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Synchronously recovering different nutrient ions from wastewater by using selective electrodialysis

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ABSTRACT

Digestive slurry normally contains various nutrient ions with high concentrations, including NH_4^+ , PO_4^{3-} , K^+ , Mg^{2+} , Ca^{2+} and SO_4^{2-} , which is a resource pool for nutrient recovery. In this study, a synchronously cationic and anionic selective electrodialysis (SCAE) was developed to recover anionic and cationic nutrient ions. Results showed that SCAE could synchronously recover more than 85.0%, 90.2% and 97.8% of PO_4^{3-} , SO_4^{2-} and other cations (including NH_4^+ , K^+ , Ca^{2+} , Mg^{2+}) from the simulated digestive slurry, respectively. The ionic permeation sequence, $NH_4^+ > K^+ > Ca^{2+} > Mg^{2+}$ for cations, and $SO_4^{2-} > PO_4^{3-}$ for anions, was affected by hydrated radius and hydration numbers, and did not alter despite the variation in electric field. High electrolyte concentration in the product streams would promote the recovery efficiency of both divalent cations and anions due to the ionic replacement effect and the demand for charge neutrality. Under continuous operation, the maximum concentrations of PO_4^{3-} , SO_4^{2-} , Mg^{2+} , Ca^{2+} , NH_4^+ and K^+ in product streams reached 231.9, 496.6, 180.7, 604.3, 9,648.4 and 4,571.4 mg·L⁻¹, respectively. By directly mixing different streams, the feasibility of producing mineral fertilizers without dosing externally precipitating chemicals was proved. Struvite, NH_4 HSO₄ and potassium chloride minerals were produced successfully. The outcome provided an optional method for nutrient recovery from wastewater.

Key words: ammonium, electrodialysis, nutrient recovery, phosphorus, slurry

HIGHLIGHTS

- A SCAE system was developed for recovering different nutrient ions synchronously.
- Ion migration sequence was determined by the hydrated radius and hydration numbers.
- The product streams were mixed to manufacture fertilizers without dosing chemicals.
- Higher batch number would increase the recovery efficiency of phosphate and sulfate.

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1. INTRODUCTION

With the growing demand for livestock production, the livestock wastewater rich in phosphorus and ammonium, has become one of the major pollution sources. Normally, anaerobic digestion is applied as the common method to treat wastewater with high-strength organics. Although the anaerobic digestion process is a low-carbon technology for energy recovery, the treatment of digestive slurry has become a difficulty. In general, the direct use of digestive slurry as fertilizer on farmland has limits, since it has a strict requirement on sufficient farmland to assimilate the digestate and prohibit environmental pollution (Gu *et al.* 2021). Besides, the digestive slurry normally possesses high salinity which might result in soil salinization in case of frequent use (Zhang *et al.* 2011). These suggested that the digestive slurry could not be widely recommended in agricultural farming in the densely-populated countries.

From another aspect, the rich nutrient components in the digestive slurry, including NH_4^+ , PO_4^{3-} , K^+ , etc., are favorable for the agricultural use. Nowadays, recovering nutrient from wastewater has been gaining wide attention worldwide. Different technologies have been developed respectively to recover NH_4^+ and PO_4^{3-} , including chemical precipitation (Kim *et al.* 2022), adsorption (Yang *et al.* 2021), and evaporation (van Lindena *et al.* 2022). The chemical precipitation of struvite or calcium phosphate is preferable to recover NH_4^+ and PO_4^{3-} from urine, swine wastewater, with high concentrations of PO_4^{3-} and NH_4^+ (He *et al.* 2020). However, it should be noticed that sufficient PO_4^{3-} concentration, pH levels, and the dosage of divalent cations (Mg^{2+} or Ca^{2+}) have complicated impacts on crystallization, which may restrict the efficacy of phosphorus recovery (Bradford-Hartke *et al.* 2021; Liu *et al.* 2021). Generally, relatively high phosphorus concentration and exogenous magnesium source are required, which undoubtedly increases the operational cost for the precipitation process and limit the application scenarios of this method. Digestive slurry normally contains various nutrient compositions, including phosphate, magnesium, sulfate, potassium, with relatively low concentrations (Lu & Xu 2021). Therefore, developing a technology to fractionate and concentrate phosphorus and other nutrients from the wastewater would significantly enhance the recovery efficiency.

