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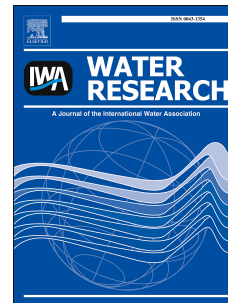
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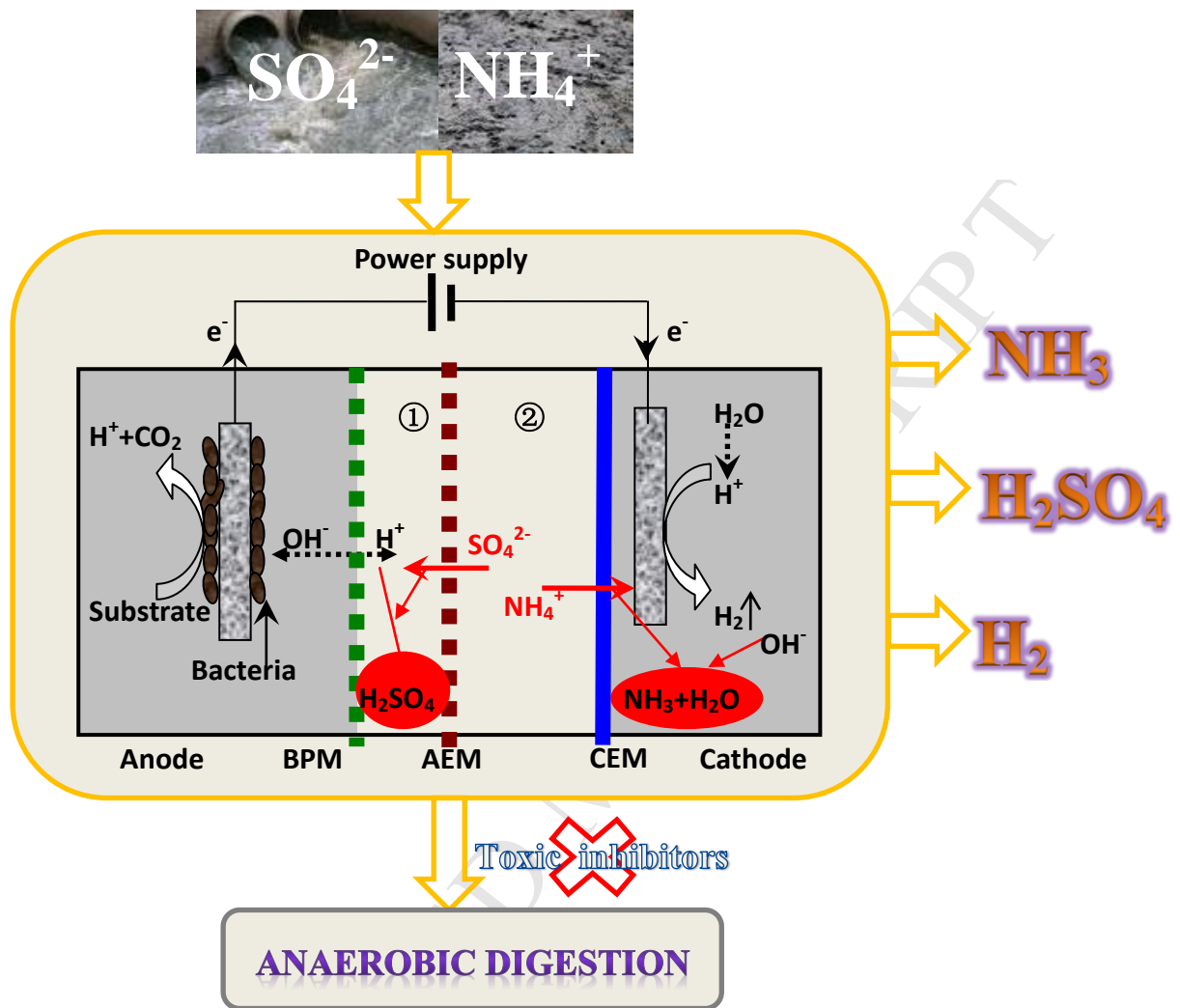
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3 Recovery of ammonia and sulfate from waste  
4 streams and bioenergy production via bipolar  
5 bioelectrodialysis

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17 **Abstract**

18 Ammonia and sulfate, which are prevalent pollutants in agricultural and industrial wastewaters,  
19 can cause serious inhibition in several biological treatment processes, such as anaerobic  
20 digestion. In this study, a novel bioelectrochemical approach termed bipolar bioelectrodialysis  
21 was developed to recover ammonia and sulfate from waste streams and thereby counteracting  
22 their toxicity during anaerobic digestion. Furthermore, hydrogen production and wastewater  
23 treatment were also accomplished. At an applied voltage of 1.2 V, nitrogen and sulfate fluxes of  
24  $5.1 \text{ g NH}_4^+\text{-N/m}^2\text{/d}$  and  $18.9 \text{ g SO}_4^{2-}\text{/m}^2\text{/d}$  were obtained, resulting in a Coulombic and current  
25 efficiencies of 23.6% and 77.4%, respectively. Meanwhile,  $\text{H}_2$  production of 0.29 L/L/d was  
26 achieved. Gas recirculation at the cathode increased the nitrogen and sulfate fluxes by 2.3 times.  
27 The applied voltage, initial  $(\text{NH}_4)_2\text{SO}_4$  concentrations and coexistence of other ions were  
28 affecting the system performance. The energy balance revealed that net energy ( $\geq 16.8 \text{ kWh/kg-N}$   
29 recovered or  $\geq 4.8 \text{ kWh/kg-H}_2\text{SO}_4$  recovered) was produced at all the applied voltages (0.8-1.4  
30 V). Furthermore, the applicability of bipolar bioelectrodialysis was successfully demonstrated  
31 with cattle manure. The results provide new possibilities for development of cost-effective  
32 technologies, capable of waste resources recovery and renewable energy production.

33 **Keywords:** Bipolar bioelectrodialysis; Bioelectrochemical system; Ammonia; Sulfate;  
34 Resources recovery; Waste streams

