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Ammonium recovery from agro-industrial digestate using bioelectrochemical systems

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ABSTRACT

Growing food and biomass production at the global scale has determined a corresponding increase in the demand for and use of nutrients. In this study, the possibility of recovering nitrogen from agro-industrial digestate using bioelectrochemical systems was investigated: two microbial electrolysis cells (MECs) were fed with synthetic and real digestate (2.5 gNH_4^+-N L^{-1}). Carbon felt and granular graphite were used as anodes in MEC-1 and MEC-2, respectively. As to synthetic wastewater, the optimal nitrogen load (NL) for MEC-1 and -2 was 1.25 and 0.75 gNH_4^+-N d^{-1}, respectively. MEC-1 showed better performance in terms of NH_4^+-N removal efficiency (39 $\pm$ 2.5%) and recovery rate (up to 70 gNH_4^+-N $m^{-2}d^{-1}$), compared to MEC-2 (33 $\pm$ 4.7% and up to 30 gN $m^{-2}d^{-1}$, respectively). At the optimal hydraulic retention time, lower NH_4^+-N removal efficiencies and recovery rates were observed when real digestate was fed to MEC-1 (29 $\pm$ 6.6% and 60 $\pm$ 13 gNH_4^+-N $m^{-2}d^{-1}$, respectively) and MEC-2 (21 $\pm$ 7.9% and 10 $\pm$ 3.6 gNH_4^+-N $m^{-2}d^{-1}$, respectively), likely due to the higher complexity of the influent. The average energy requirements were 3.6–3.7 kWh $kgN_{removed}^{-1}$, comparable with values previously reported in the literature and lower than conventional ammonia recovery processes. Results are promising and may reduce the need for costly and polluting processes for nitrogen synthesis.

Key words: circular economy, electricity-driven resource recovery, microbial electrochemical technologies, nutrients, wastewater treatment

HIGHLIGHTS

- Bio-electrochemical nitrogen recovery from agro-industrial digestate was achieved.
- Carbon felt anode allowed higher nitrogen recovery than granular graphite.
- Reducing the HRT had an opposite effect on nitrogen removal, depending on the anode material.
- Nitrogen removal rates were negatively affected by real digestate complexity.
- Specific energy consumption was competitive with conventional technologies for nitrogen recovery.

INTRODUCTION

The growing food and biomass production at the global scale has determined a corresponding increase in the demand and use of nutrients (N, P, and K). According to the Food and Agriculture Organization of the United Nations (FAO), global demand for nutrients will increase above 200 million tonnes in 2022; nitrogen will represent approximately 60% (i.e., 153 Mt) of such demand, and it will be primarily used for the synthesis of fertilisers (112 Mt). This scenario indicates the need to adopt innovative strategies to implement reactive nitrogen compounds production, especially in more sustainable and less energy-intensive ways. Ammonia synthesis mainly relies on the Haber-Bosch process, which requires up to 60 MJ kgN^{-1} (depending on which fossil fuel is used to generate syngas) and represents about 2% of the total energy use at global scale (Ledezma *et al.* 2015; Monetti *et al.* 2019), thus having a significant negative impact on the environment. Moreover, the progressive nitrogen accumulation due to inefficient agricultural practices and inadequate treatment of liquid streams is responsible for eutrophication, with the consequent worsening of water quality and human health problems (Nancharaiah *et al.* 2016). Within this framework, a circular economy-based approach should promote the development of new strategies to minimise the release of nutrients into the environment and shift toward a more competitive, resource-efficient bio-economy where the waste economic sector plays an important role (Lin *et al.* 2016). In this sense, the recovery of nutrients from wastewater using technical- and cost-effective processes should be encouraged. For

ammonium-rich wastewater streams (>0.5 gN L^{-1}), such as manure, digestate, urine, black water, landfill leachate, and sludge reject water, nitrogen recovery is possible by conventional processes such as ammonia stripping, struvite precipitation (i.e., MgNH$_4$PO$_4$·6H$_2$O), and ion exchange. Such techniques are energy-intensive and often require massive chemical dosing (Kuntke et al. 2018). The high operating costs and the relative cheapness of competing ammonia products derived from the Haber–Bosch process make the economic feasibility of conventional nitrogen recovery technologies still low.

An emerging approach for recovering ammonia is through bioelectrochemical systems (BES) (Monetti et al. 2019; Sharma & Mutnuri 2019; Zhang 2020): the oxidation of COD at the anode is catalysed by microorganisms and generates electrons, which migrate from the anode to the cathode through an external electrical circuit. This flow of electrons drives positively charged ammonium ions' migration across a cation exchange membrane (CEM) to the cathodic compartment, where several grams of nitrogen per litre can be accumulated (Kelly & He 2014; Nancharaiah et al. 2016) and subsequently recovered by stripping, chemisorption, or forward osmosis. Depending on the counter-reaction occurring at the cathode, either energy can be harvested (i.e., microbial fuel cells, MFCs), or energy needs to be supplied (i.e., microbial electrolysis cells, MECs) (Kuntke et al. 2018). Interactions between several parameters, including ammonium ion concentration in the treated wastewater, stripping removal efficiency, catholyte pH and conductivity, current density, membrane and electrode type, and concentrations of other competing ions, need to be investigated to optimise the process (Nancharaiah et al. 2016; Zhang 2020).

