



Full length article

## Application of ammonium fertilizers recovered by an Electrochemical System

Mariana Rodrigues<sup>a,b</sup>, R. Jensen Lund<sup>a</sup>, Annemiek ter Heijne<sup>b</sup>, Tom Sleutels<sup>a</sup>, Cees J. N. Buisman<sup>a,b</sup>, Philipp Kuntke<sup>a,b,\*</sup>

<sup>a</sup> *Wetsus, European Centre of Excellence for Sustainable Water Technology, Oostergoweg 9, 8911MA Leeuwarden; P.O. Box 1113, Leeuwarden, CC 8900 The Netherlands*

<sup>b</sup> *Environmental Technology, Wageningen University, Bornse Weilanden 9, 6708 WG Wageningen; P.O. Box 17, Wageningen, AA 6700, The Netherlands*



## ARTICLE INFO

## Keywords:

Circular economy  
Nitrogen recovery  
Electrochemical systems  
Ammonia fertilizers  
Re-using nutrients  
Sustainability

## ABSTRACT

Nitrogen (N) is an essential nutrient for plants and plays an important role in agriculture. However, the cycle between nitrogen input into agriculture and the nitrogen content in wastewater has been broken. Recently, nitrogen recovery from wastewater was demonstrated using an electrochemical system (ES) combined with a gas permeable membrane. Once concentrated, the ammonia is recovered into an acid, producing either ammonium sulfate (AS) or ammonium nitrate (AN). The ES was operated at different conditions while guaranteeing a certain nutrient removal and producing a concentrated fertilizer. An ammonium nitrate with 25.5 g<sub>N</sub>/L and an ammonium sulfate with 21.5 g<sub>N</sub>/L were recovered. To evaluate the performance of these nitrogen fertilizers, 5 treatments were applied to two crops, spinach and radish. The treatments were (1) AS recovered with the ES, 2) commercial AS, 3) AN recovered with the ES, 4) commercial AN, and 5) no addition (control). Between fertilized treatments, a significant difference was observed for fresh biomass of spinach leaf (consumable part of the crop) between recovered and commercial fertilizers. Effective fertilization was confirmed by a significantly higher fresh biomass in fertilized crops, both radish and spinach, compared to control. After harvest, soil pH was above 5.0 for both commercial and recovered fertilizers, despite the low pH of the recovered fertilizers (pH 1.8 - 2.4). This work demonstrates that fertilizers recovered by electrochemical systems can be used to improve crop growth and are a feasible alternative to commercial fertilizers.

### 1. Introduction

Nitrogen is essential for crop growth and is a key element of plant constituents including DNA, RNA, proteins, chlorophyll, and ATP (Andrews et al., 2013; Rütting et al., 2018). While nitrogen exists in high amounts in the atmosphere, it is less abundant in the soil (H. Sabry, 2015). Since the natural supply of nitrogen in the soil is insufficient for maximal growth of non-nitrogen-fixing crops, large-scale supplementation with synthetic fertilizer is used (Miller et al., 2007; Rockström et al., 2013). Synthetic nitrogen fertilizers are mainly produced by the Haber-Bosch (HB) process, which has led to the greatest historical increase in food production capacity (van der Hoek et al., 2018). The HB process of converting nitrogen gas to ammonia is energy intensive, because of the strong triple bond of N<sub>2</sub>, and consequently is responsible for 1–2% of the global energy consumption (Erisman et al., 2008; H. Sabry, 2015; Plett et al., 2020; Shaddel et al., 2019). Additionally, the

HB process is currently dependent on non-renewable fossil fuel (natural gas) as the source of hydrogen for the process (H. Sabry, 2015; Medford and Hatzell, 2017). Therefore, ammonia produced via the HB process contributes 1.5% to the global CO<sub>2</sub> emissions. (Datawheel, 2019; Institute for Industrial Productivity, 2011; Kyriakou et al., 2020; Liu et al., 2020).

Modern agriculture radically increases reactive nitrogen compounds in the environment (i.e., nitrate, nitrite, ammonia and ammonium) (Erisman et al., 2003; Medford and Hatzell, 2017; Scharf, 2015). Paradoxically, regions with nutrient surplus often apply the largest amounts of synthetic mineral fertilizers (European Commission, 1991a; Shi et al., 2018; Sigurnjak et al., 2019). Globally, the production of fertilizer has resulted in an 1100% increase in conversion of non-reactive N<sub>2</sub> to reactive nitrogen compounds. The surplus of reactive nitrogen from agriculture persists in the environment and results in acidification, eutrophication, hypoxia, and depletion of stratosphere ozone,

\* Corresponding author.

E-mail address: [philipp.kuntke@wur.nl](mailto:philipp.kuntke@wur.nl) (P. Kuntke).

<https://doi.org/10.1016/j.resconrec.2022.106225>

Received 16 November 2021; Received in revised form 26 January 2022; Accepted 6 February 2022

0921-3449/© 2022 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

contributing to climate change (Miller et al., 2007; Scharf, 2015). Consequently, legislation such as the comprehensive EU Water Framework Directive (WFD) of 2000 and Nitrates Directive in Europe, and the Clean Water Act (CWA) of 1972 in the United States, requires prevention of surface water pollution by wastewater and other pollutants (European Commission, 1991a, 1986; Hauck et al., 2016).

To prevent pollution and eutrophication caused by the excess nitrogen in wastewater, treatment of animal and human waste is necessary (van der Hoek et al., 2018). Wastewater treatment plants are required to treat domestic and industrial wastewater to certain standards before discharging into a receiving waterbody (Craig, 2018; European Commission, 1991b; National Research Council, 2002). The European Water Framework Directive (2000/60/EC) and the Urban Waste Water Directive (92/271/EEC) established the discharge limit to 10–15 mg<sub>N</sub>/L in sensitive areas (Hauck et al., 2016). The traditional wastewater treatment method to remove nitrogen (nitrification/denitrification) requires energy input of approximately 45 kJ/g<sub>N</sub> removed. Another process, Anammox, directly converts ammonium and nitrite to N<sub>2</sub> and requires approximately 16–19 kJ/g<sub>N</sub> removed (Hauck et al., 2016; Zamora et al., 2017). In both processes, reactive nitrogen is released into the atmosphere as N<sub>2</sub>. In addition, traditional wastewater treatment results in nitrous oxide (N<sub>2</sub>O) emissions, a small fraction of total N<sub>2</sub>O emissions (around 6%) but a significant fraction of greenhouse gas emissions within the anthropogenic water cycle (Hauck et al., 2016; Kuntke et al., 2018b; Maurer et al., 2003; US-EPA, 2021; van der Hoek et al., 2018).

The energy required by HB process and traditional wastewater treatment, dependency on fossil fuels, and greenhouse gas emissions of the current cycle have shifted the attention from nitrogen removal to nitrogen recovery (Damtie et al., 2021; Lofrano and Brown, 2010; Theregowda et al., 2019). Furthermore, distributed and decentralized alternative nitrogen fertilizer production could increase access to fertilizers and increase economic growth especially in countries with limited access to sanitation infrastructure, if scaled and implemented properly (Smith et al., 2020).

Technologies for nitrogen recovery vary in maturity and commercial availability, and there are limited full scale applications for nitrogen recovery from wastewater (Maroneze et al., 2014; Sengupta et al., 2015; van der Hoek et al., 2018). Nitrogen recovery technologies include adsorption, stripping, electrochemical recovery, ion exchange, hydrophobic and vacuum membranes (Christiaens et al., 2019; Laurenzi et al., 2013; Maroneze et al., 2014; Menkveld and Broeders, 2018; van der Hoek et al., 2018). Required chemical addition and/or high temperatures in these technologies are concerning due to cost and the necessity of a dependable chemical supply (Christiaens et al., 2019).

