Nitrogen recovery from blackwater using bioelectrochemical systems

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1. Introduction

Bioelectrochemical systems (BES) were previously reported as a **promising technology for ammonium (NH_4^+) recovery from blackwater** (BW) (Ledezma et al., 2015). The **exoelectrogenic oxidation** of the organic matter contained in BW and the resultant polarization of BES electrodes becomes the **driving force for NH_4^+ migration** from the anolyte to the catholyte **through a cation exchange membrane** (CEM). Application of external voltage to BES system can help increasing the process kinetics and NH_4^+ migration flux. A downstream separation system is then required **to recover NH_4^+ in form of fertilizer**. In this study, a stripping system has been adopted, based on air bubbling over an air-diffusion cathode. The basification of the catholyte, due to oxygen reduction, causes NH_4^+ to convert to NH_3 and its stripping and recovery outside BES reactor.

High total ammonia Nitrogen (TAN) concentrations **can inhibit biologic activity** in BES anode chamber due to NH_3 release (free ammonia nitrogen, or FAN) (Nam et al., 2010). Other factors, as medium conductivity were reported (Kuntke et al., 2018) as important factors causing inhibition. For this reason, an initial task of **acclimation to high N concentration and conductivity** is a requirement for a successful BW treatment by BES. This study has been carried out in the framework of Run 4 Life project.

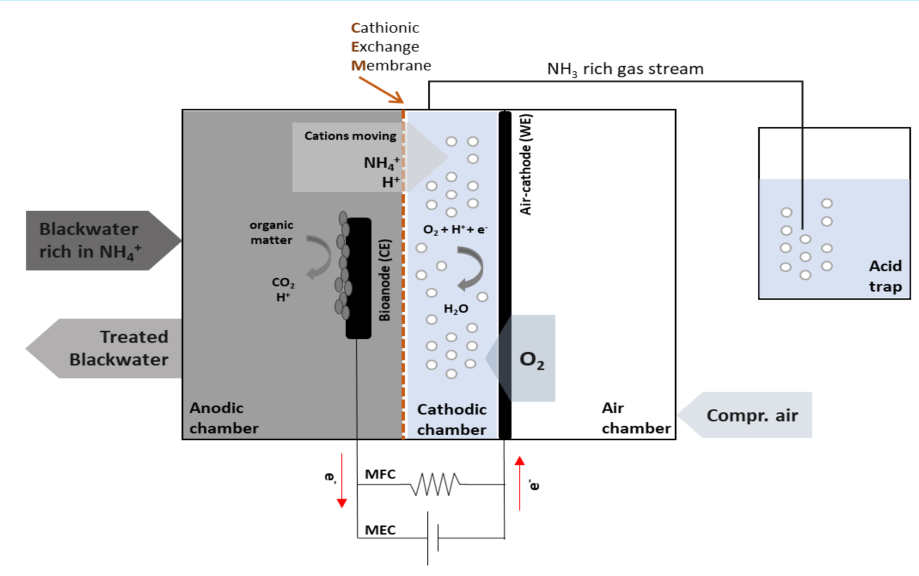


Figure 1: Adopted BES reactor design and working principle

2. Materials & Methods

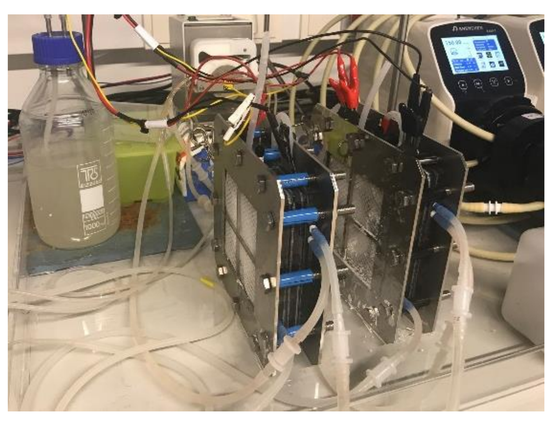


Figure 2: Air cathode MFC setup for biofilm acclimation

Figure 3: BES set up for nitrogen recovery

2.1 Biofilm acclimation to high [NH_4^+]

Reactors: 2x single chamber air-cathode Microbial Fuel Cells with electrode surface of 100 cm^2

Inoculum: Mixed culture from running MFC.