Conventionally, electrodialysis (ED) is used to desalinate brackish water and demineralize the industrial process water (Meng *et al.* 2022). During the electrochemical separation process, the ionic components are forced to move by electric field, and separated by the ion exchange membrane (Li *et al.* 2022). Recently, with the development of monovalent selective cation and anion exchange membranes (Al-Amshawee *et al.* 2020), ions can be separated by the membranes based on their various charges. Several studies have been conducted to apply monovalent ion exchange membrane to separate one or two ions, such as fractionating magnesium from seawater for struvite recovery (Ye *et al.* 2018), phosphate separation from wastewater (Tran *et al.* 2015), mercury (Sun *et al.* 2020), and lithium separation (Wen *et al.* 2022). With regard to the digestive slurry, it contains various nutrient ions with different valences, including NH⁴₄, PO³⁻₄, SO²⁻₄, K⁺, Ca²⁺ and Mg²⁺. This

suggests that in case cationic and anionic nutrient ions could be fractionated synchronously from the slurry, the downstream fertilizer manufacture might be achieved through purposedly mixing the product streams.

In this study, a synchronously cationic and anionic selective electrodialysis (SCAE) equipped with monovalent cation and anion exchange membrane was developed to fractionate different nutrient ions from the synthetic digestive wastewater. The influences of the voltage and the initial electrolyte concentration in the product streams were investigated. The factors that could affect ionic migration rates were determined. Promoting both electrical field and electrolyte concentration was helpful in divalent ions migrating. However, migration of monovalent cations was only enhanced by increasing the electrical field. The maximum capacity of nutrient fractionation was obtained under continuous operation. The recovery rates of PO_4^{3-} and SO_4^{2-} increased, while those of cations decreased with the batches due to the accumulated gradient resistance and replacement effect. After that, the product streams. The outcome of this study is significant and practical since it provides a new option for nutrient recovery with high efficiency but without dosing external chemicals.

2. MATERIALS AND METHODS

2.1. Materials

Five types of the membranes were employed in this study, i.e., standard cation exchange membrane (SK), standard anionic exchange membrane (SA), end membrane of electrode (SC), the monovalent cation exchange membrane (MVK) and monovalent anionic exchange membrane (MVA), respectively. SK, SA and SC membranes were provided by the Kening Wote Water Treat Technology Co., Ltd, while MVA and MVK membranes were bought from the AGC Engineering Co., Ltd, Japan. The properties of the membranes are displayed in Table S1.

Samples of real digestive wastewater were collected from a pig farming plant in Fujian, China, and the ion concentrations were analyzed. The concentrations of the ions were: Na⁺ 205.71 ± 81.38 mg·L⁻¹, K⁺ 891.56 ± 102.33 mg·L⁻¹, NH⁺₄-N 2,314.64 ± 40.54 mg·L⁻¹, Ca²⁺ 119.17 ± 15.27 mg·L⁻¹, Mg²⁺ 30.63 ± 4.92 mg·L⁻¹, Cl⁻ 6,414.09 ± 239.75 mg·L⁻¹, SO²⁺ 49.87 ± 2.87 mg·L⁻¹, and PO³⁻₄-P 24.57 ± 1.62 mg·L⁻¹, respectively. Accordingly, synthetically digestive wastewater was prepared by dosing the desired amounts of NaCl, KCl, CaCl₂, MgCl₂·6H₂O, NH₄Cl, (NH₄)₂SO₄, and NH₄H₂PO₄·2H₂O into pure water. All of the chemicals were of analytical grade.

2.2. SCAE equipment and stack configuration

The SCAE stack, with a size of $200 \times 400 \text{ mm}^2$, was purchased from the Kening Wote Water Treat Technology Co., Ltd, China. For the SCAE operation, the membrane stack contained five identical units, and each unit connected to four vessels, which ensured the operations of the feed stream, anionic product stream, cationic product stream, and brine stream, respectively. Two end cation exchange membrane and rinsing chamber were set at the opposite ends of the plate electrodes, which were connected to a DC power supply (eTM-3020, eTommens Co., Ltd, China). The configuration of the SCAE equipment is shown in Figure 1.