Although BES were proved as promising for ammonium nitrogen recovery from high ammonium concentration streams (Wu & Modin 2013; Gildemyn et al. 2015; Zhang & Angelidaki 2015; Zou et al. 2017), studies about nitrogen recovery from agro-industrial wastes are still limited (Cerrillo et al. 2016, 2018).

In this study, two MECs equipped with carbon felt and granular graphite as anodes were fed with a synthetic medium mimicking agro-industrial digestate with high ammonium concentrations. Different hydraulic retention times and nitrogen loads were tested to maximise system performance in terms of ammonium recovery. Carbon felt and granular graphite are relatively cheap electrodes to be used in bioelectrochemical systems, and their application was subsequently investigated with real agro-industrial digestate with the perspective of process scale-up. No modifications were made to the electrodes (e.g., chemical cleaning as described by Gildemyn et al. 2015) to keep the costs at their minimum. Results were compared in terms of, among the others, nitrogen removal efficiencies, nitrogen removal and recovery rates, and specific power consumption to find the most appropriate material for the treatment of real digestate. Results were promising and provided a comprehensive set of valuable information for the possible combination of BES and anaerobic digestion for agro-waste valorisation within a circular economy-based approach.

MATERIALS AND METHODS

Experimental setup

The experiments were carried out using two double-chamber cells made of Perspex (MEC-1 and MEC-2). Two frames with an internal dimension of $8 \times 8 \times 2$ cm were linked with screws. The hydraulic seal was ensured by linking each cell frame with a rubber sheet, appropriately cut to fit the Perspex frame. Anodic and cathodic chambers, both with a volume of 130 cm^3, were physically separated by a CEM. The MEC-1 anode was a 64 cm^2 carbon felt electrode (thickness 1.12 cm, degree of purity 99.9%, AlfaAesar, Germany), connected to a stainless-steel mesh current collector; the MEC-2 anode consisted of graphite granules (d = 2–3 mm) that filled the anode chamber for about 1/3 of the total volume, and a graphite bar was used as the current collector. For both MEC-1 and MEC-2, the cathode material was a stainless-steel mesh (AISI 316, dimensions 8×8 cm, 0.1 mm thickness), with a projected surface of 64 cm^2. The anode chamber was equipped with a reference electrode (Ag/AgCl, $+0.197$ V vs SHE, mod. MF2052, BioAnalytical Systems, USA) for both cells. The anode (working electrode), cathode (counter electrode), and reference electrode were connected to a multi-channel potentiostat (Ivium Technologies, Ivium-N-stat, NL) for process control. The cathode compartment was coupled to a stripping and an absorption column, both made of Perspex, with an inner diameter of 8 and 70 cm height, half-filled with Raschig rings (L $\times$ A 4×4 mm, Carlo Erba, Italy). The catholyte was forced to flow continuously from the cathode chamber to the stripping column. The airflow for the ammonia stripping was ensured with a membrane pump, connected in a closed loop with the two columns. A schematic setup overview is shown in Figure 1. The absorption column was filled with 1 M sulphuric acid solution.
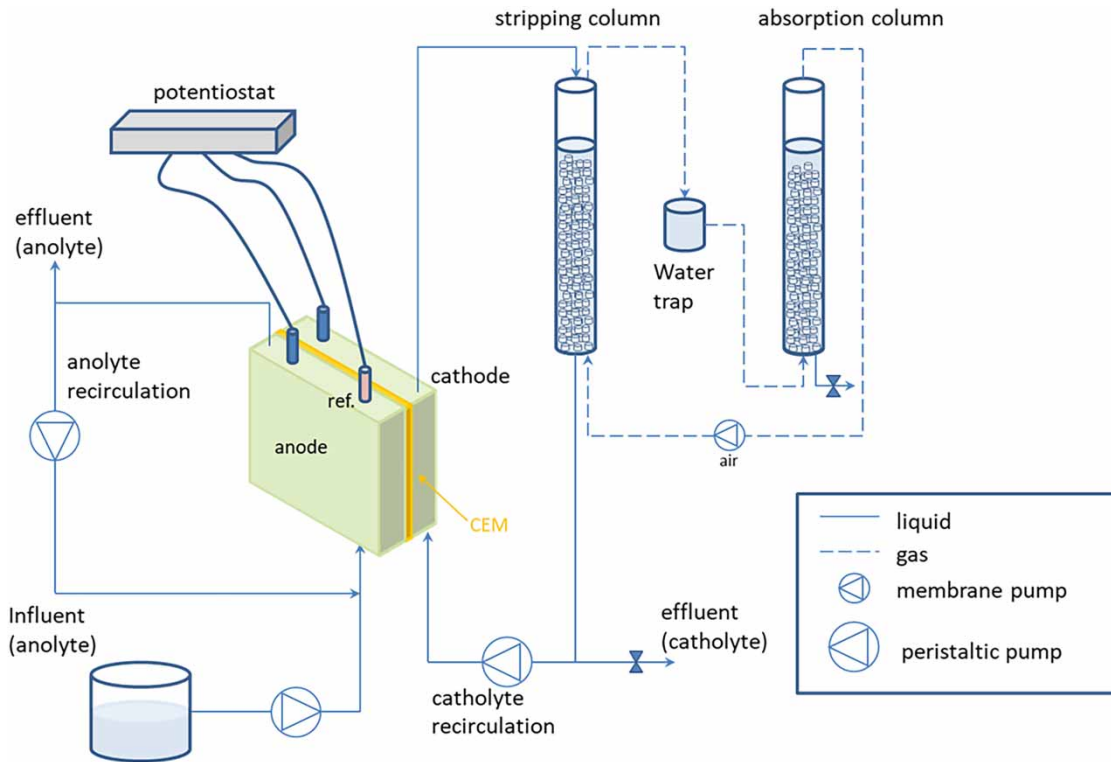
Figure 1 | Schematic representation of the BES setup.