Electrochemical system (ES) for nitrogen recovery employs electrical current and ion exchange membranes to drive the removal of ammonium ions from the influent stream to a concentrate compartment with increased pH, which forces ammonium to volatilize to ammonia gas (Christiaens et al., 2019; Kuntke et al., 2018a; Rodrigues et al., 2020b; Tarpeh et al., 2018). The resulting concentrated stream, with high ammonia concentration and pH, can be directly used or secondarily treated by a gas permeable hydrophobic membrane (TMCS, transmembrane chemisorption) (Christiaens et al., 2019; Kuntke et al., 2018b; Rodrigues et al., 2020a). When ES is combined with TMCS, ammonia is absorbed into a strong acid, creating a final product such as concentrated ammonium sulfate (AS) or ammonium nitrate (AN), depending on the acid used (Kuntke et al., 2018a,b).

Several efforts have been employed to improve nitrogen recovery technologies with regards to nitrogen removal efficiency, energy consumption and scale of treatment capacity (Damtie et al., 2021; Kuntke et al., 2018b; Tarpeh et al., 2018; Yang and Qin, 2021). However, very few studies describe the composition of the recovered fertilizers or evaluate their agronomic efficiency on crops (Laurenzi et al., 2013; Shaddel et al., 2019; Sigurnjak et al., 2019; Szymanska et al., 2019). Furthermore, the limited science-based knowledge on the performance

of alternative recovered fertilizers, also obstructs full scale adoption of new nitrogen recovery technologies (Sigurnjak et al., 2019; Szymanska et al., 2019).

In this study, we recovered several ammonium nitrate and ammonium sulfate fertilizers using a stacked ES, comprised of bipolar membranes and cation exchange membranes, followed by TMCS previously described in (Rodrigues et al., 2020a) and treating synthetic reject water. The influence of different operation conditions on the production of a fertilizer and removal and recovery of nitrogen is described herein. Two of the recovered ammonium fertilizers, AS and AN, were evaluated in a climate-controlled pot experiment. To evaluate fertilizer performance, spinach and radish were grown. The effect of recovered fertilizers on the fresh biomass (yield), nutrient uptake (N content) and deterioration of the soil (pH) were compared with commercially available fertilizers and no fertilizer addition (control).

## 2. Materials and methods

### 2.1. Electrochemical fertilizer production

An electrochemical system (ES) was used to first remove ammonium from synthetic reject water with 2.02 g/L ammonium, 1.64 g/L chloride, 0.02 g/L sulfate, 0.05 g/L total carbon, 0.35 g/L sodium and 0.40 g/L potassium, followed by recovery of ammonia into an acid (Rodrigues et al., 2020a). Two acids were used, sulfuric acid and nitric acid, resulting in ammonium sulfate (AS) and ammonium nitrate (AN) fertilizer products, respectively. An extended description of the setup, chemical analysis and calculations can be found in (Rodrigues et al., 2020a). In short, the electrochemical system included 6 cell pairs (feed and concentrate compartments). The feed and concentrated compartments were separated on one side by a cation exchange membrane on the other side by a bipolar membrane. A system outline is presented in Supplementary Information, Appendix A. The anode was separated from the feed compartment by a MEA (membrane electrode assembly) used for hydrogen oxidation. The cathode compartment was separated from the concentrate by an anion exchange membrane. The recirculation flow rate for feed, concentrate and cathode recycle systems were 360 mL/min (linear flow speed 12 cm/s). Acid recirculation rate was between 170 and 500 mL/min. The acid dosing was performed in continuous and in batch mode. For continuous experiments, acid dosing was set at approximately 15 mL/min, to be dosed when the pH of the acid recycle loop increased above pH 6. For batch experiments, the acid was a 1 L constant volume recirculated over the TMCS.

In order to study the influence of operational conditions on fertilizer product nitrogen concentration and pH, the ES was operated at different current densities (25, 75 and 100 A/m<sup>2</sup>) and Load Ratio (applied current vs nitrogen load) between 1.2 and 3.6 (Kuntke et al., 2018a; Rodríguez Arredondo et al., 2019).

### 2.2. Crops growth experiment

#### 2.2.1. Experimental strategy

To assess the effectiveness of the recovered fertilizers, pot experiments were conducted in a MyGrowthRoom climate chamber (Nijssen, Leiden, The Netherlands). The experiments were conducted with five different treatments, applied to three replicates for each of the two crops. The five treatments were: 1) AS recovered with the ES, 2) commercial AS, 3) AN recovered with the ES, 4) commercial AN, 5) no addition (control). Commercial fertilizers were ammonium sulfate (ASPure, Fibrant, Urmond, The Netherlands) and ammonium nitrate (AMNITRA, Yara Vlaardingen BV, Vlaardingen, The Netherlands). Pots were arranged with completely randomized design (Supplementary Information, Appendix B – Table B1). A second experiment was reproduced after, following the same exact setting.

Two crops were studied, radish (*raphanus raphanistrum* subsp. *sativus*) and spinach (*spinacia oleracea*). Radish was chosen due to its short

growing period (35 days), ease of cultivation in various conditions, high requirement for fertilization (Chohura and KoŁota, 2011) as well as measured correlation between growth and nitrogen application (El-D-*esu*ki et al., 2005). Spinach was chosen due to short growing period (45 days) and measured correlation between nitrogen application and yield (Jeyasubramanian et al., 2016; Prasad et al., 2012). In addition, spinach and radish are part of the Brassica family and thus require sulfur fertilization for oil synthesis (Smatanová et al., 2004).

Nitrogen fertilizer was applied such that all pots received the same amount of N (mg). Total N concentration included  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . N fertilization was split between two doses. Pot fertilization was calculated based on the recommended field fertilization rates included in the soils report and the following equation:

$$\text{Pot Fertilization} = \frac{\text{fert}_{\text{field}} \times \text{soil weight}_{\text{pot}}}{2,000,000} \quad (1)$$

Where pot fertilization is the converted fertilizer dose per pot (kg, converted to mg),  $\text{fert}_{\text{field}}$  is the recommended rate of fertilization for field application (kg/ha),  $\text{soil weight}_{\text{pot}}$  is the dry weight of soil in each pot (kg), and assuming 2000,000 (kg/ha), kilograms soil per hectare using standard furrow slice soil depth of 15–20 cm (Imakumbili et al., 2020).

The N content was calculated based on  $\text{NH}_4^+$  content for AS fertilizers, and  $\text{NO}_3^-$  and  $\text{NH}_4^+$  for AN fertilizers. A fertilizer dosing scheme is included below in Table 1. The selected recovered fertilizers (Prod.) had 25.5 g<sub>N</sub>/L and pH = 1.8 for ammonium nitrate and 21.5 g<sub>N</sub>/L and pH = 2.4 for ammonium sulfate. The commercial (Comm.) ammonium nitrate had 232.5 g<sub>N</sub>/L and pH = 7.4 while the commercial ammonium sulfate had 28.4 g<sub>N</sub>/L and pH = 5.4.

The temperature of the climate chamber was set to 16 °C and humidity was set to 60%. Day length was set to 12 h, with lamps set to an intensity of 200  $\mu\text{mol}/\text{m}^2/\text{s}$  (Rubatzky and Yamaguchi, 1997).