Operation: Constant load discharge mode at 20 Ω

Influent: Continuous feeding with Synthetic medium:

- MFC1 medium: 1.7 g COD/L; 24h HRT; fixed 0.5 g/L [N-NH_4^+].
- MFC2 medium: idem + Increasing gradient of 0.5g/L of N-NH_4^+ per cycle.

2.2 Nitrogen recovery

Reactors: 2x three chamber BES cells with controlled air-flowrate air diffusion cathode. Anode: carbon felt; Cathode: Unidirectional carbon fibers + commercial catalyst; Reference electrode: Ag/AgCl.

CEM: Membrane International (CMI 7000)

Electrode surface 100 cm^2

Air system auxiliaries: Air flowmeter; primary and secondary acid traps fed with [H_2SO_4]=0.1M

Adopted Chronoamperometric modes (BES types):

Open circuit voltage (OCV), Microbial fuel cell (MFC E=0.2V) and Microbial electrochemical cell (MEC E<0).

Inoculum: mixed culture coming from the set up described in 2.1.

Influent: anolyte: 1L of Synthetic medium (initially 1.7g COD/L, with posterior 2.5g/L of sodium acetate addition as supplementary carbon source; [N-NH_4^+]=1g/L) & Blackwater enriched with 2.5g/L of sodium acetate and 1g/L N-NH_4^+; Catholyte: 0.5L of [NaCl]=12.3 g/L.

3. Results

3.1 Biofilm acclimation results

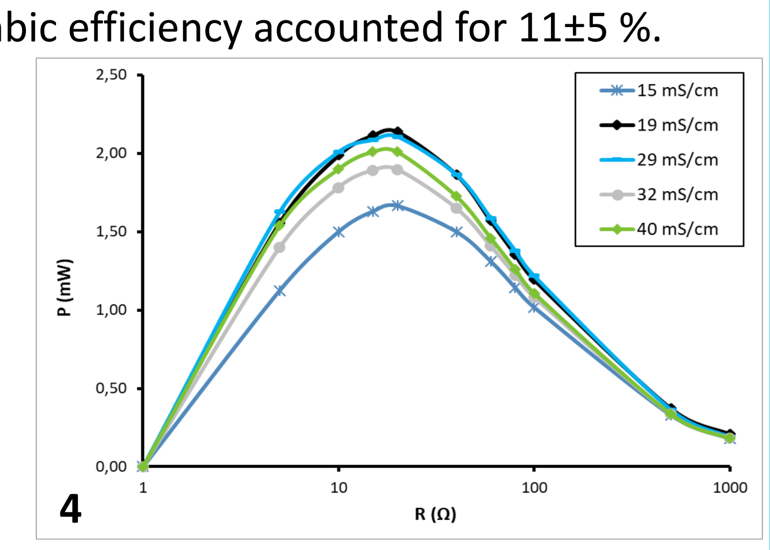
Biofilm was successfully grown and acclimated in MFC 1 and working in steady state for more than 220 days. COD and nitrogen removal remained constant. Electrically, recorded current densities were in the range 0.59-0.7 A/m^2 and coulombic efficiency accounted for 11±5 %.