2.3. Experimental procedure

Before the operation, limiting current density (LCD) was determined by referencing the method, described by a previous study (Ghyselbrecht *et al.* 2013). Accordingly, the voltages applied in this study ranged from 4 to 8 V.

2.3.1. Batch operation

The operational mode of constant voltage was applied to deal with the digestive slurry with relatively low conductivities, and prohibit water dissociation (Mohammadi *et al.* 2021). In this section, the impacts of the voltage were investigated, with the value set at 4, 5, 6, 7 and 8 V, respectively. The simulated slurry solution, $15 \text{ g} \cdot \text{L}^{-1}$ NaCl and 0.5 mol/L sodium sulfamate solutions were applied as the initial feed, product and rinsing streams, respectively. The initial volumes of feed, anionic, cationic, brine and rinsing streams were set at 4:2:2:2:2 L.

According to the literature, the electrolyte concentration in the product stream might impact the performance of ion fractionation (Ding *et al.* 2021). Therefore, the concentrations of electrolyte in the product and brine streams were investigated in the study, with the initial concentrations of NaCl set at 2.5 g·L⁻¹, 5 g·L⁻¹, 10 g·L⁻¹, 20 g·L⁻¹, 30 g·L⁻¹, respectively. The voltage was constant at 7 V.



Figure 1 | Configuration of the SCAE equipment.

2.3.2. Continuous-mode operation

In order to obtain the evolution of ion mobility and maximum capacities of the SCAE system fractionating nutrient ions from the wastewater, the continuous experiments were carried out with five subsequent batches. For every batch operation, in case the conductivity of feed stream reduced to $0.3 \text{ mS} \cdot \text{cm}^{-1}$, the liquid in the feed chamber would be discharged with 600 mL left to sustain the SCAE operation. Fresh feed solution would be immediately injected into the chamber for the next new run. For the continuous test, two levels of operational voltage, i.e., 6 and 8 V, were employed.

2.4. Downstream fertilizer production

After the continuous operation, different nutrient ions were extracted from the digestive slurry and distributed in different streams with high concentrations. PO_4^{3-} and SO_4^{2-} were located in the anionic product stream, Ca^{2+} and Mg^{2+} in the cationic product stream, and NH_4^+ and K^+ in the brine stream, respectively. In order to manufacture mineral fertilizers directly from the product streams, necessary arrangements were proceeded. After reviewing the literature on the manufacture process of mineral, struvite ($NH_4MgPO_4.6H_2O$) (Guan *et al.* 2021), KCl (Zhou *et al.* 2011) and NH_4HSO_4 were designed as the product fertilizers in this study.

The first step was to perform struvite crystallization, in which desired amounts of cationic and anionic product streams were paired and mixed together. During the operation, the pH value was kept constant at 9.5 for struvite precipitation without external magnesium addition. The residual supernatant was then subjected to the production of KCl and NH_4HSO_4 . In the second step, the pH value of supernatant was further enhanced to 11.0, and KCl crystals were obtained by vacuum evaporation in a water bath with the temperature kept at 80 °C. It should be noted that under such conditions of pH level and evaporation, NH_4^+ was automatically transformed to gaseous NH_3 and subsequently educed for H_2SO_4 absorption. Finally, NH_4HSO_4 crystallization could be obtained by evaporation and crystallization.

2.5. Analytical methods

During the SCAE operation, the current and voltage were recorded online simultaneously. The parameters of temperature, conductivity, and pH were measured with a hQ40d Multi-meter (Hach Co., USA). Cations, including Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺, were determined by an ion chromatography equipped with a conductivity detector (Aquion ICS, Thermo Fisher, America). The anions of Cl⁻, and SO₄²⁻ were analyzed by another ion chromatography (ICS-3000, DIONEX,

USA). The ammonium molybdate spectrophotometric method was used for the detection of phosphate, with an ultraviolet and visible spectrophotometer (UV-9000IC, Shanghai Metash Instrument Co., Ltd, China).