Seeds were added to each pot directly by hand. Radish seeds were sown 15 per pot, and spinach seeds 6 per pot, at a depth of 1 cm. Seedlings were thinned to 6 plants per pot for radish and 2 plants per pot for spinach, between 7 and 10 days after planting. A minimum space of 5 cm was maintained for all crops. Once seeds were planted, pots were watered every other day, up to a pre-defined weight, with tap water to maintain the optimal moisture content (70%). ‘Emergence’ was defined as 7 days after planting. Nitrogen fertilization was based on a split dose, 50% at 10 days after emergence and 50% at 20 days after emergence. Radish was harvested after 35 days (da Silva et al., 2016; Rubatzky and Yamaguchi, 1997), and spinach was harvested after 45 days after planting (Jeyasubramanian et al., 2016; Prasad et al., 2012).

### 2.2.2. Chemical analysis

All fertilizers were submitted to ion chromatography (IC) to determine cations and anions content. IC cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ) were measured using a Metrohm 930 Compact IC Flex instrument with cations column (Metrosep C 4–150/4.0). IC anions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ) were measured with a Metrohm 761 Compact IC instrument with anions column (Metrosep A Supp5–150/4.0) (Metrohm Nederland BV, Schiedam, The Netherlands). The pH and electrical conductivity were measured manually using a handheld meter (Seven Excellence S470, Mettler Toledo, Tiel, The Netherlands).

**Table 1**  
Fertilizer Dosing Scheme.

Treatment	Basal Dose $\text{P}_2\text{O}_5$ (mg/pot)	N First Dose (g/pot)	N Second Dose (g/pot)	Available (g <sub>N</sub> /L)	FertilizerDose Vol. (mL/pot)	Total Dose Volume (6 pots) (mL)
Control	16.4	–	–	–	–	–
Prod. AN	16.4	0.2	0.2	25.5	7.9	47.1
Prod. AS	16.4	0.2	0.2	21.5	9.3	55.8
Comm. AN	16.4	0.2	0.2	232.5	0.9	5.2
Comm. AS	16.4	0.2	0.2	28.4	7.1	42.3

### 2.2.3. Crop analysis

After harvest, roots and leaves were weighed individually per plant, and yield recorded as roots for radish and leaves for spinach. The leaves and roots were then dried at 60 °C for 72 h in an oven. Following drying, leaves and roots were weighed and ground for elemental analysis (Thermo Scientific FlashSmart CHNSO, Interscience BV, Breda, The Netherlands) to determine carbon, hydrogen, nitrogen and sulfur content.

Soil was collected from a farm in Roderech (The Netherlands) and classified. Soil debris was removed by sieving to 10 mm mesh size. A comprehensive soil analysis and report was performed by Eurofins Agro (Wageningen, The Netherlands). The soil report defined all available nutrients, classification, and structure, field watering capacity, as well as fertilization recommendations. The soil was classified as loamy sand at pH of 5.5. One of the essential macro-nutrients (N, P, K), P was found to be in a low range in the soils report. Therefore, phosphate pentoxide ( $\text{P}_2\text{O}_5$ ) was dissolved in Milli-Q and the recommended P dose was applied in a basal dose prior to seed planting to all soils.

Soil samples were collected before seeding, 24 h after fertilization and after harvesting. For pH measurement, the soil was dried for 24–72 h at 65 °C, ground and sieved to 2 mm. Each soil was added to Milli-Q water at a ratio of 1:5 gs to 15 mL plastic centrifuge tubes, shaken for 60 min with benchtop shaker, followed by 30 min rest before taking pH measurement with manual meter (Seven Excellence S470, Mettler Toledo, Tiel, The Netherlands).

Before elemental analysis and microwave digestion, soils were dried for 72 h at 65 °C, ground and sieved to 2 mm. All samples were assayed in duplicate. Elemental analysis was used to determine carbon, hydrogen, nitrogen and sulfur content. Microwave digestion (Ethos Easy, Milestone Srl., Sorisole BG, Italy) followed by ICP-OES (Perkin Elmer, type Optima 5300 DV, PerkinElmer, Waltham, Massachusetts, USA) was performed to determine potassium and phosphorus content.

### 2.2.3. Statistical analysis

The effect of the fertilizer treatments on each of the experimental variables was analyzed using factorial analysis of variance (ANOVA). Factorial ANOVAs were conducted using R version 3.6.1. Tukey’s HSD (honestly significant difference) test was used to control for Type I error inflation with p-value of 0.05 used as the criterion for statistical significance. The analyses were performed with Df = 14 (Degrees of Freedom). All experimental variables are included in the Supplementary Information, Appendix C - Table C1.

## 3. Results

### 3.1. Electrochemical system performance and fertilizer production

The fertilizers recovered by the ES are presented in Table 2, separated by recovering acid and ordered according to total nitrogen concentration (N Total Conc.). Table 2 also includes parameters of fertilizer quality such as pH, nutrient content, and the operating conditions at which they were produced. Fertilizers with the highest respective nitrogen concentration within each group, AS or AN, are marked with # and were used in the pot experiment.

The current density and acid dosing mode affected the composition

**Table 2**

Composition and pH of the fertilizers recovered (including total nitrogen concentration [N Total Conc.], ammonium concentration [ $\text{NH}_4^+$  Conc.], nitrate concentration [ $\text{NO}_3^-$  Conc.] and sulfate concentration [ $\text{SO}_4^{2-}$  Conc.]) and respective operation conditions that they were obtained. The commercial fertilizers were also presented. The fertilizers applied to the crops are marked with #.

Acid Used	N Total Conc. (g/L)	Acid Dosing	Current Density ( $\text{A}/\text{m}^2$ )	Actual Load Ratio	Fertilizer pH	$\text{NH}_4^+$ Conc. (g/L)	$\text{NO}_3^-$ Conc. (g/L)
#Nitric	25.5	C	100	2.3	1.8	16.3	56.7
Nitric	24.9	C	100	1.5	2.1	15.8	56.0
Nitric	24.9	C	75	1.2	2.1	15.5	56.8
Nitric	22.2	C	25	1.2	2.5	14.0	50.2
Nitric	21.4	C	75	1.2	2.1	14.0	46.7
Nitric	21.4	B	100	2.0	8.8	15.0	43.4
Comercial AN	232.5				7.4	148.0	520.0
Acid Used	N Total Conc. (g/L)	Dosing	Current Density ( $\text{A}/\text{m}^2$ )	Actual Load Ratio	Fertilizer pH	$\text{NH}_4^+$ Conc. (g/L)	$\text{SO}_4^{2-}$ Conc. (g/L)
#Sulf.	21.5	C	100	2.1	2.4	27.7	79.7
Sulf.	21.0	C	75	1.2	2.8	27.0	78.7
Sulf.	20.2	C	75	1.2	2.8	26.0	74.8
Sulf.	17.8	B	100	2.2	9.3	22.9	55.9
Sulf.	12.3	B	100	3.6	1.3	15.8	64.4
Sulf.	12.0	C	25	1.5	3.0	15.4	41.0
Sulf.	2.8	B	25	1.9	0.8	3.6	70.2
Comercial AS	28.4				5.4	36.6	101.5

of the fertilizer recovered. Concentration increased with current density, and the highest product N concentration for both AS and AN was observed at  $100 \text{ A}/\text{m}^2$ . This was expected as more nitrogen is transported over the same cation exchange membrane area at higher current density, and consequently the TMCS transport rate also changes (Rodrigues et al., 2020a; Rodríguez Arredondo et al., 2017). For continuous acid dosing mode, all products recovered were acidic with  $\text{pH} < 3.0$ . Batch acid dosing resulted in alkaline fertilizers ( $\text{pH} = 8.8$  and  $\text{pH} = 9.3$ ) and less concentrated products. As the transfer over the TMCS is concentration gradient dependent, batch mode affected the overall performance of the system and resulted in less concentrated fertilizers. The loading rate (Load Ratio) was not directly related to the obtained nitrogen concentration in the fertilizer and, therefore, it should not be the only parameter consider during ammonia recovery.