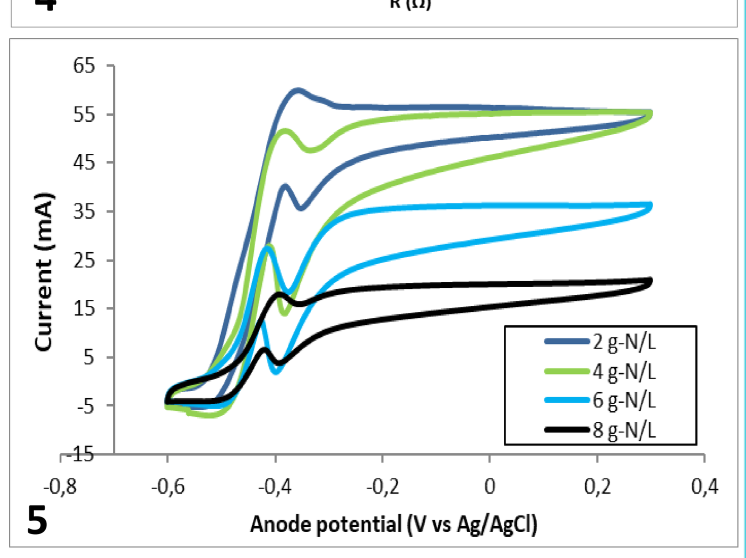
Figure 4: Influence of conductivity and Ammonium concentration on power generation: Suggests that below 40mS/cm electric conductivity has no negative effects. In contraposition it produces an increase in the power produced.

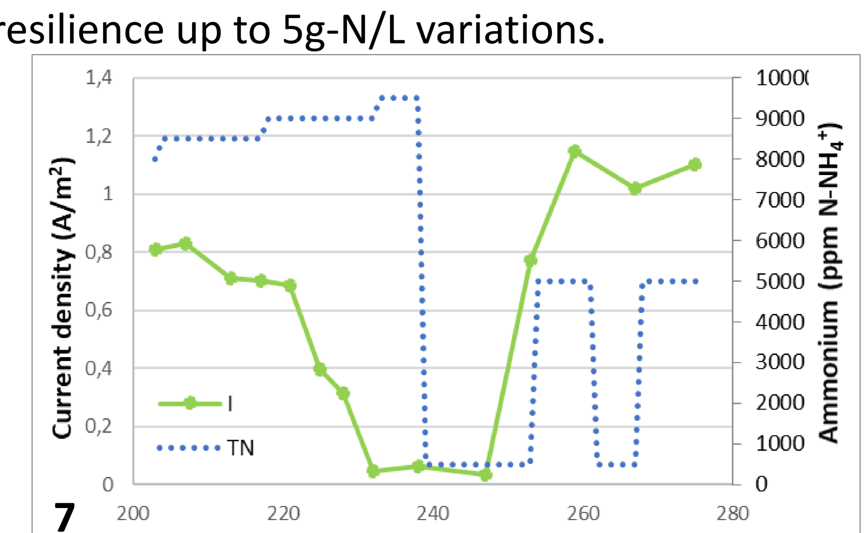
Figure 5: Influence of ammonium concentration. Cyclic voltammetries: demonstrating an exoelectrogenic activity decreasing of the biofilm with [N-NH_4^+] increasing.

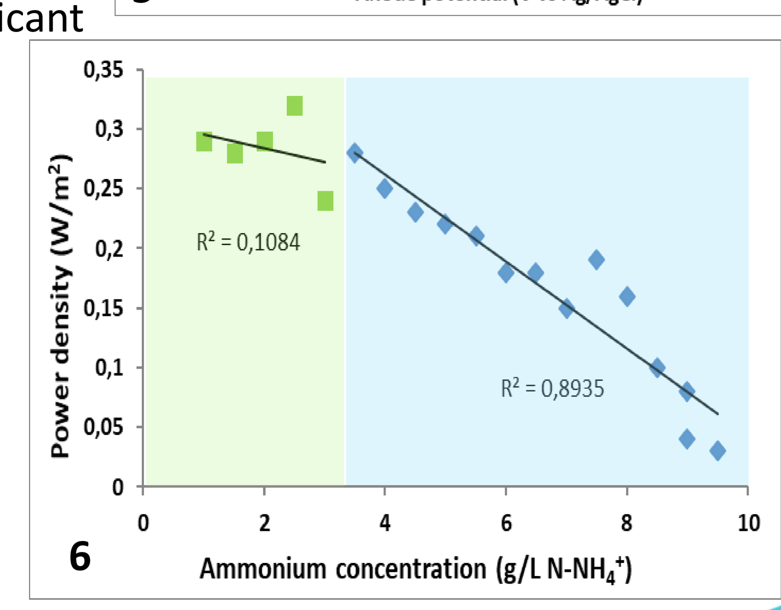
Figure 6: Influence of ammonium concentration on Maximum Power density: Polarization curves revealed a significant decreasing trend in microorganisms activity since 3.5 g/L of [N-NH_4^+].