2.6. Data analysis

The current efficiency of specific ions is calculated by the ion migration and total electrical current charge in the same period, with the equation as described by a previous study (Chen *et al.* 2021):

$$\eta_A = \frac{\Delta n_A zF}{q} \times 100\% = \frac{(C_0 \times V_0 - C_t \times V_t)zF}{\int nIdt} \times 100\%$$
(1)

where Δn_A is the amount of ion *A* migrating to the product stream in time *t*. *Z* is valence of ion *A*. *F* is the Faraday constant as 96,485 C·mol⁻¹, *q* the total electrical current charge in time *t*. C_0 and C_t are the ion concentrations, and V_0 and V_t are the volumes in the feed at t_0 and *t*. *n* is the number of the membrane units.

The ionic migration rate represents the amount of ions transport through membranes in a certain period, which is calculated by the following equation (Liu *et al.* 2017):

$$M_r = \frac{\Delta n_A}{S \times t} = \frac{C_0 \times V_0 - C_t \times V_t}{S \times t}$$
(2)

where S is the effective membrane area in the stack.

The recovery efficiency (R) is defined as the initial amount of certain ions in the feed divided by the amount of ion recovered into the brine or product streams, which is based on the following equation (Lemay *et al.* 2020):

$$R = \left| \frac{\Delta n_{P/B}}{\Delta n_F} \right| = \left| \frac{C_{P/B,0} V_{P/B,0} - C_{P/B,t} V_{P/B,t}}{C_{F,0} V_{F,0} - C_{F,t} V_{F,t}} \right|$$
(3)

where $\Delta n_{P/B}$ and Δn_F are the differences of the ions amount in the product/brine or the feed stream during t_0 and t, $C_{P/B}$ and C_F the concentrations in the product (or brine) and feed streams, $V_{P/B}$ and V_F the volume of the product/brine and feed streams, respectively.

Energy consumption is the integration of the power, which is determined by the following equation:

$$E = \int_0^t U I dt \tag{4}$$

where U is the voltage, and I the current.

3. RESULTS AND DISCUSSION

3.1. Batch operation

Previous research has revealed that different ions behaved dissimilarly in the electrodialysis process (Chen *et al.* 2018). In this section, the impacts of voltages and initial electrolyte concentration were investigated to obtain a better understanding of various ionic behaviors in the process of SCAE.

3.1.1. Influence of voltages

In the electrodialysis process, the electrical force is the key driving force for ion migration. In this section, five experimental batches with the voltage ranging 4–8 V was performed, and the results are shown in Figure 2. Higher voltages could accelerate the desalination with higher initial currents (Figure 2(a)). However, different anionic or cationic ions displayed significantly different transport behaviors under the same operational conditions. The migration rates of various ions were calculated (Figure S1). As for PO₄^{3–}, it exhibited different profiles compared to other anionic ions, where the maximum migration rates emerged close to the end of operation_o Regarding the monovalent cations, NH₄⁺ and K⁺ displayed similar migration rates with time extending, and were transported faster than divalent cationic ions. Therefore, the permeation sequence of cationic ions in the electrodialysis process was: NH₄⁺ > K⁺ > Ca²⁺ > Mg²⁺, SO₄²⁻ > PO₄³⁻, respectively.

As reported in the previous literature (Knauth *et al.* 2021), the mobility of coexisting ions could be ascribed to their hydrated radius, which is listed in Table 1. Ions with higher hydrated radiuses possessed higher resistance (Cheng *et al.* 2018), which would result in lower migration rates. As to the anionic and cationic ions, the permeation performances were compliant with the sequence of their hydrated radiuses (except NH_4^+). Although NH_4^+ possessed the maximum hydrated radius (Table 1), it displayed faster permeating behaviors compared to those of Mg^{2+} and Ca^{2+} ions (Figure S1). This was because NH_4^+ possessed less hydration number (4.0), lower than 10.0 of hydrated Mg^{2+} ion and 7.2 of hydrated Ca^{2+} ion. Similar results have been reported by Epsztein *et al.* (2019).

The recovery efficiencies of various nutrient components are shown in Figure 3(a). For voltages below 7 V, the increase of electric power would improve the efficiency of nutrient recovery. Once the voltage reached 8 V, relative declines of recovery efficiency (blue columns) were observed for all ions. This efficiency reduction could be ascribed to the temperature enhancement, due to the Joule effect. As illustrated in Table S2, the temperature discrepancy of the operation at 8 V before and after the experiment reached 1.8 °C, significantly higher than those in other runs. Figure 3(b) demonstrated the current efficiencies of various ions, which were coupled with the sequences of ion migration rates as shown in Figure S1. Such results revealed



Figure 2 | Variation of currents and ion concentrations in the feed stream under different voltages. (a) current; (b) PO_4^{3-} ; (c) SO_4^{2-} ; (d) NH_4^+ ; (e) K^+ ; (f) Ca^{2+} ; (g) Mg^{2+} (*continued*).