Thus, higher current density and continuous acid dosing resulted in production of a fertilizer with higher product nitrogen concentrations. Additionally, for the selected conditions, between 66 and 76% of the nitrogen was removed and recovered from the wastewater. This coincides with previous observations using a similar system (Kuntke et al., 2018b; Rodrigues et al., 2020a).

The most concentrated recovered N-products, also the least acidic, for both AN and AS were selected to evaluate the efficiency as fertilizers. The results are presented in the next section.

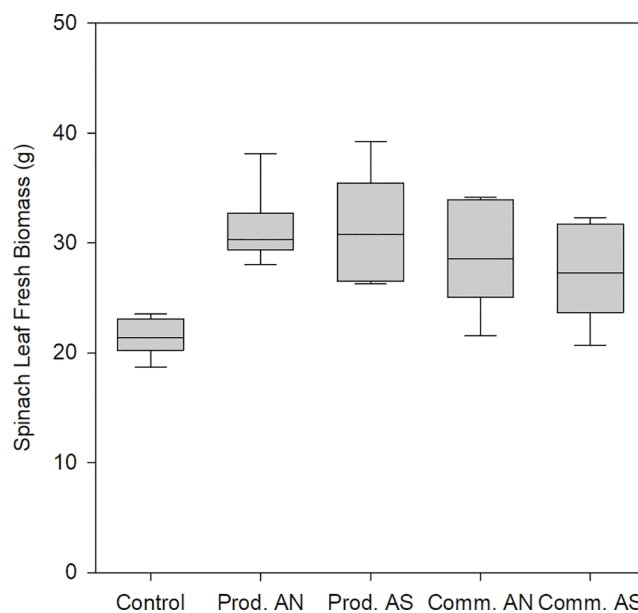
### 3.2. Crop growth

In order to establish the performance of the recovered fertilizers, Fresh Biomass (yield) and nutrient uptake (N content) are presented for the consumable parts of the plant (spinach leaf and radish root). Overall, all plants successfully grew to harvest. Fig. 1 shows the spinach fresh leaf yield.

Fig. 1 shows spinach fresh leaf biomass was higher in fertilized groups compared to control. The omnibus  $F$  test ( $p < 0.001$ ) indicated that a statistically significant mean ( $\bar{x}$ ) difference in fresh leaf biomass was present for at least one of the pairwise comparisons among treatments. Tukey's HSD indicated that the recovered AN ( $\bar{x} = 31.2$ ) and the recovered AS ( $\bar{x} = 31.3$ ) were significantly higher than control ( $\bar{x} = 21.5$ ). Commercial AS ( $\bar{x} = 27.3$ ) and commercial AN ( $\bar{x} = 28.8$ ) were between these groups with no significant difference in means. This indicates that the application of fertilizer was effective in improving spinach yield, and although higher averages were observed in recovered fertilizers over commercial, no significant difference was observed.

Fresh biomass of radish roots is presented in Fig. 2.

Fig. 2 shows fresh biomass for recovered AN ( $\bar{x} = 40.2$ ), commercial AN ( $\bar{x} = 40.3$ ), commercial AS ( $\bar{x} = 33.0$ ) and recovered AS ( $\bar{x} =$



**Fig. 1.** Spinach leaf fresh biomass median, considering all six pots, shown for the 5 different treatment groups (no addition (control), AN recovered with the ES, AS recovered with the ES, commercial AS, commercial AN). The data is presented as a Box plot. The line within each box is the median, the 25<sup>th</sup> percentile is shown as the lower boundary of the box, and the upper boundary of the box indicates the 75<sup>th</sup> percentile. The error bars above and below the box represent the 90<sup>th</sup> and 10<sup>th</sup> percentile, respectively (Systat Software, 2017).

32.2) compared to control ( $\bar{x} = 35.6$ ). There were no significant differences in radish fresh root biomass for the different treatments ( $p > 0.1$ ).

N fertilization was observed to significantly improve leaf over root growth. High N fertilization has been previously observed to significantly increase leaf number and area, believed to increase chlorophyll synthesis (Chohura and KoŁota, 2011; da Silva et al., 2016). This result is not optimal regarding radish yield. Nevertheless, the effect of recovered fertilizers was comparable to commercial treatments.

N was measured in spinach leaves and radish roots in order to assess nutrient uptake from fertilization. The detailed statistical analysis can be found in Supplementary Information, Appendix D. Fig. 3 shows N content in spinach leaves.

Fig. 3 shows the N content was higher when a fertilizer was applied. The omnibus  $F$  test ( $p < 0.0001$ ) indicated that a statistically significant



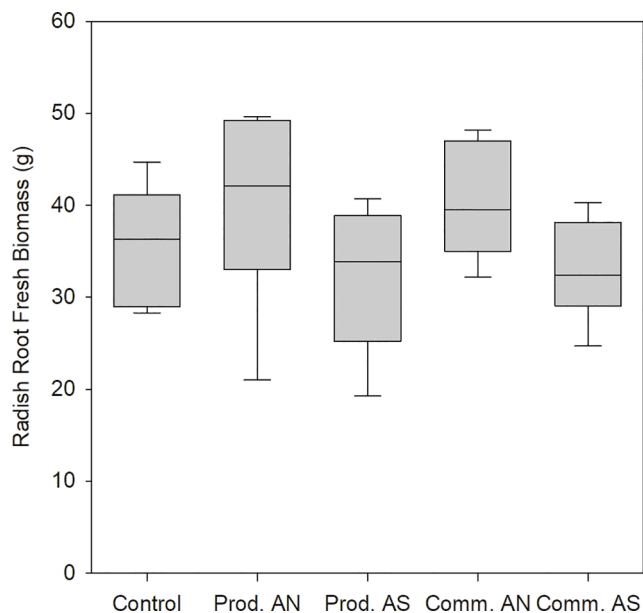


Fig. 2. Average radish root fresh biomass shown for the 5 different treatment groups (no addition (control), AN recovered with the ES, AS recovered with the ES, commercial AS, commercial AN) considering all six pots of the treatment.

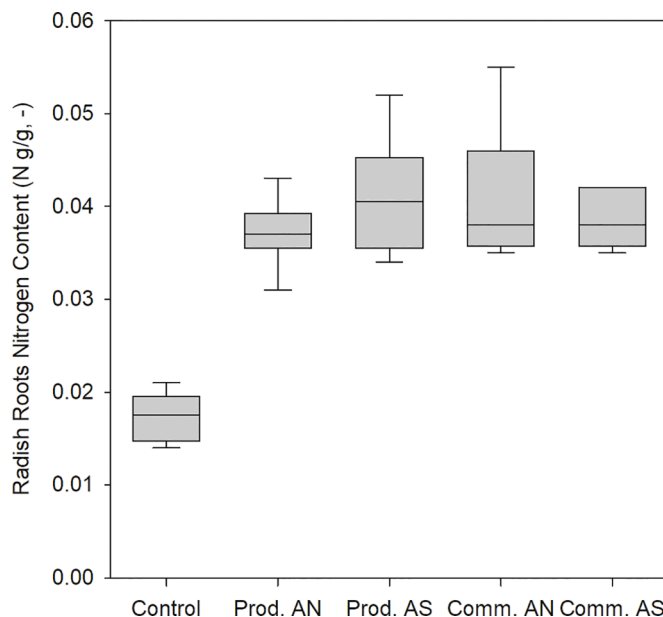


Fig. 4. Nitrogen content in radish roots (weight percentage) shown for the 5 different treatment groups (no addition (control), AN recovered with the ES, AS recovered with the ES, commercial AS, commercial AN) considering all six pots of the treatment.