Influent and media composition

The synthetic anolyte (Medium A) composition was prepared according to Gildemyn *et al.* (2015). The concentrations of ammonium (dosed as NH_4HCO_3) and acetate were 2.5 gNH_4^+-N L^{-1} and 3.0 g L^{-1}, respectively. The real anolyte consisted of the digestate produced by an anaerobic digester treating corn silage, livestock manure, and other agro-industrial residues. The 3-stage continuous wet digestion plant consists of three anaerobic mixed reactors working in series for a total digestion volume of approximately 4,200 m^3. The first reactor (i.e., primary digester) works in the low range of thermophilic process temperature. It is fed with biomass, while the second stage (i.e., post-digester) works in the high thermophilic range to boost the methanogenic conversions. The digestate is subsequently stored in the final tank, where the undigested residues are further processed in mesophilic conditions. The daily feedstock is composed of approximately 7 t of dedicated crop silage (corn and weed), 2 t of bran, 1 t of sheep manure and 15 m^3 of bovine slurry, partially replaced by olive pomace during the olive harvesting season. When available, small amounts of other agro-industrial by-products could also be fed during the year. The digestate was sieved at 125 μm, and the main composition was: NH_4^+-N, up to 2,500 mg L^{-1}; $COD_{filtered}$, up to 4,600 mg L^{-1}; total solids, up to 0.95%. The catholyte consisted of 0.1 M NaCl solution (Medium B).

BES operation

The cells were initially batch-fed using Medium A and operated as MFCs to monitor the growth and activity of the electroactive biomass (results not shown). The anodic chamber of each cell was inoculated with a mixture (50:50 v:v) consisting of the activated sludge drawn from the wastewater treatment plant of Cagliari (Italy) and the effluent sludge from the 3-stage anaerobic digester treating agro-industrial residues. After the process start-up, both cells were switched to MEC mode. The working electrode (i.e., the anode) was poised at −200 mV vs the reference electrode (Ag/AgCl) using the potentiostat. The anodic compartments were fed continuously with intense recirculation, and the cathodic chambers were batch-operated. Different hydraulic retention times (HRT) and nitrogen loads (NL: 0.75, 1.0, and 1.25 gNH_4^+-N d^{-1}) were tested in MEC1 and 2 fed with synthetic anolyte, and the optimal ones were chosen to treat the real agro-industrial digestate.

Analytical methods

Samples were collected from the anolyte (influent and effluent), the catholyte, and the absorption column. Anolyte samples were analysed in terms of chemical oxygen demand (COD), pH, acetate, and ammonia concentrations. Catholyte and absorption column samples were analysed in terms of ammonia concentration. Acetate concentration was measured through high-performance liquid chromatography (P680, Dionex, USA) equipped with a UV lamp detector and an organic acid column. COD was determined using a spectrophotometer (DR-2800, Hach, USA) after filtration of samples (1.2 μm). The anolyte conductivity was measured with an HQ30d meter (Hach, USA), equipped with an intellical CDC-401 probe (Hach, USA). NH_4^+-Nitrogen concentration was determined by spectrophotometric analysis (U-2000, Hitachi, Japan) at a wavelength of 420 nm. The pH was measured for all samples through a pH meter (GLP 22, Crison, Spain). X-ray diffractometry (XRD) analysis was performed on ammonium sulfate crystals recovered from the absorption column.