Figure 2 | Continued.

that although the application of higher voltages augmented the electric field, it did not mean that the sequent movability of different ions was altered. In addition, higher voltage also suggested more energy consumption. The operation run at 4 V possessed 4.87 kW·h·m⁻³, and a stepwise increase of energy consumption was detected, 5.75, 6.90, 7.99 and 8.81 kW·h·m⁻³ at 5, 6, 7, 8 V, respectively.

3.1.2. Influence of initial electrolyte concentration

Normally, for the real use, the SCAE system would be operated continuously, which indicated that nutrient ions would increase stepwise in the product and brine streams. Such ion accumulation might hinder ion migration and reduce the nutrient recovery efficiency due to osmotic effects. In addition, the properties of real wastewaters might significantly fluctuate due to season change or the operational strategy of anaerobic treatment. This variation implied that different initial concentrations of electrolytes should be considered for the SCAE operation.

In this section, the impacts of initial NaCl concentration in the product and brine streams on SCAE operation were investigated. The recovery efficiencies of cations and anions in the product streams and brine stream (NH₄⁺ and K⁺) were determined. As displayed in Figure 4(a), the multivalent cations (Mg²⁺ and Ca²⁺) and anions (SO₄²⁻ and PO₄³⁻) displayed the increased trend of recovery efficiency (above 80% in final), coupled with the enhancement of NaCl concentrations in

lon	lonic radius (Å ^a)	Hydrated radius (Å)	Reference
Na ⁺	1.02	2.18	Marcus (2013)
NH_4^+	1.48	3.31	Li et al. (2016), Korolev (2014)
K^+	1.38	2.13	Marcus (2013)
Mg^{2+}	0.72	2.97	Marcus (2013)
Ca^{2+}	1.00	2.69	Marcus (2013)
Cl^{-}	1.81	2.25	Marcus (2013)
SO_4^{2-}	2.30	2.75	Marcus (2013)
PO ₄ ³⁻	2.38	2.95	Marcus (2013)

Table 1 | Properties of ions in the aqueous solution

^aLength unit, 1 Å = 0.1 nm.





Figure 3 | Recovery efficiency (a) and current efficiency (b) of different nutrient components under different voltages.



Figure 4 | Recovery efficiency (a) and current performance (b) under different electrolyte concentrations.

the product streams. As to the monovalent ions $(NH_4^+ \text{ and } K^+)$ in the brine stream, they displayed a decline down to 60%. Figure 4(b) depicts the variation of current efficiency in the experiments, where the increase of NaCl concentration resulted in a decrease in the ionic current efficiency. This was because more current was wasted in resisting ion diffusion caused by the high concentration gradients among different chambers (Liu & Cheng 2020), which also could be confirmed by the increase in energy consumption. The energy consumption was 6.78, 7.03, 7.34, 8.15 and 9.10 kWh·m⁻³ when electrolyte concentration was 2.5, 5, 10, 20 and 30 g-NaCl·L⁻¹, respectively. It should be noted that higher NaCl concentrations resulted in faster ion migration, especially for divalent ions like Ca²⁺, Mg²⁺, SO₄²⁻ and PO₄³⁻, as shown in Figure 5. Such rate enhancement was attributed to the increase of electrical conductivity reflected as the current increase in the early stage, which is observed in Figure 5(a).

It has been reported that the existence of monovalent anion or cation exchange membrane in the electrodialysis could alter the migration behavior of various ion under the electric field, since they merely allow positively or negatively monovalent ions to pass through the product stream to reach the brine stream (Tran *et al.* 2015). In order to keep the charge neutrality in the product stream, divalent ions migrating from the feed stream to the product stream would therefore displace the monovalent ions (Na⁺ or Cl⁻) in the product streams. Previous research revealed that the addition of sodium or chloride ions in the product streams could improve the competitive migration of other ions. Therefore, an enhancement in the recovery efficiencies of multivalent ions (Ca²⁺, Mg²⁺, SO²₄⁻, PO³⁻₄) in the product streams was observed, as shown in Figure 4(a). With regard to



Figure 5 | Changes of current and ion migration rates in the feed streams with different electrolyte concentrations. (a) current; (b) PO_4^{3-} ; (c) SO_4^{2-} ; (d) NH_4^+ ; (e) K^+ ; (f) Ca^{2+} ; (g) Mg^{2+} (*continued*).