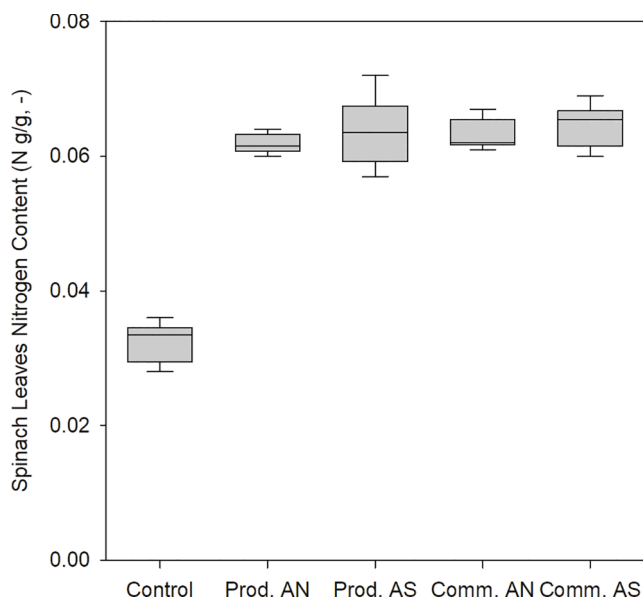


Fig. 3. Nitrogen content in spinach leaves (weight percentage) shown for the 5 different treatment groups (no addition (control), AN recovered with the ES, AS recovered with the ES, commercial AS, commercial AN) considering all six pots of the treatment.

mean difference in spinach leaf N content was present for at least one of the pairwise comparisons among treatments. Tukey's HSD indicated that spinach leaf N content for all fertilizer treatments: recovered AN ( $\bar{x} = 6.2$ ), commercial AN ( $\bar{x} = 6.3$ ), recovered AS ( $\bar{x} = 6.4$ ) and commercial AS ( $\bar{x} = 6.5$ ) were significantly higher than control ( $\bar{x} = 3.2$ ). Radish root N content is presented in Fig. 4.

Fig. 4 indicates no significant difference was observed between recovered and commercial fertilizers regarding nitrogen uptake: recovered AN ( $\bar{x} = 3.7$ ), commercial AN ( $\bar{x} = 3.8$ ), recovered AS ( $\bar{x} = 3.8$ ) and commercial AS ( $\bar{x} = 3.9$ ). All fertilizer treatments were significantly higher than control ( $\bar{x} = 1.7$ ). The omnibus F test ( $p < 0.0001$ ) indicated that a statistically significant mean difference radish root N

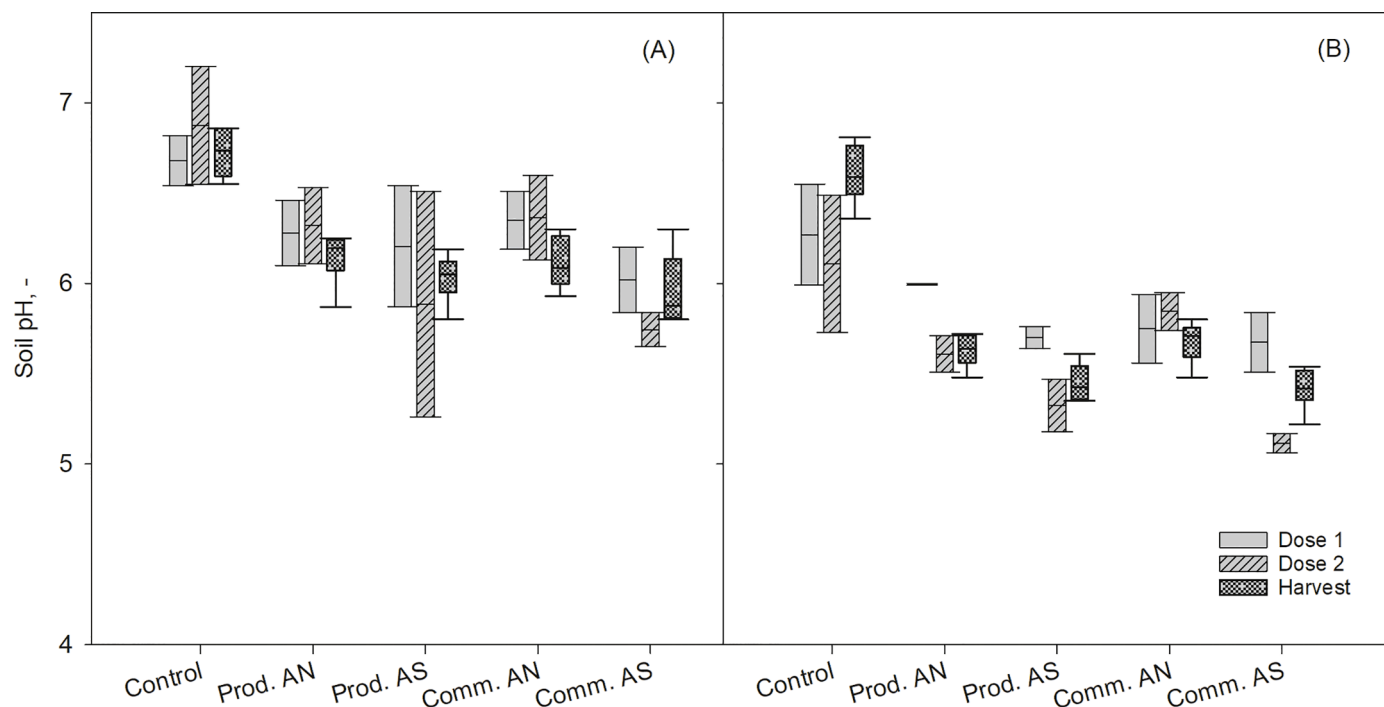
content was present for at least one of the pairwise comparisons among treatments.

The N content of fertilized groups for both radish roots and spinach leaves indicated that the plants increased their nitrogen uptake (higher than control) and this was comparable among treatments. Interestingly, AS-fertilized groups showed the highest N content, both in radish and spinach. While S is not included in the well-known N, P, K nutrients, it is equally as important, especially for certain crop families. S fertilization in combination with N results was previously demonstrated to increase yield of spinach (Smatanová et al., 2004), and other brassicas (Jamal et al., 2010). Generally, other studies demonstrated overall effective performance of recovered AS produced by stripping on maize, grass and lettuce (Sigurnjak et al., 2016; Szymanska et al., 2019; Yetilmezsoy and Sapci-Zengin, 2009). Stripped AS has been proven to result in higher nitrogen use efficiency, higher N, P, K uptake and less leaching compared to commercial fertilizer (Chen, 2012; Sigurnjak et al., 2016; Szymanska et al., 2019; Vaneekhaute et al., 2013, 2014)).