Figure 7: Resilience in current production to [N-NH_4^+] fluctuations achieved after acclimation: Once the biofilm inhibited, MFC 2 was fed with low [N-NH_4^+] medium. After two weeks the biofilm recovered the exolelectrogenic activity and demonstrates significant resilience up to 5g-N/L variations.









3.2 Nitrogen Recovery results

Figure 8: BES operation mode: Operation in MEC mode led to higher N removal reaching 75-80% (13.7-19.2 g-N/m^2/d).

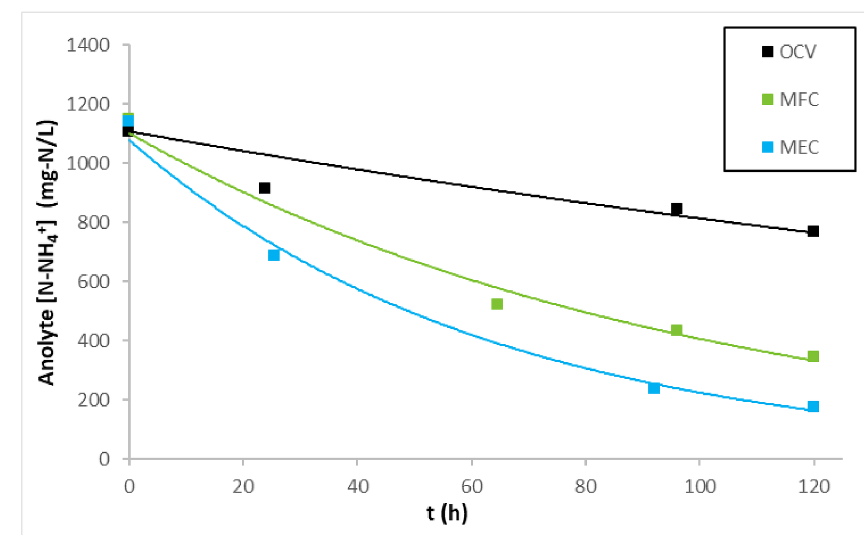
Also, higher current densities achieved 2.22-2.78 A/m^2, almost doubling the ones achieved in MFC mode. OCV represents the diffusion through the CEM only due to the concentration gradient.

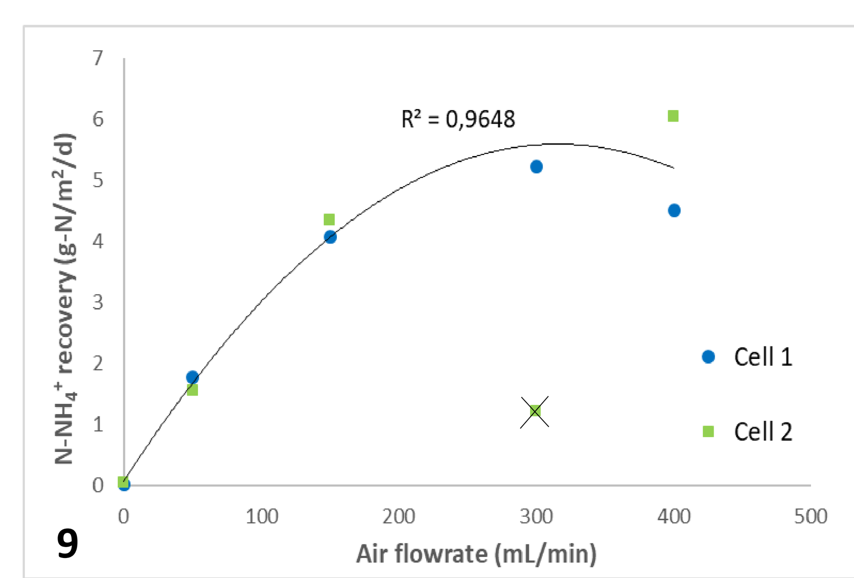
Figure 9: Air flowrate effect on N-NH4+ recovery:

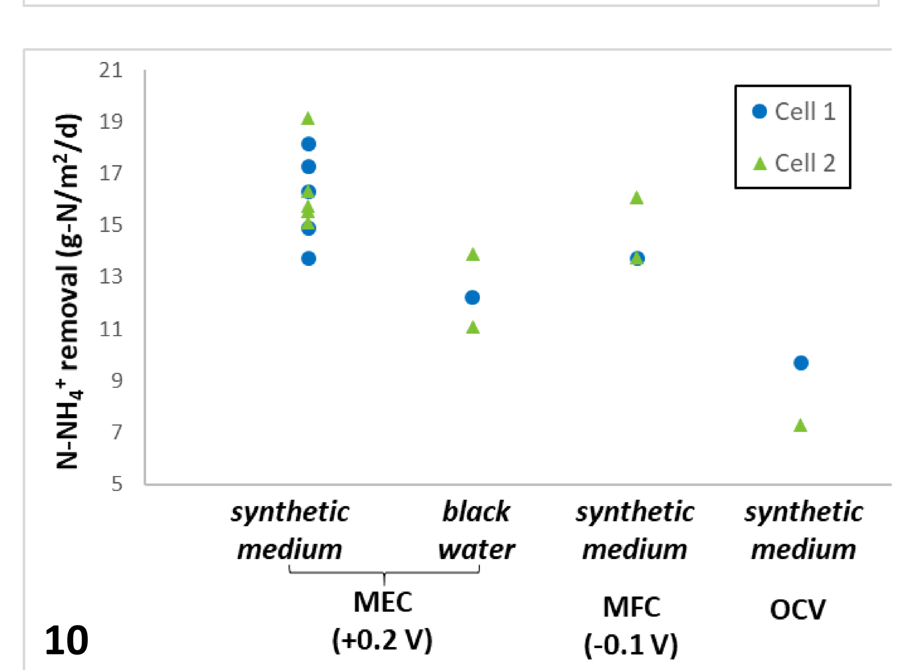
A likely-linear increase trend of N recovery can be observed for air flowrates lower or equal to 150 mL/min. Similar behaviours were observed in terms of current generated and N removal. Despite higher recovery could be reached, 150mL/min is the most cost-effective option.

MEC (0.2V) + 150 mL/min → allowed to remove 74-80% of N from the anolyte in 5 days, recovering 36-47% in the (first) acid trap. The remaining N was trapped in the cathode chamber. Moreover, neither anode nor cathode chamber presented suitable conditions for N-NH_4^+ oxidation to NOx forms (not detected).

Figure 10: Synthetic medium vs Black water: as expected, treating black water removal decreased (and also current and N recovery associated). Even though, around 12 g-N/m^2/d could be removed from the anolyte while treating 50-100 kg COD/m^2/d.







4. Conclusions:

- It has been studied the behaviour of two anodic biofilms at high NH_4^+ concentrations.
- Complete inhibition was observed when reaching 9.5 g-N/L, but significant inhibitory effects detected since 3.5 g-N/L.
- Acclimated biofilm presents resilience to short-term variations of N load. That is a useful characteristic for its operation with real BW streams.
- The feasibility of BES approach for N recovery has been proven.
- Higher N recovery achieved when BES was operated in MEC.
- A few parameters optimization allowed to remove up to 74-80% of N from the anolyte, recovering almost 50% in the acid traps as liquid fertilizer. Moreover, treating enriched Black water around 12 g-N/m^2/d could be removed.
- N recovery achieved is in the range of the state of the art of other BES systems using other N-rich wastewater (Kuntke et al., 2018).