Figure 5 | Continued.

 NH_4^+ and K^+ , relatively less recovery levels were detected in the brine stream, since they underwent longer migration distance in the product stream (Figure 4(a)). The same phenomenon was also reported in previous research (Chen *et al.* 2021).

3.2. Continuous operation

The nutrient recovery efficiency of SCAE system under continuous operation was investigated by setting voltages at 6 and 8 V, respectively. The desalination of digestive slurry and the conductivities in different chambers are listed in Figure S3. Through the SCAE operation, the significant performance of nutrient recovery was achieved, as illustrated in Figure 6. Under the operational voltage at 6 V, the maximumly accumulative concentrations of PO_4^{3-} , SO_4^{2-} , Mg^{2+} , Ca^{2+} , NH_4^+ and K^+ in the product and brine streams were 215.9, 470.3, 180.7, 604.3, 9,648.4 and 4,220.7 mg·L⁻¹, respectively, which were 9.88, 9.50, 6.19, 4.67, 4.15 and 4.87 times higher than those in the initial wastewater. As to the SCAE operation under 8 V, the fractionation of PO_4^{3-} , SO_4^{2-} , Mg^{2+} , Ca^{2+} , NH_4^+ and K^+ ions in the product and brine streams could reach 231.9, 496.6, 114.8, 300.1, 8,183.7 and 4,571.4 mg·L⁻¹, respectively.

During the continuous operation, the variation in conductivity in every batch displayed similar profiles throughout the experiments (Figure S3). By contrast, the occupation of recovered nutrient components in every batch to the total recovered



Figure 6 | Concentrations of different ions accumulated in the target streams. (a) PO_4^{3-} and SO_4^{2-} in the anionic product stream; (b) NH_4^+ and K^+ in the brine stream; (c) Ca^{2+} and Mg^{2+} in the cationic product stream.

amounts showed different trends (Table 2). When the batch number increased, small percentage increases of PO_4^{3-} and SO_4^{2-} were detected in the anionic product stream, which indicated that more batch operation would result in higher phosphate and sulfate recovery rates. However, for the monovalent (NH₄⁺ and K⁺) and divalent (Mg²⁺ and Ca²⁺) cations, downtrends were observed. This result suggested that with the increase in the batch number, the transportation of cations would undergo much more resistance by higher concentration gradient.

For the continuous operation of the SCAE system in this study, more and more monovalent nutrient ions would transport and accumulate in the brine chamber, while multivalent anions (PO_4^{3-} and SO_4^{2-}) or cations (Mg^{2+} and Ca^{2+}) would respectively migrate and substitute Na^+ or Cl^- ions in the anionic or cationic product chamber due to the displacement effects, as described in the above text. Such discrepancy in ion movement would therefore result in a significant augment of conductivity in the brine stream, along with relatively small changes in the product streams. As shown in Figure S3, the conductivity in the brine chamber was enhanced from 24.0 mS/cm to 129.1 mS/cm, whereas the conductivity in the cationic and anionic product chambers ranged to 16.9–24.9 mS/cm and 24.3–36.5 mS/cm, respectively. It should be pointed out that the cationic and anionic chambers was located adjacent to the left or right side of the brine chamber, respectively. With time passing, the osmotic pressures both in cationic and anionic chambers were augmented, which subsequently elevated the resistance of ion migration (Yao *et al.* 2020). Hence, the increase in the batch number would result in less ion migration in the latter stages, especially for cations (Table 2). With regard to multivalent anions, i.e. PO_4^{3-} and SO_4^{2-} , a different result was observed,