### 3.3. Soils pH

Soil pH was measured for all treatments throughout the experiments, Fig. 5. Low pH was a parameter of concern regarding fertilizer product quality, as recovered fertilizers were more acidic than commercial fertilizers. Additionally, with S remaining in the soil, for AS fertilization in general, acidification is a concern (Szymanska et al., 2019; Vaneekhaute et al., 2013).

Fig. 5 shows soil pH was significantly higher in control over fertilized soils for both radish and spinach ( $p < 0.0001$ ). The soil pH decreased after both recovered and commercial fertilizers were applied. The lowest soil pH during radish growth was 5.8, while for spinach it was 5.2. In radish, all fertilized treatment groups had similar soil pH averages and no treatment was significantly different. For spinach, only commercial AS decreased significantly the pH compared to the other treatments. Ultimately, the low soil pH did not affect negatively the crop growth, as higher fresh biomass was achieved for the pots using fertilizer. Moreover, it was observed that recovered fertilizers do not differ from commercial regards to soil acidification. Additionally, the lower pH of the recovered fertilizers can present an advantage as the need of



**Fig. 5.** A) Soil pH after dose 1, dose 2 and radish harvest shown for the 5 different treatment groups (no addition (control), AN recovered with the ES, AS recovered with the ES, commercial AS, commercial AN) considering all six pots of the treatment. B) Soil pH after dose 1, dose 2 and spinach harvest for the 5 different treatment groups.

acidification of other streams of nutrients has been previously reported to avoid the emission of ammonia (Sigurnjak et al., 2017).

The recovered ammonium nitrate was 4.2% N concentration by weight. The recovered ammonium sulfate was 6% N. This was comparable to a previously reported ammonium sulfate recovered from manure by stripping at a bio-refinery (6.6%  $(\text{NH}_4)_2\text{SO}_4$ ) (Szymanska et al., 2019). More concentrated N recovered fertilizers were only achieved while using caustic addition and high temperatures during stripping ammonium sulfate from digestate (25–40%) (Menkveld and Broeders, 2018) or from manure (40–60%) (Laureni et al., 2013).

While electrochemical systems concentrate the nitrogen removed from wastewater and increase the pH, the N transport rate over the TMCS is lower. However, it was previously demonstrated that using a two-step process, including cation exchange membranes and gas permeable membranes (TMCS), the transport of undesired substances such as organic micropollutants to the final product is reduced (Christiaens et al., 2019). Using ES for ammonium recovery is one possible step towards a future of sustainable fertilizer production and secured global food supply, and advances development within the water-energy-food nexus.

#### 4. Conclusion

Current research demonstrates that reactive nitrogen can be recovered with electrochemical (ES) systems. However, while most studies claim that ES-recovered ammonium products are potential crop fertilizers, few studies on applying recovered fertilizers on crops have been performed. This study demonstrates that ES-recovered AS and AN fertilizers can be effectively used as nitrogen fertilizers for crops. While supplying the same amount nitrogen for crop growth, the recovered fertilizers perform similarly compared to commercial fertilizers considering growth parameters such as fresh biomass and nitrogen nutrient. Therefore, electrochemical nitrogen recovery has significant potential to not only reduce nitrogen loads within wastewater treatment but to produce valuable fertilizer products. Nevertheless, energy and economic costs associated with the treatment of reactive nitrogen in traditional

wastewater treatment and the Haber-Bosch process should be further studied.

#### CRediT authorship contribution statement

**Mariana Rodrigues:** Conceptualization, Methodology, Data curation, Writing – original draft, Supervision, Visualization, Validation. **R. Jensen Lund:** Investigation, Software, Writing – original draft. **Anne-miek ter Heijne:** Writing – review & editing. **Tom Sleutels:** Writing – review & editing. **Cees J.N. Buisman:** Writing – review & editing, Funding acquisition. **Philipp Kuntke:** Conceptualization, Writing – review & editing, Project administration, Funding acquisition, Supervision.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Research data

The research data underlying this work is available at [doi:10.4121/19064378](https://doi.org/10.4121/19064378).

#### Acknowledgements

This work was performed in the cooperation framework of Wetsus, European centre of Excellence for Sustainable Water Technology ([www.wetsus.eu](http://www.wetsus.eu)). Wetsus is co-funded by the Dutch Ministry of Economic Affairs and Ministry of Infrastructure and Environment, the European Union Regional Development Fund, the Province of Fryslân, and the Northern Netherlands Provinces. This work was also supported by the LIFE-NEWBIES project. The LIFE-NEWBIES project (LIFE17 ENV/NL/000408) has received funding from the LIFE Programme of the European

Union. The authors like to thank the participants of the research theme “Resource Recovery” for the fruitful discussions and their financial support. The authors would also like to thank Vania Chavez Rico and Yujia Luo (Wetsus & Wageningen University) for their valuable input in the crops growth protocol. The authors would like to thank Dr. Hani Sewilan (RWTH Aachen University) for his input. Finally, the authors would like to thank Dr. Michael Zweifel for his help on the statistical analysis.

## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.resconrec.2022.106225](https://doi.org/10.1016/j.resconrec.2022.106225).