Calculations

The concentrations of NH_4^+-N measured in the influent anolyte ($C_{An,inf}$, mg L^{-1}) and effluent ($C_{An,eff}$, mg L^{-1}) were used for the calculation of the removal efficiency (RE, %), according to Equation (1):

$$RE = \frac{C_{An,inf} - C_{An,eff}}{C_{An,inf}} \times 100 \tag{1}$$

The nitrogen flux across the cation exchange membrane (i.e., the removal rate) was calculated according to Equation (2):

$$J_N = \frac{(C_{An,inf} - C_{An,eff}) \cdot Q}{A_m} \tag{2}$$

where J_N = flow of NH_4^+-N through the membrane (g m^{-2}d^{-1}); $C_{An,inf}$ = concentration of NH_4^+-N in the influent anolyte (g L^{-1}); $C_{An,eff}$ = concentration of NH_4^+-N in the effluent anolyte (g L^{-1}); Q = influent anolyte flowrate (L d^{-1}); A_m = surface of the membrane (m^2).

The recovery rate of NH_4^+-N (R_{NH4-N}^+, g m^{-2}d^{-1}) in the absorption column was calculated according to Equation (3):

$$R_{NH_4^+-N} = \frac{C_{abs.col.}}{A_m \cdot t} \tag{3}$$

where $C_{abs.col.}$ = NH_4^+-N accumulated in the absorption column (g L^{-1}); A_m = surface of the membrane (m^2); t = operating time (d).

The current density (j, A m^{-2}) was calculated according to Equation (4):

$$j = \frac{I}{A_m} \tag{4}$$

where I = current produced (A); A_m = surface of the membrane (m^2).

The specific energy consumption (SEC, kWh kgN$_{removed}^{-1}$) for ammonium transfer through the membrane was calculated according to Equation (5):

$$SEC = \frac{j \cdot A_m \cdot \Delta V \cdot 24}{(C_{An,inf} - C_{An,eff}) \cdot Q} \tag{5}$$

where j = current density (mA m^{-2}); A_m = surface of the membrane (m^2); ΔV = potential difference between anode and cathode (V); $C_{An,inf}$ = NH_4^+-N concentration in the influent anolyte (g L^{-1}); $C_{An,eff}$ = NH_4^+-N concentration in the effluent anolyte (g L^{-1}); Q = flowrate of influent anolyte (L d^{-1}).

Finally, the current efficiency (CE, %) was calculated according to Gildemyn et al. (2015).

RESULTS AND DISCUSSION

BES performance treating synthetic agro-industrial digestate

The operating conditions applied in the experimental phases with synthetic digestate (Medium A) are summarised in Table 1.

Process performances in terms of acetate and ammonium removal efficiency, current efficiency, and SEC for MEC-1 and MEC-2 are summarised in Table 2. Acetate removal efficiency did not change significantly in MEC-1 from Phase I onward, while a progressive decrease was observed in MEC-2, indicating the worsening of process performance with lower HRTs.

Figure 2 shows BES performance in terms of ammonium removal efficiency and removal rates. The highest values of NH_4^+-N removal rates were 78 ± 3.8 gN m^{-2}d^{-1} for MEC-1 (Phase III) and 33 ± 4.7 gN m^{-2}d^{-1} for MEC-2 (Phase I), respectively. As for MEC-1, a slight decrease in NH_4^+-N removal efficiency (from 48 ± 5.2 to $39 \pm 2.5\%$) was observed, as the NL was increased from 0.75 to 1.25 gNH_4^+-N d^{-1}. However, the resulting NH_4^+-N removal rates increased from 49 ± 5.0 to 78 ± 3.8 gNH_4^+-N m^{-2}d^{-1}

Table 1 | Experimental phases using synthetic wastewater

Phase	Acetate [g L^{-1}]	NH_4^+-N [g L^{-1}]	NL [gNH_4^+-N d^{-1}]	Anolyte conductivity [mS cm^{-1}]	Anolyte pH [–]	HRT (MEC-1) [h]	HRT (MEC-2) [h]
I	3.0	2.5	0.75	22.9 ± 0.5	8.2 ± 0.2	12	8
II	3.0	2.5	1	22.9 ± 0.5	8.2 ± 0.2	8	6
III	3.0	2.5	1.25	22.9 ± 0.5	8.2 ± 0.2	6	4