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## 38 1. Introduction

39 Anaerobic digestion is an attractive technology widely used for organic waste treatment and  
40 production of energy in the form of biogas (Weiland, 2010). However, the stability of the  
41 processes is hard to maintain due to a wide variety of toxic substances, among which free  
42 ammonia ( $\text{NH}_3$ ) and hydrogen sulphide ( $\text{H}_2\text{S}$ ) produced from sulfate reduction are two most  
43 significant inhibitors (Angelidaki and Ahring, 1994; Siles et al., 2010). Ammonia ( $\text{NH}_3/\text{NH}_4^+$ )  
44 and sulfate ( $\text{SO}_4^{2-}$ ) are often found at high levels ( $\geq 3\text{g NH}_4^+\text{-N/L}$  and up to  $13\text{g SO}_4^{2-}\text{-S/L}$ ,  
45 respectively) in the livestock manures and industry residues (Siles et al., 2010). As notorious  
46 environmental pollutants, these substances are often found in concentrations much higher than  
47 the inhibition levels. Inhibition can start at  $1.5\text{g-NH}_4^+\text{-N/L}$  and/or  $1.4\text{g-SO}_4^{2-}/\text{L}$  while 100%  
48 inhibition can be found at  $6\text{-}13\text{g-NH}_4^+\text{-N/L}$  and/or  $1.8\text{g-SO}_4^{2-}/\text{L}$  (El Hadj et al., 2009; Siles et  
49 al., 2010). Beside causing inhibition,  $\text{H}_2\text{S}$  derived from sulfate reduction can cause serious  
50 corrosion in compressors, gas storage tanks and engines, which need to be removed from biogas  
51 through energy-extensive processes (Ryckebosch et al., 2011). Several biological, chemical and  
52 physical techniques such as bioaugmentation, air stripping and chemical precipitation have been  
53 developed to remove or recover excess ammonia and thereby preventing the inhibition  
54 (Angelidaki and Ahring, 1994; Angeles De la Rubia et al., 2010; Ippersiel et al., 2012;  
55 Westerholm et al., 2012). However, most of the methods are uneconomical, requiring high  
56 energy input, have low efficiency, or need of additional chemicals. Most importantly, none of  
57 these methods can recover both ammonia and sulfate.

58 Recently, microbial electrochemical systems (MES) such as Microbial fuel cell (MFC) and  
59 microbial electrolysis cell (MEC) have been demonstrated as promising alternatives to  
60 conventional air-stripping for ammonia recovery (Kelly and He, 2014; Kuntke et al., 2012; Wu

61 and Modin, 2013). Though promising, there are still several challenges need to be addressed  
62 before field application. For example, anodic bacteria might be inhibited at high ammonia levels  
63 ( $>4$  g  $\text{NH}_4^+\text{-N/L}$ ) (Kim et al., 2011; Nam et al., 2010). To meet this challenge, microbial  
64 desalination cell (MDC) has recently been proposed to recover ammonia from anaerobic reactors  
65 (Zhang and Angelidaki, 2014). The principle of MDC has also been successfully applied to  
66 upconcentrate nutrients from diluted urine (Tice and Kim, 2014). Nevertheless, the dramatic pH  
67 drop in the anode during recovery needs to be prevented before practical application (Qu et al.  
68 2012). Sulfate is potential electron acceptor in MES (Sun et al., 2009; Zhao et al., 2008), but  
69 direct recovery of sulfate (e.g., as sulfuric acid) has never been reported. Therefore, it is of great  
70 importance to explore the feasibility of sulfate recovery using MES. Furthermore, an advanced  
71 system that can combine ammonia and sulphide recovery should be pursued. An MES namely  
72 microbial electrolysis desalination and chemical production cell (MEDCC) was recently  
73 developed for water desalination, acid and alkali production (Chen et al., 2012). With an applied  
74 voltage ( $\sim 1.2$  V),  $\text{Cl}^-$  and  $\text{Na}^+$  in the desalination chamber are driven across an anion exchange  
75 membrane (AEM) and a cation exchange membrane (CEM) into acid-production and cathode  
76 chambers, where they are recovered as HCl and NaOH (Chen et al., 2012). It has been reported  
77 that  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  have higher ionic conductivity and diffusivity to transport through  
78 membranes than that of  $\text{Na}^+$  and  $\text{Cl}^-$  (Tice and Kim, 2014). Thus,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  could be  
79 captured in the form of  $\text{NH}_3$  (from  $\text{NH}_4^+$  and  $\text{OH}^-$ ) and  $\text{H}_2\text{SO}_4$ . In light of the above, the MEDCC  
80 could fulfill the requirements for ammonia and sulfate recovery, which has never been reported.  
81 Nevertheless, the extensive aeration in the cathode of MEDCC might be one of the key  
82 challenges for such new application.

83 In this study, we developed a bioelectrochemical system, called in the later as “bipolar  
84 bioelectrodialysis”, on the basis of MEDCC, for a brand new application with respect to  
85 simultaneous ammonia and sulfate recovery from waste streams and hydrogen production.  
86 Beside different application scopes, the main advantage of the bipolar bioelectrodialysis over the  
87 previous MEDCC is that the energy-intensive aeration at the cathode was replaced with cost-  
88 effective hydrogen production, which could offset the energy costs during recovery or be stored  
89 for further use. The objective of this study was to investigate the feasibility of the bipolar  
90 bioelectrodialysis system by varying operational parameters such as applied voltage, initial  
91 ammonia and sulfate concentration, and ionic species. Whereas the synthetic wastewater  
92 containing varied ammonia and sulfate concentrations was used for the investigation, also cattle  
93 manure was used as a proof of concept to demonstrate its applicability. This work demonstrates a  
94 new avenue to recover valuable resources from waste streams, produce bioenergy, and  
95 potentially prevent inhibitions during anaerobic digestion.

## 96 **2. Materials and methods**

### 97 **2.1 Experimental setup**

98 The bipolar bioelectrodialysis system composed of four chambers (inside dimensions 5 cm×5  
99 cm×2 cm for each, Figure 1) was made of nonconductive polycarbonate. A bipolar membrane  
100 (BMP, fumasep® FBM, FuMA-Tech GmbH, Germany), an AEM (AMI 7001, Membrane  
101 international, NJ) and a CEM (CMI 7000, Membrane international, NJ) were placed between the  
102 anode and cathode chambers. The acid-production chamber was close to the anode side for  
103 sulfate recovery. The working chamber was close to the cathode side for receiving waste streams.  
104 The liquid volume of each chamber except anode was 40 mL. There were several openings on  
105 each chamber connected with rubber tube for feeding and sampling. The anode electrode was



106 made of a carbon fiber brush (5.0 cm diameter, 5.0 cm length, Mill-Rose, USA), which was  
107 pretreated at 450 °C for 30 min prior to use (Al Atraktchi 2014). The pretreated anode was pre-  
108 acclimated with mature biofilm in a MFC operated with wastewater. The cathode was a stainless  
109 steel woven mesh (4.0 x 4.0 cm, 0.24 mm wire diameter, 1.57 mm aperture, The Mesh Company,  
110 United Kingdom) coated with 0.5 mg/cm<sup>2</sup> Pt. All the electrical connection and electrode  
111 pretreatment were performed according to previous study (Zhang and Angelidaki, 2012a).