## References

- Andrews, M., Raven, J.A., Lea, P.J., 2013. Do plants need nitrate? the mechanisms by which nitrogen form affects plants. *Ann. Appl. Biol.* <https://doi.org/10.1111/aab.12045>.
- Chen, A., 2012. Optimizing nutrient use efficiency in agriculture by utilizing manure and digestate derivatives as bio-based fertilizer.
- Chohura, P., Kofota, E., 2011. The effect of nitrogen fertilization on radish yielding. *Acta Sci. Pol. Hortorum Cultus* 10, 23–30.
- Christiaens, M.E.R., Udert, K.M., Arends, J.B.A., Huysman, S., Vanhaecke, L., McAdam, E., Rabaey, K., 2019. Membrane stripping enables effective electrochemical ammonia recovery from urine while retaining microorganisms and micropollutants. *Water Res.* 150, 349–357. <https://doi.org/10.1016/j.watres.2018.11.072>.
- Craig, R.K., 2018. Water quality law in the US and EU: a comparison of the clean water act and water framework directive. *Eur. Now* 1–10.
- da Silva, P.F., de Matos, R.M., Borges, V.E., de Alencar, A.E.V., Neto, J.D., 2016. Growth and plant mass of radish fertirrigated with different doses nitrogen. *Rev. Ceres* 63, 122–128. <https://doi.org/10.1590/0034-737x201663020002>.
- Damtie, M.M., Volpin, F., Yao, M., Tijging, L.D., Hailemariam, R.H., Bao, T., Park, K.D., Shon, H.K., Choi, J.S., 2021. Ammonia recovery from human urine as liquid fertilizers in hollow fiber membrane contactor: effects of permeate chemistry. *Environ. Eng. Res.* 26, 1–9. <https://doi.org/10.4491/eeer.2019.523>.
- Datawheel, 2019. Nitrogenous fertilizers [WWW document]. URL <https://oec.world/en/profile/hs92/nitrogenous-fertilizers>.
- El-Desuki, M., Salman, S.R., El-Nemr, M.A., Abdel-Mawgoud, A.M.R., 2005. Effect of Plant Density and Nitrogen Application on the Growth, Yield and Quality of Radish (*Raphanus sativus* L.). *Journal of Agronomy* 4 (3), 225–229. <https://doi.org/10.3923/ja.2005.225.229>.
- Erisman, J.W., Grennfelt, P., Sutton, M., 2003. The European perspective on nitrogen emission and deposition. *Environ. Int.* 29, 311–325. [https://doi.org/10.1016/S0160-4120\(02\)00162-9](https://doi.org/10.1016/S0160-4120(02)00162-9).
- Erisman, J.W., Sutton, M.A., Galloway, J., Klimont, Z., Winiwarter, W., 2008. How a century of ammonia synthesis changed the world. *Nat. Geosci.* 1, 636–639. <https://doi.org/10.1038/ngeo325>.
- European Commission, 1991a. ‘Nitrates’ directive. *Off. J. Eur. Communities*.
- European Commission, 1991b. The urban waste water treatment directive. *Off. J. Eur. Communities* <https://doi.org/01991L0271-20140101>.
- European Commission, 1986. Protection of the Environment, and in particular of the soil, when sewage sludge is used in agriculture. *Off. J. Eur. Communities*.
- H Sabry, A.-K., 2015. Synthetic fertilizers, role and hazards. *Fertil. Technol.* 111–133. <https://doi.org/10.13140/RG.2.1.2395.3366>.
- Hauck, M., Maalcke-Luesken, F.A., Jetten, M.S.M., Huijbregts, M.A.J., 2016. Removing nitrogen from wastewater with side stream anammox: what are the trade-offs between environmental impacts? *Resour. Conserv. Recycl.* 107, 212–219. <https://doi.org/10.1016/j.resconrec.2015.11.019>.
- Imakumbili, M.L.E., Semu, E., Semoka, J.M.R., Abass, A., Mkamilo, G., 2020. Plant tissue analysis as a tool for predicting fertiliser needs for low cyanogenic glucoside levels in cassava roots: an assessment of its possible use. *PLoS ONE* 15, e0228641. <https://doi.org/10.1371/journal.pone.0228641>.
- Institute for Industrial Productivity, 2011. Ammonia.
- Jamal, A., Moon, Y.S., Abdin, M.Z., 2010. Sulphur - a general overview and interaction with nitrogen. *Aust. J. Crop Sci.* 4, 523–529.
- Jeyasubramanian, K., Gopalakrishnan Thoppey, U.U., Hikku, G.S., Selvakumar, N., Subramania, A., Krishnamoorthy, K., 2016. Enhancement in growth rate and productivity of spinach grown in hydroponics with iron oxide nanoparticles. *RSC Adv.* 6, 15451–15459. <https://doi.org/10.1039/c5ra23425e>.
- Kuntke, P., Rodrigues, M., Sleutels, T., Saakes, M., Hamelers, H.V.M., Buisman, C.J.N., 2018a. Energy-efficient ammonia recovery in an up-scaled hydrogen gas recycling electrochemical system. *ACS Sustain. Chem. Eng.* 6, 7638–7644. <https://doi.org/10.1021/acssuschemeng.8b00457>.
- Kuntke, P., Sleutels, T., Rodrigues, T.H.J.A., Arredondo, M., Georg, S., Barbosa, S.G., ter Heijne, A., Hamelers, H.V.M., Buisman, C.J.N., 2018b. Bioelectrochemical ammonia recovery: progress and perspectives. *Appl. Microbiol. Biotechnol.* 102, 3865–3878. <https://doi.org/10.1007/s00253-018-8888-6>.
- Kyriakou, V., Garagounis, I., Vourros, A., Vasileiou, E., Stoukides, M., 2020. An electrochemical Haber-Bosch process. *Joule* 4, 142–158. <https://doi.org/10.1016/j.joule.2019.10.006>.
- Laureni, M., Palatsi, J., Llovera, M., Bonmati, A., 2013. Influence of pig slurry characteristics on ammonia stripping efficiencies and quality of the recovered ammonium-sulfate solution. *J. Chem. Technol. Biotechnol.* 88, 1654–1662. <https://doi.org/10.1002/jctb.4016>.
- Liu, X., Elgowainy, A., Wang, M., 2020. Life cycle energy use and greenhouse gas emissions of ammonia production from renewable resources and industrial by-products. *Green Chem.* 22, 5751–5761. <https://doi.org/10.1039/d0gc02301a>.
- Lofrano, G., Brown, J., 2010. Wastewater management through the ages: a history of mankind. *Sci. Total Environ.* 408, 5254–5264. <https://doi.org/10.1016/j.scitotenv.2010.07.062>.
- Maroneze, M.M., Zepka, L.Q., Vieira, J.G., Queiroz, M.I., Jacob-Lopes, E., 2014. A tecnologia de remoção de fósforo: gerenciamento do elemento em resíduos industriais. *Rev. Ambient. e Agua* 9, 445–458. <https://doi.org/10.4136/1980-993X>.
- Maurer, M., Schwegler, P., Larsen, T.A., 2003. Nutrients in urine: energetic aspects of removal and recovery. *Water Sci. Technol.* 48, 37–46. <https://doi.org/10.2166/wst.2003.0011>.
- Medford, A.J., Hatzell, M.C., 2017. Photon-driven nitrogen fixation: current progress, thermodynamic considerations, and future outlook. *ACS Catal.* 7, 2624–2643. <https://doi.org/10.1021/acscatal.7b00439>.
- Menkveld, H.W.H., Broeders, E., 2018. Recovery of ammonia from digestate as fertilizer. *Water Pract. Technol.* 13, 382–387. <https://doi.org/10.2166/wpt.2018.049>.
- Miller, S.A., Landis, A.E., Theis, T.L., 2007. Environmental trade-offs of biobased production. *Environ. Sci. Technol.* 41, 5176–5182. <https://doi.org/10.1021/es072581z>.
- National Research Council, 2002. Privatization of Water Services in the United States, Privatization of Water Services in the United States. National Academies Press, Washington, D.C. <https://doi.org/10.17726/10135>.
- Plett, D.C., Ranathunge, K., Melino, V.J., Kuya, N., Kuya, Y., Kronzucker, H.J., 2020. The intersection of nitrogen nutrition and water use in plants: new paths toward improved crop productivity. *J. Exp. Bot.* 71, 4452–4468. <https://doi.org/10.1093/jxb/eraa049>.
- Prasad, R., Pandey, A., Singh, K.P., Singh, V.P., Mishra, R.K., Singh, D., 2012. Retrieval of spinach crop parameters by microwave remote sensing with back propagation artificial neural networks: a comparison of different transfer functions. *Adv. Sp. Res.* 50, 363–370. <https://doi.org/10.1016/j.asr.2012.04.010>.
- Rockström, J., Steffen, W., Noone, K., Persson, Å., Chapin, F.S., Lambin, E.F., Lenton, T.M., Scheffer, M., Folke, C., Joachim, H., Schnellhuber, Nykvist, B., de Wit, C.A., Hughes, T., van der Leeuw, S., Rodhe, H., Sörlin, S., Snyder, P.K., Costanza, R., Svedin, U., Falkenmark, M., Karlberg, L., Corell, R.W., Fabry, V.J., Hansen, J., Walker, B., Liverman, D., Richardson, K., Crutzen, P., Foley, J.K., 2013. A safe operating space for humanity. *Future Nat.: Documents Glob. Change* 491–501. <https://doi.org/10.1126/science.281.5374.190>.
- Rodrigues, M., De Mattos, T.T., Sleutels, T., Ter Heijne, A., Hamelers, H.V.M., Buisman, C.J.N., Kuntke, P., 2020a. Minimal bipolar membrane cell configuration for scaling up ammonium recovery. *ACS Sustain. Chem. Eng.* 8, 17359–17367. <https://doi.org/10.1021/acssuschemeng.0c05043>.
- Rodrigues, M., Sleutels, T., Kuntke, P., Hoekstra, D., ter Heijne, A., Buisman, C.J.N., Hamelers, H.V.M., 2020b. Exploiting Donnan Dialysis to enhance ammonia recovery in an electrochemical system. *Chem. Eng. J.* 395, 125143. <https://doi.org/10.1016/j.cej.2020.125143>.
- Rodríguez Arredondo, M., Kuntke, P., ter Heijne, A., Buisman, C.J.N., 2019. The concept of load ratio applied to bioelectrochemical systems for ammonia recovery. *J. Chem. Technol. Biotechnol.* 94, 2055–2061. <https://doi.org/10.1002/jctb.5992>.
- Rodríguez Arredondo, M., Kuntke, P., ter Heijne, A., Hamelers, H.V.M., Buisman, C.J.N., 2017. Load ratio determines the ammonia recovery and energy input of an electrochemical system. *Water Res.* 111, 330–337. <https://doi.org/10.1016/j.watres.2016.12.051>.
- Rubatzky, V.E., Yamaguchi, M., 1997. *World Vegetables*. Springer US, Boston, MA. <https://doi.org/10.1007/978-1-4615-6015-9>.
- Rütting, T., Aronson, H., Delin, S., 2018. Efficient use of nitrogen in agriculture. *Nutr. Cycl. Agroecosystems*. <https://doi.org/10.1007/s10705-017-9900-8>.
- Scharf, P.C., 2015. Understanding nitrogen 1–24. <https://doi.org/10.2134/2015.managing-nitrogen.c1>.
- Sengupta, S., Nawaz, T., Beaudry, J., 2015. Nitrogen and phosphorus recovery from wastewater. *Curr. Pollut. Rep.* 1, 155–166. <https://doi.org/10.1007/s40726-015-0013-1>.
- Shaddel, S., Bakhtyari-Davijany, H., Kabbe, C., Dadgar, F., Østerhus, S.W., 2019. Sustainable sewage sludge management: from current practices to emerging nutrient recovery technologies. *Sustain* 11. <https://doi.org/10.3390/su11123435>.
- Shi, L., Hu, Y., Xie, S., Wu, G., Hu, Z., Zhan, X., 2018. Recovery of nutrients and volatile fatty acids from pig manure hydrolysate using two-stage bipolar membrane electrodialysis. *Chem. Eng. J.* 334, 134–142. <https://doi.org/10.1016/j.cej.2017.10.010>.
- Sigurnjak, I., Brienza, C., Snauwaert, E., De Dobbelaere, A., De Mey, J., Vaneckhaute, C., Michels, E., Schoumans, O., Adani, F., Meers, E., 2019. Production and performance of bio-based mineral fertilizers from agricultural waste using ammonia (stripping)-scrubbing technology. *Waste Manag* 89, 265–274. <https://doi.org/10.1016/j.wasman.2019.03.043>.
- Sigurnjak, I., Michels, E., Crappé, S., Buysens, S., Biswas, J.K., Tack, F.M.G., Neve, S., De Meers, E., 2017. Does acidification increase the nitrogen fertilizer replacement value of bio-based fertilizers? *J. Plant Nutr. Soil Sci.* 180, 800–810. <https://doi.org/10.1002/jpln.201700220>.