Table 2 | Overall BES performance with synthetic influent

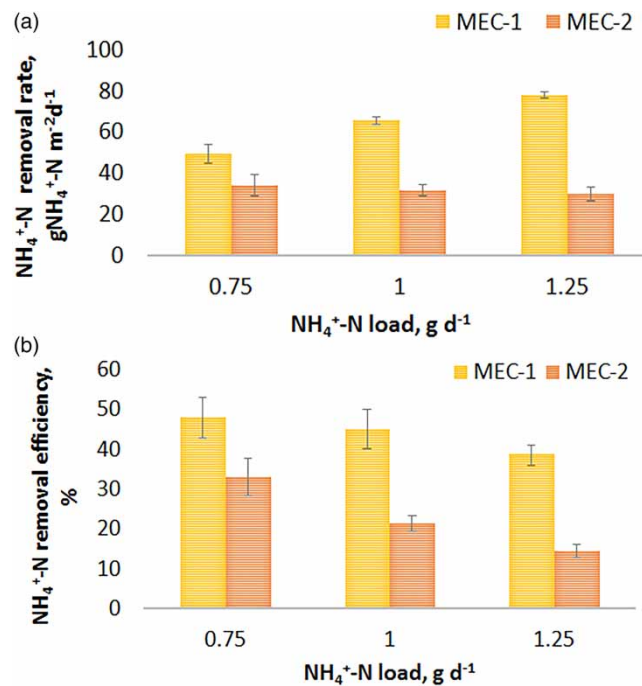| Phase	Acetate RE [%]		Ammonium RE [%]		Current efficiency [%]		SEC [kWh kgN^{-1}]	
	MEC-1	MEC-2	MEC-1	MEC-2	MEC-1	MEC-2	MEC-1	MEC-2
I	50 ± 10	36 ± 11	48 ± 5.2	33 ± 4.7	52 ± 6.6	48 ± 11	5.7 ± 0.8	4.9 ± 1.6
II	51 ± 10	34 ± 11	45 ± 4.9	21 ± 1.9	62 ± 8.5	50 ± 6.4	3.6 ± 0.8	5.2 ± 0.6
III	49 ± 3	24 ± 11	39 ± 2.5	14 ± 1.6	69 ± 2.8	63 ± 17	3.6 ± 0.1	3.9 ± 0.2

Figure 2 | NH_4^+-N removal rate (a) and removal efficiency (b) in MEC-1 and 2, with different applied NL.

due to the higher amount of influent treated per day. Correspondingly, the average SEC progressively decreased from 5.7 to 3.6 kWh kgN^{-1}. As for MEC-2, the NH$_4^+$-N removal efficiency decreased significantly (from 33 ± 4.7 to $14 \pm 1.6\%$) as the NL increased. Such decrease was not counterbalanced by the increasing amount of influent treated per day, therefore, the observed nitrogen removal rate slightly decreased from 34 ± 5.2 to 30 ± 3.3 gNH$_4^+$-N m^{-2}d^{-1}. The average SEC was in the range 3.9–5.2 kWh kgN^{-1}. For both MECs, open circuit tests were used as controls and showed negligible NH$_4^+$-N removal (below 4%), suggesting that bioelectrochemically driven NH$_4^+$-N removal was the main process involved.

The highest nitrogen recovery rates were consistently observed during Phase III (up to 70 gNH$_4^+$-N m^{-2}d^{-1}, corresponding to 3.5 kgNH$_4^+$-N m^{-3}d^{-1}) in MEC-1 and during Phase I in MEC-2 (up to 30 gNH$_4^+$-N m^{-2}d^{-1}, corresponding to 2.3 kgNH$_4^+$-N m^{-3}d^{-1}).

The difference in overall process performance between MEC-1 and 2 may be ascribed to the different anode materials. As previously reported by Vilà-Rovira et al. (2015), the biofilm growth between granular graphite particles may block the fluid flow path and produce clogging, negatively affecting the electrogenic microbial activity. Ceballos-Escalera et al. (2021) indicated the proper control of fluid dynamics in granular graphite-based electrodes as a key for minimising the effects of mass transfer limitations on catalytic rates and the transfer of charge-balancing ions outwards from the electroactive biofilm. In our study, the physical continuity of the carbon felt electrode in MEC-1 may have caused less hydraulic and electrical interferences than discontinuous granular graphite, with consequent better performance.

BES performance treating real agro-industrial digestate

MEC-1 and 2 were operated at their optimal HRT, as determined using the synthetic anolyte (i.e., 6 and 8 h, respectively). The average COD removal efficiencies were 32.7 ± 8.1 and $22 \pm 6.6\%$ in MEC-1 and 2, respectively, suggesting that most of the organic matter in the influent was slowly or not degradable. Low COD removal efficiencies ($12 \pm 1.8\%$, corresponding to 37% of the biodegradable organic matter) due to substrate complexity were also reported by Cerrillo et al. (2016) in an MEC fed with anaerobically digested pig slurry and operated in steady-state conditions at high HRT (30 h).

A progressive decrease in nitrogen removal rates and efficiencies was observed in MEC-1 (Figure 3_top) and MEC-2 (Figure 3_bottom) as real digestate was fed. This decrease was more evident in MEC-2 and ascribed to progressive clogging of intergranular pores due to the presence of solids in the influent. For this reason, cleaning and unclogging of the anodic compartment was performed on day 15. However, the consequent increase in process performance was only temporary, and nitrogen removal decreased as solids accumulated again. As reported by Bolognesi et al. (2021), the accumulation of solid particles in an MFC anodic compartment filled with granular graphite influences the contact between substrates and electrodes, and significantly modifies the distribution of the influent in the cell compartment, thus reducing process performance. However, MEC-1 and 2 showed similar performances in terms of NH$_4^+$-N removal efficiency ($29 \pm 6.6\%$ and $21 \pm 7.9\%$, respectively), while average nitrogen removal rates were 59 ± 15 and 19 ± 7.6 gN m^{-2}d^{-1}, due to the difference in NL applied. Such values were lower than those achieved with synthetic digestate, likely due to the much higher complexity of the real digestate (e.g., lower availability of readily degradable organic substrates, progressive clogging due to high solids content), as previously described also by Zeppilli et al. (2017) with the anaerobically digested organic fraction of municipal solid wastes (OFMSW). As reported by Cerrillo et al. (2016), the daily supply of mixed volatile fatty acids (namely acetate, propionate, and butyrate) led to an increase in ammonium removal efficiencies from 12 up to 60% in a MEC fed with pre-filtered and diluted pig slurry digestate, due to the higher availability of readily degradable organic substrate and the corresponding higher currents involved.

