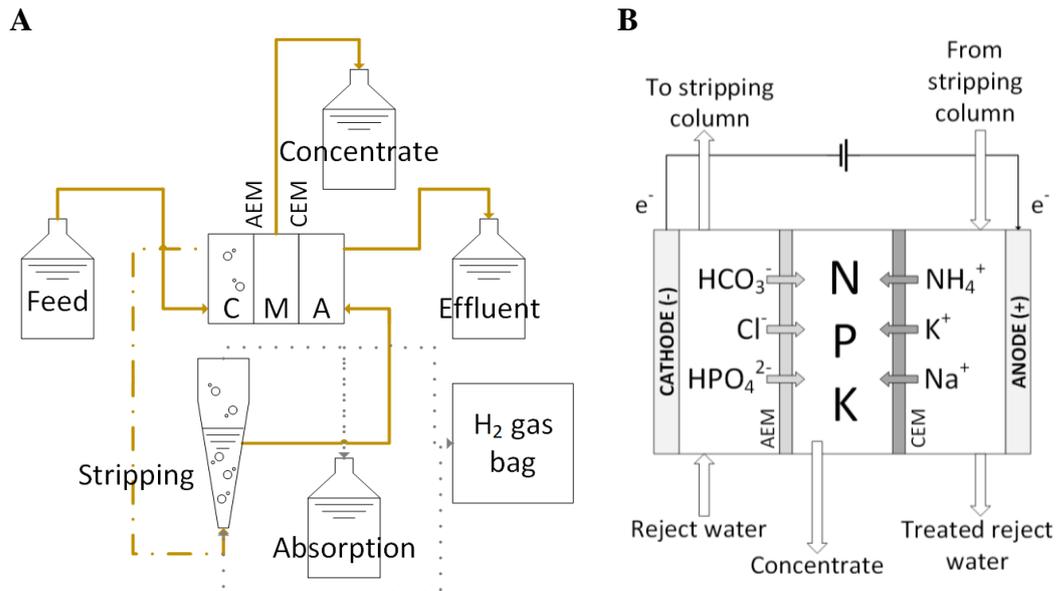


Figure 1.1 (A) Schematic presentation of the experimental system combining electroconcentration and ammonia stripping. Solid yellow lines represent the liquid flows and grey dot lines the gas flows. Yellow dash dot line represents a combined liquid and gas stream. (B) Detailed presentation of the 3-chamber electrochemical cell indicating the principal nutrient and gas flows. C=cathode; A=anode; M=middle chamber; CEM=cation-exchange membrane; AEM=anion-exchange membrane.

Results

The studied electrochemical system removed nitrogen from the influent reject water with high efficiencies of 93–96 % with synthetic and 96–99 % with real reject water, showing no significant differences in the performance with the different cathode materials (Fig 1.2). Nitrogen recovery into the middle chamber concentrate was very similar with both cathode materials: 51–52 % with synthetic and 56–57 % with real reject water. With UHSASSM, slightly higher cathodic pH values of 10.0 ± 0.0 and 10.5 ± 0.0 were obtained with synthetic and real reject water, respectively, compared to 9.8 ± 0.1 and 9.9 ± 0.0 obtained with NDACF, creating better conditions for NH₃ stripping. However, the NDACF cathode exhibited a more efficient H₂ generation, with initial tests indicating a H₂ generation rate of 80–90 mL H₂ d⁻¹ at 47 % efficiency in relation to the applied current. The H₂ production rate and efficiency of UHSASSM was estimated to be ca. 67 % of that of NDACF. The amount of nitrogen recovered via stripping at the cathodes, however, varied significantly between 10–35 % for synthetic and 4–32 % for real reject water and no clear trend could be seen in the results (Fig 1.2). The total cell voltage increased from 3.6 V with synthetic to 4.2 V with real reject water using NDACF as the cathode and from 3.0 V to 5.8 V with the UHSASSM cathode.

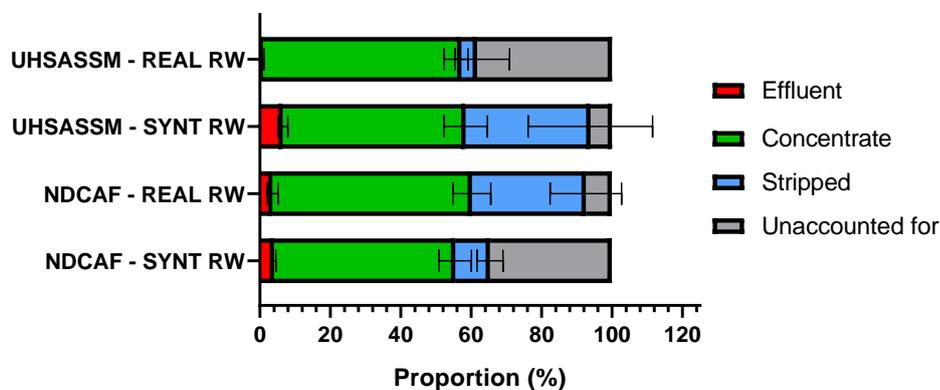


Figure 1.2 Distribution of the influent N between the different recovery and effluent streams with the two studied cathode materials (UHSASSM and NDACF) and real and synthetic reject waters (RW).

Discussion

The studied electrochemical nitrogen recovery system proved to be efficient in nitrogen removal from the influent reject water, with <1 % of the influent nitrogen escaping the system with the effluent in the best case with real reject water and UHSASSM cathode. The total removal efficiencies were significantly higher than the 72 % removal/recovery efficiency previously obtained with synthetic reject water in a previous version of the same concentration system where stripping and capture was not included (data not shown). The nitrogen concentration efficiency into the liquid concentrate was slightly lower here compared to the previously obtained 72 % in the bioelectroconcentration cell but the additional nitrogen stripping increased the overall nitrogen recovery to 61–89 %. The large variations and inconsistencies in the NH_3 stripping results are likely largely due to the system not being fully gas-tight, leading to loss of NH_3 gas, as well as the analytical methods being restricted to measuring only soluble NH_4^+ , possibly leading to overlooking some NH_3 . The results demonstrate, however, that it was possible to concentrate NH_4^+ and concomitantly strip NH_3 by recirculating only the *in situ* generated H_2 gas to the stripping column. Wu and Modin (2013) were able to obtain higher nitrogen recovery efficiencies via stripping, namely 94 % with synthetic and 79 % with real reject water, but only after a 20 h aeration period at the end of a batch test carried out in a 2-chamber bioelectrochemical cell.

While the results are promising, it is clear that measured cell voltages are too high for larger scale implementation and would need to be decreased via reactor optimisation (e.g. reduction of inter-electrode distance) or even using electroactive biomass as biocatalysts on the anode and/or cathode, i.e. turning the system into a bioelectrochemical cell with a much lower power consumption. The energy balance could also be improved by more efficient utilisation of the H_2 generated at the cathode. For example, the presented electrochemical recovery system could be further integrated with the anaerobic digestion of sewage sludge by re-injecting the H_2 generated at the cathode to the digester for biogas upgrading via hydrogenotrophic methanogenesis.

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