112 **Figure 1 is here**

## 113 **2.2 Domestic wastewater, synthetic ammonia and sulfate-rich wastewater and cattle** 114 **manure**

115 Domestic wastewater was collected from primary clarifier (Lyngby Wastewater Treatment Plant,  
116 Copenhagen, Denmark). The characteristics of the wastewater were as following: chemical  
117 oxygen demand (COD) 296 mg/L, pH 7.8, conductivity 1.4 mS/cm, nitrogen 0.07 g NH<sub>4</sub><sup>+</sup>-N/L,  
118 phosphorus 0.01 g PO<sub>4</sub><sup>2-</sup>-P/L, Na<sup>+</sup> 0.20 g/L, K<sup>+</sup> 0.07 g/L, Cl<sup>-</sup> 0.19 g/L, and SO<sub>4</sub><sup>2-</sup> 0.04 g/L. The  
119 synthetic wastewater was prepared with deionized water containing (pH 6.5): glucose 10 g/L,  
120 NaCl 0.10 g/L, MgCl<sub>6</sub>•H<sub>2</sub>O 0.10 g/L, CaCl<sub>2</sub> 0.05 g/L, NaHCO<sub>3</sub> 0.50 g/L and trace mineral  
121 metals solution (≤0.01 g/L in total). NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> were added at different concentrations  
122 according to the tests. The cattle manure was collected from Vegger biogas plant, Denmark. The  
123 manure was sieved to remove coarse materials and stored at 4 °C before use. The characteristics  
124 of the manure were: pH 8.1, total solids 79.23 g/L, volatile solids 60.55 g/L, total Kjeldahl  
125 nitrogen 3.27 g/L, NH<sub>4</sub><sup>+</sup>-N 2.15 g/L, SO<sub>4</sub><sup>2-</sup> 0.03 g/L, Cl<sup>-</sup> 8.23 g/L, Ca<sup>2+</sup> 0.82g/L, K<sup>+</sup> 3.5 g/L,  
126 Na<sup>+</sup>0.83 g/L. The manure was amended with Na<sub>2</sub>SO<sub>4</sub> to mimic a mixture of ammonia and  
127 sulfate-rich waste, obtaining a final SO<sub>4</sub><sup>2-</sup> concentration of 5 g/L.

## 128 **2.3 Reactor operation**

129 The domestic wastewater amended with acetate (2 g-COD/L in total) was recirculated from a  
130 feed reservoir (liquid volume of 500 mL) through anode at a recirculation rate of 50 mL/min  
131 using a peristaltic pump (OLE DICH, Instrucmentmakers APS, Denmark). Acetate was used  
132 here to eliminate the impact of substrate availability on the system performance. Synthetic  
133 wastewater or manure was fed into the working chamber. NaCl solution (0.1 M, pH 6.9) was  
134 used as catholyte. Unless stated otherwise, the gas phase of the cathode was internally  
135 recirculated at a rate of 50 mL/min. The feed reservoirs and all the chambers of the system were  
136 refilled when the current was lower than 0.2 mA, resulting in a single batch cycle. The reactor  
137 and reservoir were purged with nitrogen before starting each batch cycle. External voltage (0.8-  
138 1.4 V) was supplied by a power supply (HQ PS3003, Helmholtz Elektronik A/S, Denmark). The  
139 gas stream from cathode passed through adsorption bottle filled with 20 g/L boric acid before  
140 being collected into foil gas sampling bag. The acid solutions were renewed periodically. Control  
141 reactors either operated in open circuit or without gas recirculation were also set up. The external  
142 resistance was fixed at 10  $\Omega$ . All experiments were carried out in duplicate at ambient  
143 temperature ( $22\pm 3$  °C).

#### 144 **2.4 Electrochemical analysis and calculations**

145 Kjeldahl nitrogen (KN),  $\text{NH}_4^+$  and COD were measured according to Standard method (APHA,  
146 1998).  $\text{H}_2$  was analyzed by a GC-TCD fitted with a 4.5 m  $\times$  3 mm s-m stainless column packed  
147 with Molsieve SA (10/80).  $\text{Na}^+$  and  $\text{K}^+$  were measured using Flame atomic absorptions  
148 spectrophotometer (FAAS, Shimadzu).  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were quantified by ion chromatography  
149 equipped with AS-9-HC column and conductivity detector (Dionex DX-300, Dionex Co.,  
150 Sunnyvale, CA). pH was measured with a PHM 210 pH meter (Radiometer). Conductivity was  
151 determined using a CDM 83 conductivity meter (Radiometer).

152 The voltage ( $V$ ) was monitored every 30 min using a digital multimeter (Model 2700, Keithley  
 153 Instruments, Inc., Cleveland, OH, USA). Current ( $I$ ), power ( $P=IV$ ) and Coulombic efficiency  
 154 (CE) were calculated as previously described (Zhang and Angelidaki, 2012b). Current density  
 155 was calculated based on the projected surface area of cathode. The ammonia flux ( $R_N$ ), sulfate  
 156 flux ( $R_S$ ), cathodic hydrogen recovery ( $R_{H_2}$ ), current efficiency (CTE) and hydrogen production  
 157 rate ( $H_{2pr}$ ) were calculated as below:

$$158 \quad R_N = \frac{\Delta(m_N)}{At} \quad (1)$$

$$159 \quad R_S = \frac{\Delta(m_S)}{At} \quad (2)$$

$$160 \quad R_{H_2} = \frac{2FV_{H_2}}{RT \int_0^t Idt} \quad (3)$$

$$161 \quad CTE = \frac{bF\Delta(m_S)}{\int_0^t Idt} \times 100\% \quad (4)$$

$$162 \quad H_{2pr} = \frac{V_{H_2}}{tV} \quad (5)$$

163 Where  $\Delta(m_N)$  and  $\Delta(m_S)$  are the transported moles of ammonia and sulfate through membrane,  $t$   
 164 is operation time;  $A$  is the projected surface area of AEM or CEM.  $V$  is total liquid volume of  
 165 cathode chamber;  $I$  is current;  $V_{H_2}$  is the measured hydrogen volume;  $T$  is the absolute  
 166 temperature;  $R$  is the gas constant;  $F$  is Faraday's constant;  $b$  is the mole number of electrons  
 167 transferred per mole of  $SO_4^{2-}$ .

### 168 3. Results and discussion

#### 169 3.1 The performance of bipolar bioelectrodialysis

170 The system performance was studied at batch mode at a voltage of 1.2 V. In the reactor without  
171 cathode gas recirculation, the concentration of ammonia in the working chamber decreased from  
172 6 to 0.8 g-NH<sub>4</sub><sup>+</sup>-N/L, while the concentration of sulfate decreased from 20.6 to and 2.5 g-SO<sub>4</sub><sup>2-</sup>/L  
173 after one batch cycle (266 h), resulting in a nitrogen and sulfate flux of 5.1 g-NH<sub>4</sub><sup>+</sup>-N/m<sup>2</sup>/d and  
174 18.9 g-SO<sub>4</sub><sup>2-</sup>/m<sup>2</sup>/d (Figure 2A). When gas recirculation was employed at the cathode, the  
175 ammonia and sulfate fluxes increased to 11.7 g-NH<sub>4</sub><sup>+</sup>-N/m<sup>2</sup>/d and 40.7 g-SO<sub>4</sub><sup>2-</sup>/m<sup>2</sup>/d (Figure 2).  
176 In addition, gas circulation increased the final sulfate concentration in the recovery chamber,  
177 while it lowered the final ammonia concentration in the cathode. The enhanced ammonia and  
178 sulfate recovery when gas recirculation was applied at the cathode could be due to accelerated  
179 mass transfer and improved circuit current (Hou et al., 2014). The gas recirculation at cathode  
180 might also have resulted in NH<sub>3</sub> stripping from catholyte (discussed later), which could explain  
181 the reduced final ammonia concentration in the cathode. In the control reactor under open circuit,  
182 ammonia and sulfate concentrations in the working chamber decreased only slightly ( $\leq 19\%$ ),  
183 indicating the importance of current for driving the transportation of the ions. There were no  
184 significant changes in glucose concentration in either condition (data not shown), excluding the  
185 diffusion of glucose through membranes. Mass balance for the main ions was established to  
186 further elucidate the working mechanism of the bipolar bioelectrodialysis. As shown in Table 1,  
187 85% of ammonia and 81% of sulfate were recovered without gas recirculation, while 90% and  
188 93% were achieved with gas recirculation. In the reactor without gas recirculation, about 48% of  
189 the recovered ammonia remained at the cathode and another 52% was finally captured in the acid  
190 absorption bottle. However, only 20% of the recovered ammonia remained at the cathode with  
191 gas recirculation and another 80% was captured in the acid bottle, which supported our earlier  
192 assumption that NH<sub>3</sub> stripping from the cathode was enhanced with gas recirculation. The