	lons	Voltage (V)	Percentage				
Stream			Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
Anionic product	PO_4^{3-}	6	18.89%	18.85%	19.49%	19.93%	22.85%
		8	18.45%	19.18%	19.91%	20.65%	21.82%
	SO_4^{2-}	6	16.32%	18.16%	20.61%	20.69%	24.21%
		8	15.18%	19.40%	22.09%	19.21%	24.12%
Cationic product	Mg^{2+}	6	35.08%	24.09%	15.92%	13.18%	11.72%
		8	38.26%	23.78%	15.04%	12.95%	9.98%
	Ca^{2+}	6	30.41%	21.98%	17.27%	15.22%	15.11%
		8	33.25%	22.29%	17.05%	14.70%	12.71%
Brine	$\rm NH_4^+$	6	30.87%	23.40%	17.74%	16.49%	11.50%
		8	29.50%	21.76%	18.13%	15.94%	14.67%
	\mathbf{K}^+	6	24.02%	26.64%	21.13%	18.19%	10.03%
		8	22.79%	24.13%	20.89%	17.77%	14.41%

 Table 2 | Occupation of recovered nutrient components in every batch to the total recovered amounts calculated in the continuous operation

where increasing batch number would result in smaller increases in phosphate and sulfate recovery rates (Table 2). This could be explained by a weak repulsion effect due to relatively low accumulative concentrations and a small reduction in volume in the anionic product stream, as observed in Figure S4D. In Figure 6, there were obvious gaps in accumulated concentration for all kinds of nutrient ions between high and low applied voltages. However, the behaviors of ions were not the same. For PO_4^{3-} and SO_4^{2-} , the final concentration made no significant differences. High applied voltage merely improved the migration rate. As for cations, the accumulated concentration increased with the voltage except for potassium. It was worth noting, in the brine stream, the increase in NH₄⁺ concentration was higher than K⁺. Nevertheless, in the cationic product stream, the increment in Ca²⁺ concentration was higher than Mg²⁺, which matched with the permeation sequence in Section 3.1.1. Under higher voltage, NH₄⁺ and Ca²⁺ were more likely to be recovered compared with K⁺ and Mg²⁺.

It is a common knowledge that the osmotic pressure in the SCAE system could also be annotated by the significant enhancement of working volume in the brine chamber (Figure S4), coupled with reductions in the cationic and anionic chambers. However, a small increase in the volume in the cationic product chamber (Figure S4C) was detected. This could be attributed to the migration of Mg^{2+} and Ca^{2+} ions from the feed chamber to the neighboring cationic product chamber. According to the literature, Mg^{2+} and Ca^{2+} ions had a higher hydration number, as displayed in Table 1. Their movements in the SCAE process could carry more water molecules and compensate for the loss of water transport to the brine stream due to the osmotic pressure (Song *et al.* 2021).

3.3. Production of mineral fertilizer

Conventionally, the manufacture processes of different fertilizers require rigorous reaction conditions, such as high temperature, specific catalyst, high pressure and high energy consumption, also a large number of non-renewable mineral resources. After the continuous SCAE operation, the nutrient components in the product and brine streams were measured, and a technical roadmap of manufacturing fertilizers by pairing the streams was designed as shown in Figure 7. The fertilizer products generated were subjected to X-ray diffraction (XRD) analyses for mineral determination, as illustrated in Figure 55.

As shown in Figure 7, the first step was conducted for phosphorus recovery. The phosphorus-rich anionic product stream and magnesium-rich cationic product stream were mixed with a specific ratio for struvite (NH₄MgPO₄) precipitation. As displayed in Table 3, phosphate recovery from digestive slurry could reach more than 96% without dosing external chemicals. In real use, magnesium sources and relatively low phosphate in the wastewater are two of the important factors (Li *et al.* 2019; Siciliano *et al.* 2020) which limit the application of struvite recovery from wastewater. This study revealed that the SCAE process could overcome the limits, and recover phosphorus from wastewater with higher efficiency.

Considering that the brine stream was rich in NH_4^+ (>8,000 mg·L⁻¹) and K⁺(>4,000 mg·L⁻¹), rotary evaporation and crystallization were adopted for the production of ammonium and potassium fertilizers. In this stage, the stream was subjected to rotary evaporation by using sulfuric acid as the adsorbent. The adsorbent, containing 28,647.77 mg·L⁻¹ NH_4^+ -N, was further evaporated to generate NH_4HSO_4 , which was confirmed by the XRD spectrum (Figure S5). Since the residue of the brine



Figure 7 | Flow diagram of fertilizer manufacture by mixing the SCAE product steams.