The average CE in our study was 70 ± 7.9 and $33 \pm 24\%$ in MEC-1 and -2, respectively. Again, open circuit tests showed that bio-electrochemically driven NH$_4^+$-N removal was the main process involved.

Both in MEC-1 and 2, ammonium was successfully recovered as (NH$_4$)$_2$SO$_4$, as confirmed by XRD analysis performed on crystals collected from the absorption system (Figure 4).

The NH$_4^+$-N recovery rate achieved in MEC-1 was much higher than MEC-2 (60 ± 13 vs 10 ± 3.6 gNH$_4^+$-N m^{-2}d^{-1}, corresponding to 3.0 ± 0.7 and 0.8 ± 0.3 kgNH$_4^+$-N m^{-3}d^{-1}, respectively), due to the higher NL applied. Such values were lower than those achieved with the synthetic anolyte, in accordance with the nitrogen removal rates.

Nevertheless, the SEC observed in MEC-1 and -2 (3.6 ± 0.4 kWh kgN^{-1} and 3.7 ± 1.1 kWh kgN^{-1}, respectively) were still comparable with other published results (Wu & Modin 2013; Cerrillo et al. 2018) and lower than those reported for conventional ammonia removal techniques, such as the nitrification-denitrification process (13 kWh kgN^{-1}), the Sharon-Anammox process (5 kWh kgN^{-1}), and ammonia stripping (9 kWh kgN^{-1}) (Cerrillo et al. 2018). As reported by Wu & Modin (2013), electric energy requirements as high as 3.8–8.6 kWh kgN^{-1} still led to a positive energy balance of 6.5–1.7 kWh kgN^{-1}
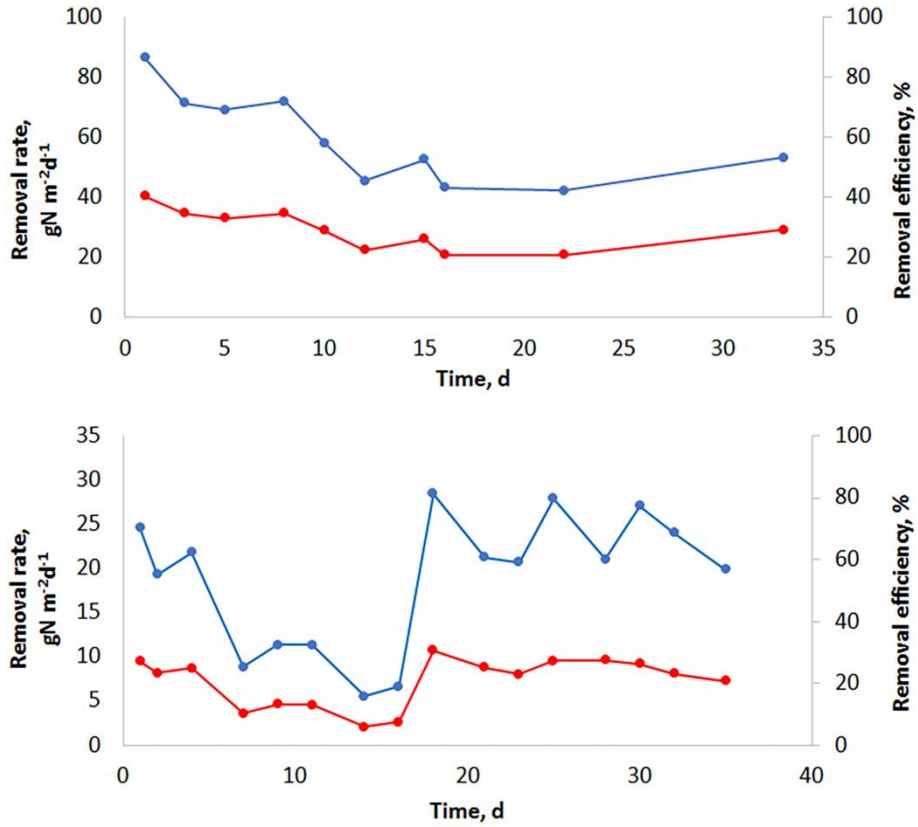
Figure 3 | Trend of NH_4^+-N removal efficiency (red) and removal rates (blue) observed in MEC-1 (top) and MEC-2 (bottom) fed with real digestate.