193 concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  in the working chamber increased slightly after one batch cycle  
194 (Table 1). It was consistent with control experiment (open circuit), in which slight transportation  
195 of  $\text{Na}^+$  and  $\text{Cl}^-$  (1.9 and 2.5 g/L, data not shown) toward working chamber were detected along  
196 with slightly decrease of  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$ , respectively. The results imply that ion exchange  
197 might also contribute to the transportation of ammonia and sulfate (Jacobson et al., 2011).

198 **Figure 2 and Table 1 are here**

199 The pH in the different chambers is shown in Figure 2B. No significant changes in the anolyte  
200 pH were observed throughout the batch cycle, while the cathode pH increased from 6.9 to above  
201 9.6 within 24 h and kept that level until end of operation in both reactors. The pH in the cathode  
202 with gas recirculation (9.99) was slightly higher than that without gas recirculation (9.80). The  
203 cathodic pH is the combination effect of hydrogen evolution and ammonia stripping. The  
204 hydrogen evolution could lead to the increase of pH while ammonia stripping could consume  
205  $\text{OH}^-$  and decrease pH. The gas recirculation could accelerate both processes. According to the  
206 result here, it can be deduced that the contribution of gas recirculation to the improvement of  
207 hydrogen evolution was more effective than that to the air stripping. Thus, the cathode with gas  
208 recirculation showed relatively higher pH. The gas recirculation at cathode also led to  
209 significantly lower pH in the recovery and working chambers (pH 0.9 and pH 1.7, respectively)  
210 compared to that without gas recirculation (1.1 and 3.82, respectively). The drop of pH in the  
211 working chamber was probably due to the diffusion/leakage of  $\text{H}^+$  through AEM (Chen et al.,  
212 2012). To avoid the influence of low pH on the following anaerobic digestion, the effluent from  
213 the working chamber could be mixed with some other alkaline substrate or with the effluent from  
214 the cathode to adjust the pH. As shown in Figure 2C, the maximum stable current density in the  
215 reactor with cathode gas recirculation was approx.  $2.7 \text{ A/m}^2$ , which was higher than that without

216 gas recirculation ( $2.4 \text{ A/m}^2$ ). In both reactors, current density reached its maximum level at the  
217 beginning, and then decreased continuously until the end of batch cycle. This phenomenon was  
218 probably attributed to the ions depletion in the working chamber which increased the internal  
219 resistance (Cao et al. 2009). The COD consumption (approx. 50%) in the anode could also partly  
220 contribute to the decrease of current density. As expected from the current density,  $\text{H}_2$  production  
221 was also improved with gas recirculation at cathode. 146 mL of  $\text{H}_2$  was produced with gas  
222 recirculation while only 128 mL was produced without gas recirculation after a batch cycle. The  
223 increase in hydrogen production with gas recirculation was consistent with the increase of pH at  
224 the cathode (Figure 2B). In general, the reactor with cathode gas recirculation showed higher  
225  $\text{RH}_2$ , CE and CTE compared to that without gas recirculation (Figure 2D). These parameters  
226 reached their maximum level at the beginning and then decreased with time in both reactors. For  
227 example,  $\text{RH}_2$ , CE and CTE reached to 92.7%, 36.3%, and 88.7% in the first 24 h in the reactor  
228 with gas recirculation. Overall, the results in this section demonstrated the feasibility of the  
229 bipolar bioelectrodialysis for ammonia and sulfate recovery along with  $\text{H}_2$  production.

230 **Figure 3 and Table 2 are here**

### 231 **3.2 The system performance at different applied voltages**

232 Circuit current was the main driving force of ions transportation, thus it is of great importance to  
233 elucidate the correlation between different current levels and recovery process by varying the  
234 applied voltage. The system performance at different applied voltages is shown in Figure 3. All  
235 the parameters including current density,  $R_N$ ,  $R_S$ ,  $\text{H}_{2\text{pr}}$ , CE, and  $\text{RH}_2$  increased with the increasing  
236 of applied voltage (0.8-1.4 V). For example, current density,  $R_N$ ,  $R_S$ ,  $\text{H}_{2\text{pr}}$ , CE, and  $\text{RH}_2$  increased  
237 respectively by 76.5%, 158%, 154%, 350%, 114% and 70% after increasing the voltage from 0.8  
238 to 1.4 V. It is likely that the increasing of system performance might continue at even higher

239 voltage. However, the electric energy consumption would probably increase with voltage and  
240 thereby affecting net energy gain. Therefore, energy balance analysis was made (Table 2). The  
241 analysis revealed that net energy ( $\geq 16.8$  kWh/kg-N or  $\geq 4.8$  kWh/kg-H<sub>2</sub>SO<sub>4</sub>) was produced  
242 during ammonia and sulfate ions recovery at all the voltages (0.8-1.4 V). The energy gain  
243 increased with the voltage till 1.2 V. However, further increasing voltage to 1.4 V decreased  
244 energy production due to increased electric energy consumption in the system. Thus, the  
245 optimum voltage for energy recovery in the bipolar bioelectrodialysis system was 1.2 V. The  
246 energy produced at 1.2 V with initial ammonia and sulfate concentration of 6 g-N/L and 20.6 g-  
247 SO<sub>4</sub><sup>2-</sup>/L was higher than that obtained with 4 g-N/L and 13.7 g-SO<sub>4</sub><sup>2-</sup>/L. The increased  
248 conductivity at relatively higher ammonia and sulfate concentration could be a possible  
249 explanation. It was also noticed that the gas recirculation at the cathode didn't reduce the overall  
250 energy gain. Instead, more energy was gained due to high H<sub>2</sub> production at the cathode. The net  
251 energy gained here was higher than that reported in the previous studies concerning MES with  
252 ammonia recovery (Kuntke et al., 2012; Wu and Modin, 2013, Zhang and Angelidaki, 2014).  
253 Beside the different operation conditions, sulfate recovery could improve energy production. In  
254 the light of above, the applied voltage was an important factor affecting the system performance  
255 and the system could with advantage be operated at 1.2 V. It should be noted that this  
256 preliminary energy analysis didn't include the purification costs for the recovered sulfuric acid,  
257 since presence of other ions (i.e., NaCl in this study) in the recovery chamber could be avoided  
258 in continuous operation. In that case, deionized water or low concentration of H<sub>2</sub>SO<sub>4</sub> instead of  
259 NaCl could be just needed at the beginning to initiate the process, but its feasibility needs to be  
260 further studied.