- Sigurnjak, I., Michels, E., Crappé, S., Buysens, S., Tack, F.M.G., Meers, E., 2016. Utilization of derivatives from nutrient recovery processes as alternatives for fossil-based mineral fertilizers in commercial greenhouse production of *Lactuca sativa* L. *Sci. Hortic. (Amsterdam)*. 198, 267–276. <https://doi.org/10.1016/j.scienta.2015.11.038>.
- Smatanová, M., Richter, R., Hlušek, J., 2004. Spinach and pepper response to nitrogen and Sulphur fertilization. *Plant, Soil Environ.* 50, 303–308. <https://doi.org/10.17221/4036-pse>.
- Smith, C., Hill, A.K., Torrente-Murciano, L., 2020. Current and future role of Haber-Bosch ammonia in a carbon-free energy landscape. *Energy Environ. Sci.* 13, 331–344. <https://doi.org/10.1039/c9ee02873k>.
- Systat Software, 2017. *SigmaPlot Version 14.0 User Guide*. Systat Software Inc. (SSI), San JoseCA.
- Szymanska, M., Sosulski, T., Szara, E., Was, A., Sulewski, P., Van Pruissen, G.W.P., Cornelissen, R.L., 2019. Ammonium sulphate from a bio-refinery system as a fertilizer-agronomic and economic effectiveness on the farm scale. *Energies* 12. <https://doi.org/10.3390/en12244721>.
- Tarpeh, W.A., Barazesh, J.M., Cath, T.Y., Nelson, K.L., 2018. Electrochemical stripping to recover nitrogen from source-separated urine. *Environ. Sci. Technol.* 52, 1453–1460. <https://doi.org/10.1021/acs.est.7b05488>.
- Theregowda, R.B., González-Mejía, A.M., Ma, X., Garland, J., 2019. Nutrient recovery from municipal wastewater for sustainable food production systems: an alternative to traditional fertilizers. *Environ. Eng. Sci.* 36, 833–842. <https://doi.org/10.1089/ees.2019.0053>.
- US-EPA, 2021. Greenhouse gas emissions [WWW document]. URL <https://www.epa.gov/ghgemissions/overview-greenhouse-gases>.
- van der Hoek, J.P., Duijff, R., Reinstra, O., 2018. Nitrogen recovery from wastewater: possibilities, competition with other resources, and adaptation pathways. *Sustain* 10. <https://doi.org/10.3390/su10124605>.
- Vaneekhaute, C., Ghekiere, G., Michels, E., Vanrolleghem, P.A., 2014. The use of digestates and recovered ammonium sulfate from NH<sub>3</sub>-scrubbing as sustainable substitutes for chemical fertilizers: a field-scale assessment. *Glob. Challenges Sustain. Wastewater Treat. Resour. Recover. IWA Spec. Conf. Pap.* 1–8.
- Vaneekhaute, C., Meers, E., Michels, E., Ghekiere, G., Accoe, F., Tack, F.M.G., 2013. Closing the nutrient cycle by using bio-digestion waste derivatives as synthetic fertilizer substitutes: a field experiment. *Biomass Bioenergy* 55, 175–189. <https://doi.org/10.1016/j.biombioe.2013.01.032>.
- Yang, K., Qin, M., 2021. The application of cation exchange membranes in electrochemical systems for ammonia recovery from wastewater. *Membranes (Basel)* 11, 494. <https://doi.org/10.3390/membranes11070494>.
- Yetilmezsoy, K., Sapci-Zengin, Z., 2009. Recovery of ammonium nitrogen from the effluent of UASB treating poultry manure wastewater by MAP precipitation as a slow release fertilizer. *J. Hazard. Mater.* 166, 260–269. <https://doi.org/10.1016/j.jhazmat.2008.11.025>.
- Zamora, P., Georgieva, T., Ter Heijne, A., Sleutels, T.H.J.A., Jeremiasse, A.W., Saakes, M., Buisman, C.J.N., Kuntke, P., 2017. Ammonia recovery from urine in a scaled-up microbial electrolysis cell. *J. Power Sources* 356, 491–499. <https://doi.org/10.1016/j.jpowsour.2017.02.089>.