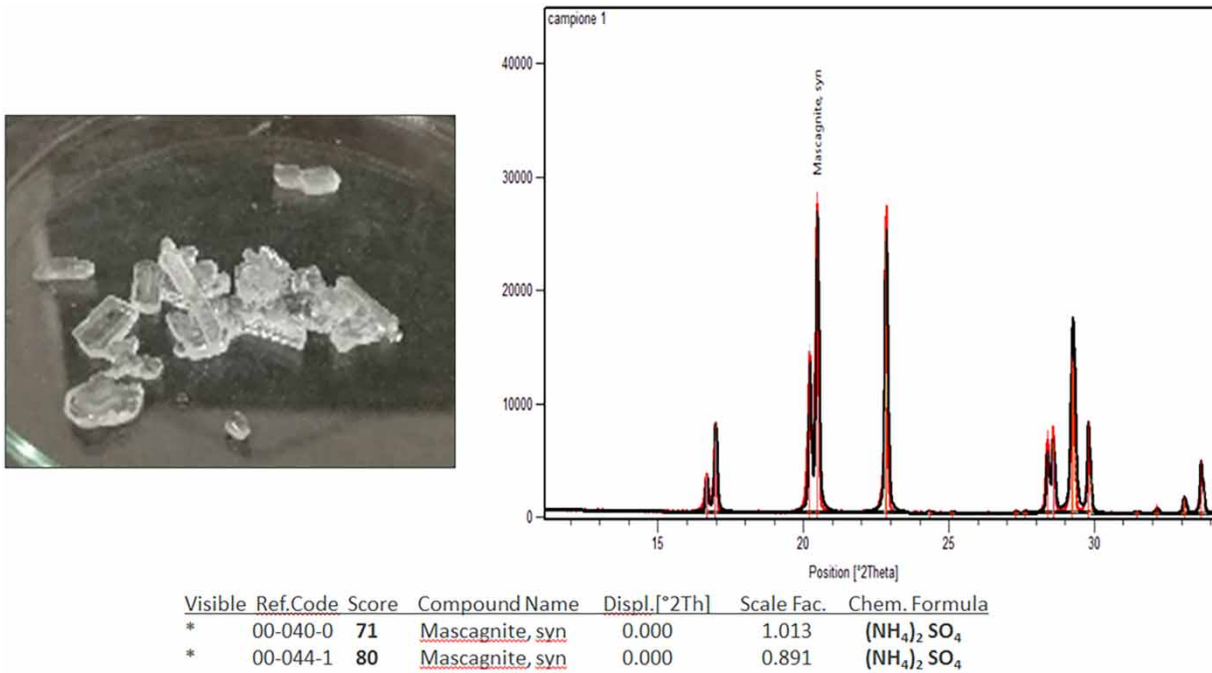| Visible	Ref.Code	Score	Compound Name	Displ.[°2Th]	Scale Fac.	Chem. Formula
*	00-040-0	71	Mascagnite, syn	0.000	1.013	$(NH_4)_2SO_4$
*	00-044-1	80	Mascagnite, syn	0.000	0.891	$(NH_4)_2SO_4$

Figure 4 | Typical XRD analysis on ammonium sulfate crystals collected from the absorption line of MEC-1 (fed with real digestate). Red line represents PDF card #00-044-1 (Mascagnite).

Table 3 | Comparison among different studies concerning ammonium recovery from digestate using bioelectrochemical and electrochemical systems

	Influent type	Reactor Type	Anode	Cathode	Influent NH_4^+-N	Nitrogen removal rate (gN m^{-2}d^{-1}; *kgN m^{-3}d^{-1}*)	Nitrogen recovery rate (gN m^{-2}d^{-1}; *kgN m^{-3}d^{-1}*)	SEC (kWh kgN^{-1})
This study	Synthetic agro-industrial digestate	2-chamber MEC	Graphite felt	Stainless steel mesh	2,500	78 ± 3.8; *3.9 ± 0.2*	up to 70; *up to 3.5*	3.6 ± 0.1
	Real agro-industrial digestate	2-chamber MEC	Graphite felt	Stainless steel mesh	2,447 ± 121	59 ± 15; *3.0 ± 0.8*	60 ± 13; *3.0 ± 0.6*	3.6 ± 0.4
Cerrillo *et al.* (2018)	Filtered digested pig slurry	2-chamber MEC	Carbon felt	Granular graphite	1,590–2,970	14.5	–	3
Cerrillo *et al.* (2016)	Filtered digested pig slurry	2-chamber MEC	Carbon felt	Stainless steel mesh	2,190	3.7 ± 0.5	–	–
Wu & Modin (2013)	Real reject water	2-chamber MEC	Carbon felt	Steel wire	1,000	–	–	3.8–20.5
Zeppilli *et al.* (2017)	Digested OFMSW	2-chamber MEC	Graphite granules	Graphite granules	932 ± 95	*0.04 ± 0.01*	–	–
	OFMSW fermentate-digestate mix.	2-chamber MEC	Graphite granules	Graphite granules	818 ± 51	*0.23 ± 0.03*	–	–
Desloover *et al.* (2012)	Digestate	2-chamber electrochemical cell	Ti-MMO	Stainless steel mesh	2,120	90	–	13–26