### 261 **3.3 The effect of initial NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> concentrations on system performance**

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was added into the synthetic wastewater at different concentrations to explore the influence of initial ammonia and sulfate concentration on the system performance (Figure 4). Current density increased from 1.7 to 2.7 A/m<sup>2</sup> with the increasing of initial (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> concentrations from 9.4 to 28.3 g/L (corresponding to 2~6 g NH<sub>4</sub><sup>+</sup>-N/L or 6.9~20.6 g-SO<sub>4</sub><sup>2-</sup>/L). The high conductivity contributed by the high (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> concentration might explain the high current density. Along with current density, R<sub>N</sub>, R<sub>S</sub>, H<sub>2pr</sub>, CE, and RH<sub>2</sub> also increased with initial (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> concentration. For example, R<sub>N</sub> of 7.6g-N/m<sup>2</sup>/d, R<sub>S</sub> of 24.5 g-SO<sub>4</sub><sup>2-</sup>/m<sup>2</sup>/d, H<sub>2pr</sub> of 0.27 L/L/d, CE 19.6%, and RH<sub>2</sub> of 56.4% were obtained at (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> concentration of 9.4 g/L, while much higher values of 11.7 g-N/m<sup>2</sup>/d, 40.5 g-SO<sub>4</sub><sup>2-</sup>/m<sup>2</sup>/d, 0.54 L/L/d, 28.9%, and 68.6% were achieved at (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> concentration of 28.3 g/L. The results indicate that the bipolar bioelectrodialysis could be applicable to waste streams with wide range of ammonia and sulfate concentrations. The bipolar bioelectrodialysis was targeting the waste streams with high concentration of ammonia and sulfate which can cause severe inhibition during anaerobic digestion, such as livestock manures and industrial wastewaters (or mixture of two by co-digestion). Thus, the synthetic wastewater was used to mimic those waste streams. The system could also be applied to the wastewater with low level of ammonia and sulfate (e.g., domestic wastewater), which could be a new application for future study.

Figure 4 is here

### 3.4 The effect of other ionic species on NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> transportation

Although SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> are dominant ions in ammonia and sulfate-rich wastewaters, other ions such as Cl<sup>-</sup> and Na<sup>+</sup> might also move through membranes and thereby affecting the recovery processes. Thus, Cl<sup>-</sup> and Na<sup>+</sup> (150 mM each) were added into the synthetic wastewater containing 300 mM NH<sub>4</sub><sup>+</sup> and 150 mM SO<sub>4</sub><sup>2-</sup> to investigate their impact on the system



285 performance (Figure 5). In the working chamber,  $\text{NH}_4^+$  concentration decreased sharply from  
286 300 to 19 mM within 120 h, while  $\text{Na}^+$  concentration decreased slightly from 150 to 124 mM  
287 during the same period. Thereafter,  $\text{Na}^+$  concentration decreased dramatically and at the end of  
288 batch cycle approached a level lower than 24 mM. Similarly,  $\text{SO}_4^{2-}$  concentration in the working  
289 chamber decreased fast in the first 72 h (150 to 57 mM), while  $\text{Cl}^-$  concentration was around 125  
290 mM during this period. Nevertheless,  $\text{Cl}^-$  concentration decreased continuously along with  $\text{SO}_4^{2-}$   
291 from 72 h till the end of the batch cycle. Correspondingly,  $\text{NH}_4^+$  transportation to the cathode  
292 was faster than that of  $\text{Na}^+$ , while  $\text{SO}_4^{2-}$  transportation to the recovery chamber was faster than  
293 that of  $\text{Cl}^-$  (Figure 5B). The initial lag period of the  $\text{Na}^+$  and  $\text{Cl}^-$  transportation could be due to the  
294 lack of concentration gradient between the membrane. It has been reported that same level of  
295 ionic concentration between membranes can prevent ions diffusion (Desloover et al., 2012). The  
296 higher equivalent ionic conductivity of  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  over other ions (e.g.,  $\text{Na}^+$  and  $\text{Cl}^-$ ) could  
297 also be responsible for the selective  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  transportation (Tice and Kim, 2014). Unlike  
298  $\text{Na}^+$ , ammonia was continuously leaving from the reactor (cathode) in terms of volatile  $\text{NH}_3$ ,  
299 which might be favorable for selective  $\text{NH}_4^+$  transportation. This could also explain the relatively  
300 longer lag phase of  $\text{Na}^+$  transportation. It should be noted that current density,  $\text{H}_2$ , CE and  $\text{R}_{\text{H}_2}$   
301 observed here (Figure S1, Supplementary data) was much higher than that without NaCl addition  
302 in the working chamber shown in Figure 3 (at 1.2 V). This was probably due to the increased  
303 conductivity after adding NaCl. Thus, the coexistence of other ions didn't affect the ammonia  
304 recovery, but it may influence the purity of  $\text{H}_2\text{SO}_4$  recovered at the recovery chamber (e.g., in  
305 terms of HCl). The acids mixture could be used directly in industries or further purified. It could  
306 be interesting to investigate the effect of other cations such as  $\text{Ca}^{2+}$  and  $\text{K}^+$  which could also be  
307 found in most of waste streams. However,  $\text{Ca}^{2+}$  and  $\text{K}^+$  are quite similar to  $\text{Na}^+$  in terms of

308 transportation property through cation exchange membrane. It can be expected that  $\text{Ca}^{2+}$  and  $\text{K}^{+}$   
309 have similar effect as  $\text{Na}^{+}$  on the system. Thus, the ammonia transportation would not be  
310 adversely affected no matter which cation ( $\text{Ca}^{2+}$ ,  $\text{K}^{+}$ , or  $\text{Na}^{+}$ ) presented. Specialized anion  
311 exchange membranes that are selective for  $\text{NH}_4^{+}$  and  $\text{SO}_4^{2-}$  ions could be developed in future to  
312 enhance selective recovery from complex waste streams.