Table 3 | Performance of manufacturing different fertilizers with the product streams as the substrates

Nutrient	Voltage (V)	Concentration ^a (mg·L ^{-1})	Fertilizer product	Weight ^b (mg)	Recovery ratio (%)
PO ₄ ^{3–} -P	6 8	215.9 231.9	NH4MgPO4·6H2O	167.0 176.7	96.58 97.94
SO_4^{2-}	6 8	470.3 496.6	NH ₄ HSO ₄	55.2 55.7	93.14 95.44
Mg^{2+}	6 8	180.7 114.8	NH4MgPO4·6H2O	111.3 117.8	37.81 50.36
Ca^{2+}	6 8	604.3 300.1	CaCl ₂	164.4 83.2	45.78 39.81
NH_4^+	6 8	9,648.4 8,183.7	NH ₄ HSO ₄	6,639.5 5,940.4	34.78 35.96
\mathbf{K}^+	6 8	4,220.7 4,571.4	KCl	897.2 1,024.2	54.24 63.15

^aThe concentrations of nutrient ions were determined after the SCAE process.

^bThe fertilizer production was calculated on the basis of a 1 L feed stream.

stream contained high concentrations of K^+ and NH_4^+ , it was treated to evaporation to produce raw fertilizer, mixing with KCl and NH_4Cl crystals. For nutrient ions in the digestive slurry, their concentrations after the SCAE and recovery rate are listed in Table 3. Since the fertilizer manufacturing process only extracted the monovalent ions in the brine stream, the recovery ratio of NH_4^+ and K^+ was relatively lower. However, they could be recovered from the anionic product stream by the same method as from the brine. As for Ca^{2+} and Mg^{2+} , they were recovered by forming a chemical precipitation with PO_4^{3-} in specific molar ratio. Thus, their recovery ratio was limited by PO_4^{3-} concentration in the feed stream.

It should be admitted that the technical roadmap of manufacturing fertilizers (Figure 7) in this study was imperfect. However, since the streams obtained after the SCAE process contained high concentrations of nutrient ions with less impurities, it was feasible to produce other fertilizer minerals, such as $Ca_3(PO_4)_2$, $Mg_3(PO_4)_2$, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, and K_2SO_4 . Undoubtedly, precise process design should be adopted to enhance the purity of the products.

4. CONCLUSIONS

This study was aimed at synchronously recovering nutrient ions from digestive slurry, including NH_4^+ , PO_4^{3-} , K^+ , Mg^{2+} , Ca^{2+} and SO_4^{2-} , and subsequently manufacturing different mineral fertilizer. A SCAE process was constructed by introducing the monovalent cation- and anion-selective membranes into the electrodialysis process. Results from the batch experiments revealed that SCAE could remove more than 85.0%, 90.2% and 97.8% of PO_4^{3-} , SO_4^{2-} and cations from the simulated digestive slurry, respectively. Higher applied voltage would improve the recovery efficiency. More divalent ions are recovered with higher initial electrolyte concentrations. The ionic permeation sequence, $NH_4^+ > K^+ > Ca^{2+} > Mg^{2+}$ for cations, and

 $SO_4^{2-} > PO_4^{3-}$ for anions was found due to the combined effects of hydrated radius and hydration numbers. Higher concentrations of electrolyte in the product streams would promote the migration of both divalent cations and anions, which could be ascribed to the ionic replacement effect due to the charge neutrality in the relevant streams. In the continuous operation, the SCAE system recovered 231.9, 496.6, 180.7, 604.3, 9,648.4 and 4,571.4 mg·L⁻¹ of PO_4^{3-}, SO_4^{2-}, Mg^{2+}, Ca^{2+}, NH_4^+ and K^+ in product streams, respectively. After that, the manufacture of different fertilizers, including NH₄MgPO₄, KCl and (NH₄) HSO₄, was performed by purposefully mixing the product streams, without dosing external precipitating chemicals. Future experiments will be carried out by using the real digestive slurry, and the parameters of pH, ion concentration and flow velocity will be investigated. Also, the feasibility of other technical routes of manufacturing fertilizers will be examined.

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DATA AVAILABILITY STATEMENT

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

CONFLICT OF INTEREST

The authors declare there is no conflict.

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