Numbers in italics are expressed as kgN m^{-3} d^{-1}.

compared with the Haber-Bosch process in a 2-chambered MEC fed with real reject wastewater (1,000 mgNH$_4^+$-N L^{-1}) at the cathode and synthetic municipal wastewater at the anode, and operated in galvanostatic mode (5–10 mA). Although calculations do not take into account the energy consumption related to the air stripping, it should be considered that other much more energy-efficient methods can be used for capturing ammonia, such as diffusion through a membrane (Rothrock *et al.* 2010; Wu & Modin 2013).

Some practical considerations

A comparison between the results of this study with agro-industrial digestate and previous studies concerning ammonium recovery from digestate using (B)ES is summarised in Table 3. Though the results of our study were promising, it is interesting to notice that further improvement of MEC performance can still be achieved. As reported by Zeppilli *et al.* (2017), a significant increase in volumetric nitrogen removal rates (from 0.04 ± 0.01 to 0.23 ± 0.03 kgN m^{-3}d^{-1}) in a methane-producing MEC fed with the effluent of a two-phase anaerobic digester was achieved, as the feeding was switched from anaerobic digestate to a fermentate-digestate mixture (ratio of 1:10). The high concentration of volatile fatty acids in the fermentate (80% of soluble COD) led to increasing currents (from 23 ± 4 to 60 ± 4 mA) and enhanced NH$_4^+$-N contribution to ionic transport from the anodic to the cathodic compartment (up to 20%). A similar approach can be used in our study by mixing digestate with VFA-rich fermentate taken from the primary digester, thus enhancing ammonium recovery. However, such a strategy would lower biogas production potential and reduce the plant's overall energy efficiency. MEC application for ammonium recovery looks particularly suitable if applied to 1-stage digestion plants that usually have a low conversion efficiency and work with a typical 30-day hydraulic retention time. Biomasses are considered costless for such systems, while major concerns are usually about nitrogen-induced methanogenic suppression (Ramm *et al.* 2020) and slurry/digestate distribution cost. The readily degradable organic acids content in filtered digestate should be sufficient to sustain nitrogen recovery using MEC. A fraction of the filtration residues, still rich in complex organic compounds, could also be recirculated into the digester to virtually increase its HRT and partially recover the biogas production potential loss, even if further field studies should be performed to evaluate the energetic balance of this last step.

Another option, designed for large utility-scale plants and prone to reduce transportation costs, is based on manure processing directly in the production site, to obtain a manure-thickened fraction, which can be sold to the biogas plant, and a filtered fraction which can be treated by MEC and, thanks to the reduced nitrogen content, could be applied to the nearest field, dramatically reducing energy consumption and pollution related to transportation. Manure or digestate filtration represents the step that mainly impacts process energetic yield; therefore, the ideal application of the process described in our study is on already pre-filtered matrices, according to standard industry practices. Bolognesi *et al.* (2021) observed that colloidal and small solid particles gradually accumulated in the anodic chamber of a microbial fuel cell filled with granular graphite and fed with pre-screened mature leachate and dairy wastewater. The progressive accumulation of solid particles limited the contact between substrate and electrode surface, reduced the net free volume in time with consequent reduction of HRT, and likely caused partial fouling of the cation exchange membrane, negatively affecting ion transfer efficiency between anodic and cathodic compartments. In this sense, implementing a more particle-selective influent screening was suggested to minimise clogging and avoid the worsening of process performance. If this is not possible, the recovery of nitrogen and other potential advantages like reduced transportation and distribution costs (filtered residues can be distributed by fertirrigation) should compensate for the extra costs related to filtration.

Since the effluent of both MECs still had a relatively high nitrogen concentration, the possible integration with a completely autotrophic post-treatment system (e.g., one- and two-step anammox) may represent an attractive solution. The integration of these processes would allow obtaining, in addition to the economic advantage generated by the partial recovery of nitrogen (MEC), also a significant reduction in the operating costs associated with its completely autotrophic removal downstream.

CONCLUSION

Bioelectrochemically driven ammonium recovery was successfully achieved in two microbial electrolysis cells fed with agro-industrial digestate. The carbon felt anode allowed higher and more stable nitrogen removal and recovery rates than granular graphite due to better hydraulic distribution and electrical continuity. Although the complexity of real digestate in terms of organic matter and total solids content led to worse nitrogen removal and recovery rates compared to the synthetic influent, the results were promising. They proved BES as a viable, cost-effective option for recovering nitrogen from agro-industrial digestate instead of conventional processes aimed at nitrogen recovery or synthesis.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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