313 **Figure 5 is here**

### 314 **3.5 The system performance with cattle manure**

315 The applicability of the bipolar bioelectrodialysis was further verified with cattle manure. As  
316 shown in Figure 6, the concentration of  $\text{NH}_4^{+}$  and  $\text{SO}_4^{2-}$  in the working chamber decreased  
317 continuously until the end of batch cycle, while constant accumulation of  $\text{NH}_4^{+}$  and  $\text{SO}_4^{2-}$  was  
318 observed respectively in the cathode and recovery chamber. Consistent with previous  
319 observation,  $\text{NH}_4^{+}$  concentration in the cathode was much lower than the level removed from the  
320 working chamber due to free  $\text{NH}_3$  volatilization. More than 94% of  $\text{NH}_4^{+}$  and  $\text{SO}_4^{2-}$  in the cattle  
321 manure were finally recovered at the end of batch cycle. Current density reached maximum level  
322 (approx.  $2.3 \text{ A/m}^2$ ) at the beginning and thereafter decreased to  $0.8 \text{ A/m}^2$  after 182 h, resulting in  
323 an average CE of 27.7%. The remained current density at the end of recovery process could be  
324 due to the presence of other ions in the cattle manure which support the conductivity inside of  
325 the system. Along with ammonia and sulfate recovery,  $\text{H}_2$  production at the cathode increased  
326 gradually to 150 mL with an average  $R_{\text{H}_2}$  of 68.2%. The above results demonstrated the  
327 applicability of the bipolar bioelectrodialysis to the complex waste streams. The cattle manure  
328 amended with  $\text{SO}_4^{2-}$  was used in this test, further investigation with waste streams originally  
329 containing both ammonia and sulfate (e.g., urine) may promote the industrial application of the

330 technology. Co-digestion of two waste streams rich either in ammonia or sulfate may also fit  
331 well with the application.

332 **Figure 6 is here**

#### 333 **4. Conclusion**

334 Ammonia and sulfide derived from sulfate reduction are two notorious toxic compounds in  
335 anaerobic digestion processes. Removal or recovery of these inhibitors is always energy-  
336 intensive and inefficient, and a method that can achieve simultaneous ammonia and sulfate  
337 recovery has never been reported so far. It was shown in this study that bipolar bioelectrodilysis  
338 was an attractive alternative method to recover ammonia and sulfate and produce hydrogen,  
339 allowing the counteraction of their toxicity during anaerobic digestion. The bipolar  
340 bioelectrodilysis offers several advantages over conventional methods: (1) This is the first  
341 technology which can recover two inhibitors (or its precursor) simultaneously; (2) In-situ  
342 recovery without additional chemicals. Instead, hydrogen was produced to make the process self-  
343 sustainable; (3) The recovered sulphuric acid could be used to capture ammonia which make the  
344 technology even economic feasible; (4) No risk of inhibition on exoelectrogens, as the waste will  
345 not be fed into the anode; (5) No need of further H<sub>2</sub>S removal from the biogas, since its precursor  
346 (i.e., sulfate) is recovered, and thereby reducing the biogas upgrading costs; (6) Wastewater  
347 treatment can be accomplished through the oxidation in the anode. The extent of recovery could  
348 be further optimized by addressing the challenges related to materials (e.g., selective membrane),  
349 operation (continuous mode), and microbiology. Especially, the quality of the effluent in each  
350 chamber should be considered and optimized. The COD removal in the anode could be further  
351 improved by regulating the hydraulic retention time and other operational parameters (e.g., type  
352 of wastewater). The catholyte could be reused for several times, which needs to be further

353 studied. Furthermore, the NaCl solution could be replaced by deionized water or H<sub>2</sub>SO<sub>4</sub> as  
354 electrolyte in the recovery chamber in continuous operation to initiate the recovery process and  
355 thereby improving the purity of the recovered H<sub>2</sub>SO<sub>4</sub>. Besides, while the ratio of N/S was fixed  
356 in this study to prove the concept, the influence of different N/S ratios along with individual  
357 substance concentrations should be investigated in future to better understand the system.  
358 According to the results regarding different initial ammonia and sulfate concentrations, it can be  
359 expected that the system could also work at varied ammonia and sulfate ratios. In addition, the  
360 bipolar bioelectrodialysis could be linked to anaerobic digestion process for further exploring its  
361 effectiveness on biogas enhancement. Considering that large amount of world's biogas plants are  
362 suffering economic and energy losses caused by ammonia and sulfide inhibition, there is  
363 significant potential for bipolar bioelectrodialysis.

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**Table 1** Mass balance on the main ions

Test		AC	RC	WC	CC	AB <sup>d</sup>	Total	Balance (100%)		
1 <sup>a</sup>	NH <sub>4</sub> <sup>+</sup> (mg)	In	<sup>b</sup> 0	308.6±1.1	0	0	308.6±1.1	98.3±0.5		
		out	-	41.1±0.3	128.6±0.6	133.7±0.3	303.4±0.6			
	SO <sub>4</sub> <sup>2-</sup> (mg)	In	-	0	822.9±0.7	0	0	822.9±0.7	97.7±0.3	
		out	-	668.0±0.4	136±0.7	0	0	804.0±1.5		
	Na <sup>+</sup> (mg)	In	-	92.0±2.9	0.4±0.1	92.0±2.9	0	184.4±2.9	95.7±7.5	
		out	-	88.0±5.7	36.4±5.7	52.0±11.3	0	176.4±11.3		
	Cl <sup>-</sup> (mg)	In	-	140.0±8.5	0.2±0.1	140.0±8.5	0	280.2±8.5	97.8±4.3	
		out	-	116.0±5.7	20.1±4.5	138.0±2.8	0	274.1±3.9		
	2 <sup>c</sup>	NH <sub>4</sub> <sup>+</sup> (mg)	In	-	0	308.6±1.1	0	0	308.6±1.1	98.0±4.1
			out	-	0	25.7±7.3	57.1±13.8	219.6±9.1	302.4±15.6	
SO <sub>4</sub> <sup>2-</sup> (mg)		In	-	0	822.9±0.7	0	0	822.9±0.7	99.6±4.5	
		out	-	764.0±19.8	56±16.9	0	0	820.0±36.8		
Na <sup>+</sup> (mg)		In	-	92.0±2.5	0.4±0.1	92.0±2.5	0	184.4±2.9	102.2±3.1	
		out	-	96.0±11.3	28.3±11.3	64.0±5.7	0	188.3±5.7		
Cl <sup>-</sup> (mg)		In	-	140.0±8.5	0.2±0.1	140.0±8.5	0	280.2±8.5	98.0±3.4	
		out	-	120±9.6	16.2±3.4	138.4±3.4	0	274.6±9.6		

<sup>a</sup> Without recirculation in the cathode. The data was taken at the end of batch run (266 h)

<sup>b</sup> The ions in the anolyte was not considered, as some of ions might be consumed and their migration to/from the other chambers could be ignored due to BPM separation.

<sup>c</sup> With recirculation in the cathode. The data was taken at the end of batch run (181 h)

<sup>d</sup> Adsorption bottle filled with boric acid.



**Table 2** Energy balance analysis based on the batch test

Voltage (V)	Normalized Units	Input		Output			Net energy balance
		Electric energy <sup>a</sup>	Pumping <sup>b</sup>	NH <sub>3</sub> energy equiv <sup>c</sup>	H <sub>2</sub> SO <sub>4</sub> energy equiv <sup>d</sup>	H <sub>2</sub>	
0.8	kWh/kg-N	-2.04 <sup>i</sup>	-0.42	10.30	7.57 <sup>e</sup>	1.53	16.94
	kWh/kg-H <sub>2</sub> SO <sub>4</sub>	-0.59	-0.12	2.96 <sup>e</sup>	2.18	0.44	4.87
1.0	kWh/kg-N	-2.54	-0.27	10.30	7.58 <sup>e</sup>	1.92	16.99
	kWh/kg-H <sub>2</sub> SO <sub>4</sub>	-0.73	-0.08	2.96 <sup>e</sup>	2.18	0.55	4.88
1.2	kWh/kg-N	-2.95	-0.19	10.30	7.60 <sup>e</sup>	2.35	17.11
	kWh/kg-H <sub>2</sub> SO <sub>4</sub>	-0.85	-0.05	2.95 <sup>e</sup>	2.18	0.67	4.90
1.2 <sup>f</sup>	kWh/kg-N	-2.75	-0.16	10.30	7.69 <sup>e</sup>	2.40	17.48
	kWh/kg-H <sub>2</sub> SO <sub>4</sub>	-0.78	-0.04	2.92 <sup>e</sup>	2.18	0.68	4.96
1.2 <sup>g</sup>	kWh/kg-N	-2.67	- <sup>h</sup>	10.30	7.58 <sup>e</sup>	2.11	17.32
	kWh/kg-H <sub>2</sub> SO <sub>4</sub>	-0.77	-	2.96 <sup>e</sup>	2.18	0.61	4.98
1.4	kWh/kg-N	-3.56	-0.16	10.30	7.64 <sup>e</sup>	2.58	16.80
	kWh/kg-H <sub>2</sub> SO <sub>4</sub>	-1.02	-0.04	2.94 <sup>e</sup>	2.18	0.74	4.80

<sup>a</sup> Based on the current over the batch cycle

<sup>b</sup> Estimated according to hydraulic head loss and theoretic equation (in Supplementary data).

<sup>c</sup> Assumed energy consumption for Haber-Bosch process

<sup>d</sup> Assumed energy consumption for wet sulfuric acid process

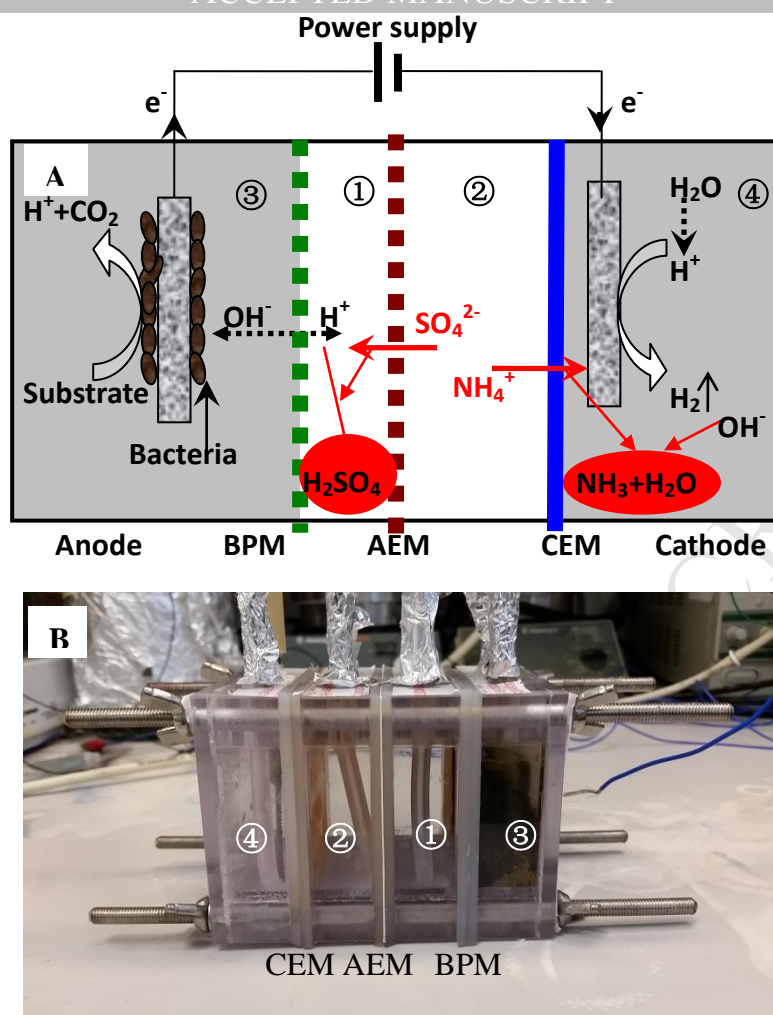
<sup>e</sup> Calculated based on the mole ratio of recovered NH<sub>3</sub> and SO<sub>4</sub><sup>2-</sup> in each batch

<sup>f</sup> The initial NH<sub>4</sub><sup>+</sup>-N and SO<sub>4</sub><sup>2-</sup> concentration in the WC was 6 and 20.6 g/L (mole ratio of 2:1).

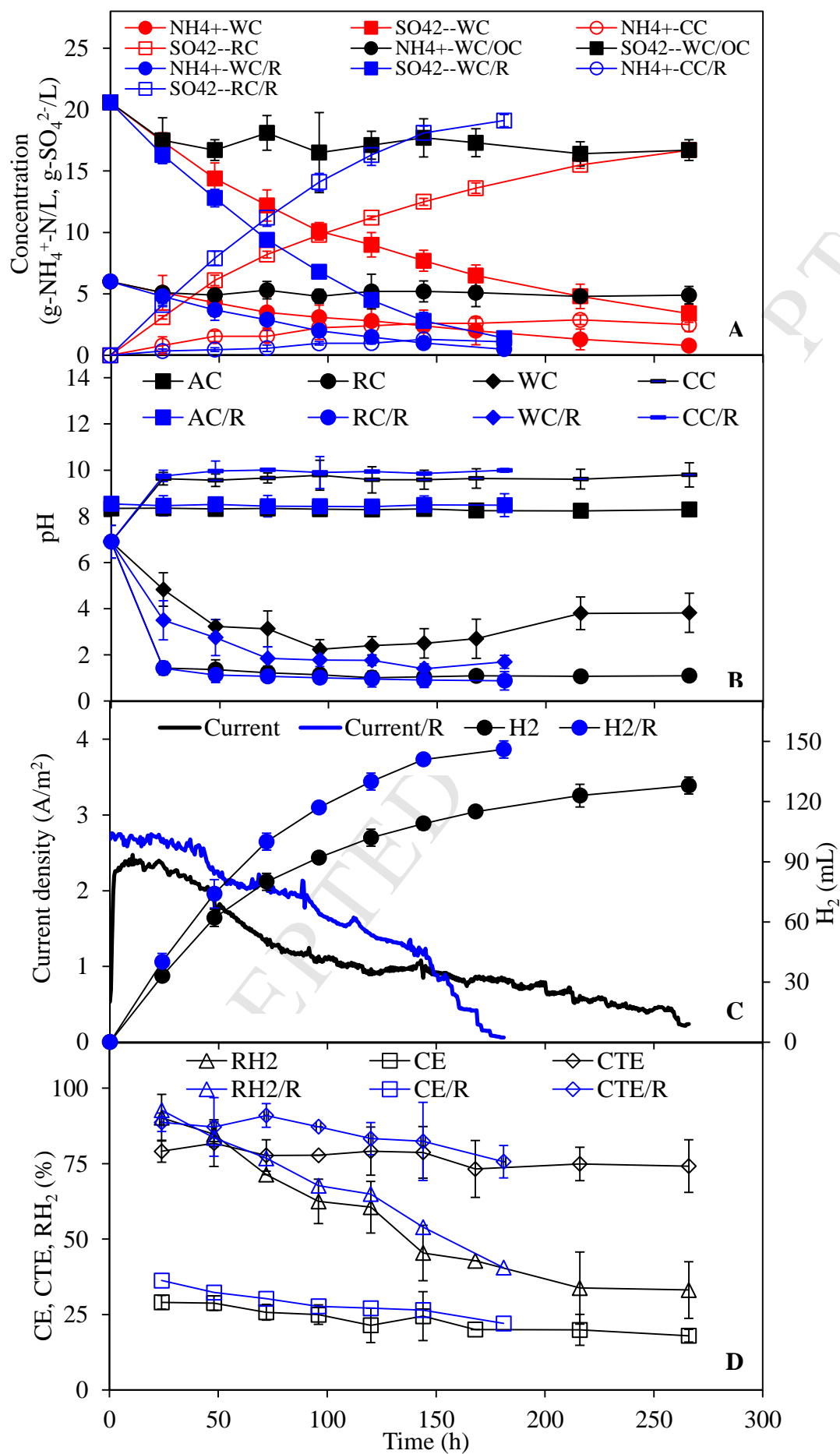
<sup>g</sup> The initial NH<sub>4</sub><sup>+</sup>-N and SO<sub>4</sub><sup>2-</sup> concentration in the WC was 6 and 20.6 g/L (mole ratio of 2:1), but without cathode recirculation.

<sup>h</sup> not applicable

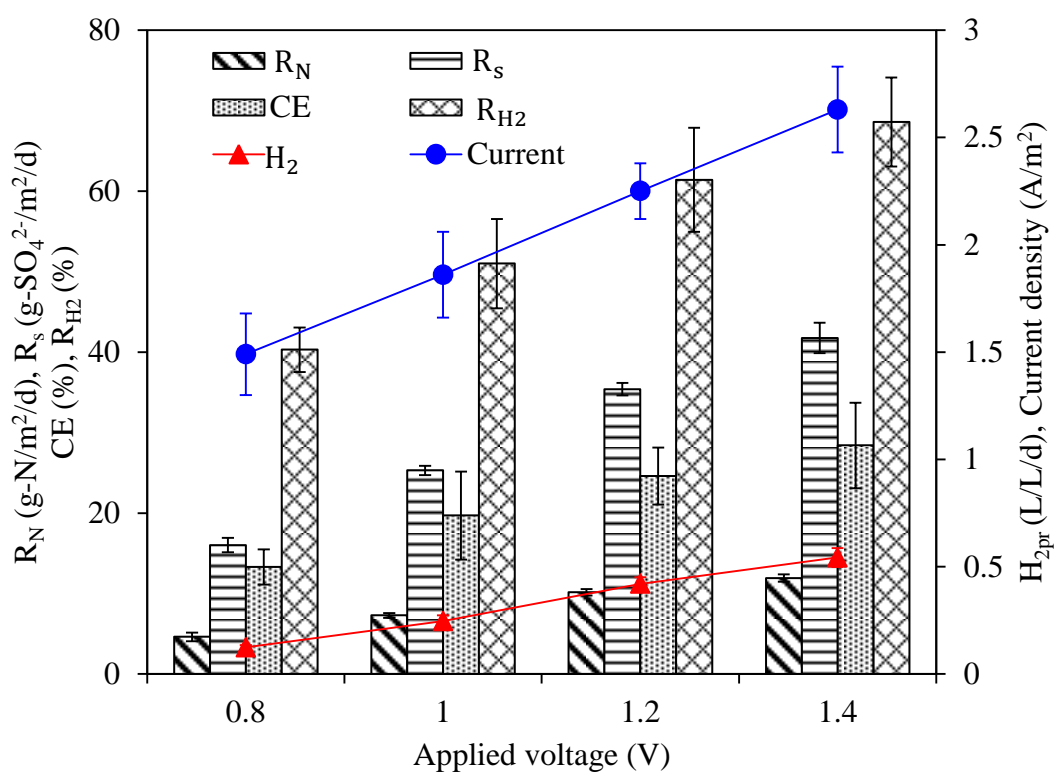
<sup>i</sup> Minus means energy cost, while positive means energy gain



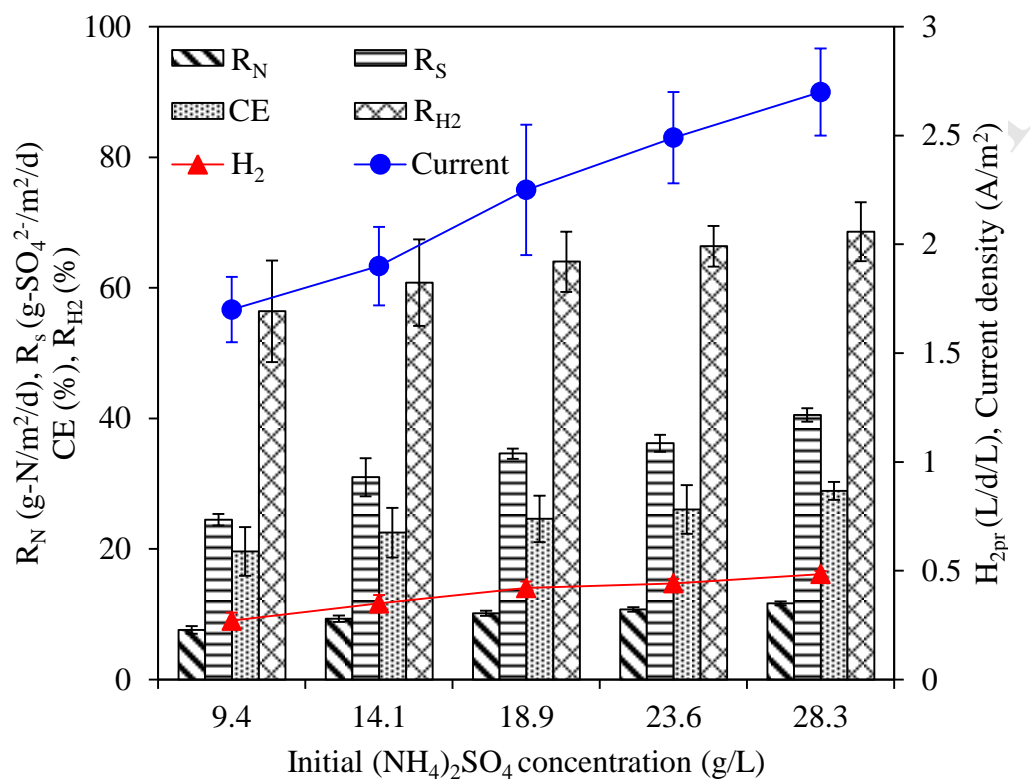
**Figure 1** Schematic illustration (A) and image (B) of the bipolar bioelectrodialysis from opposite view. ① Recovery chamber, ② Working chamber, ③ Anode, ④ Cathode.



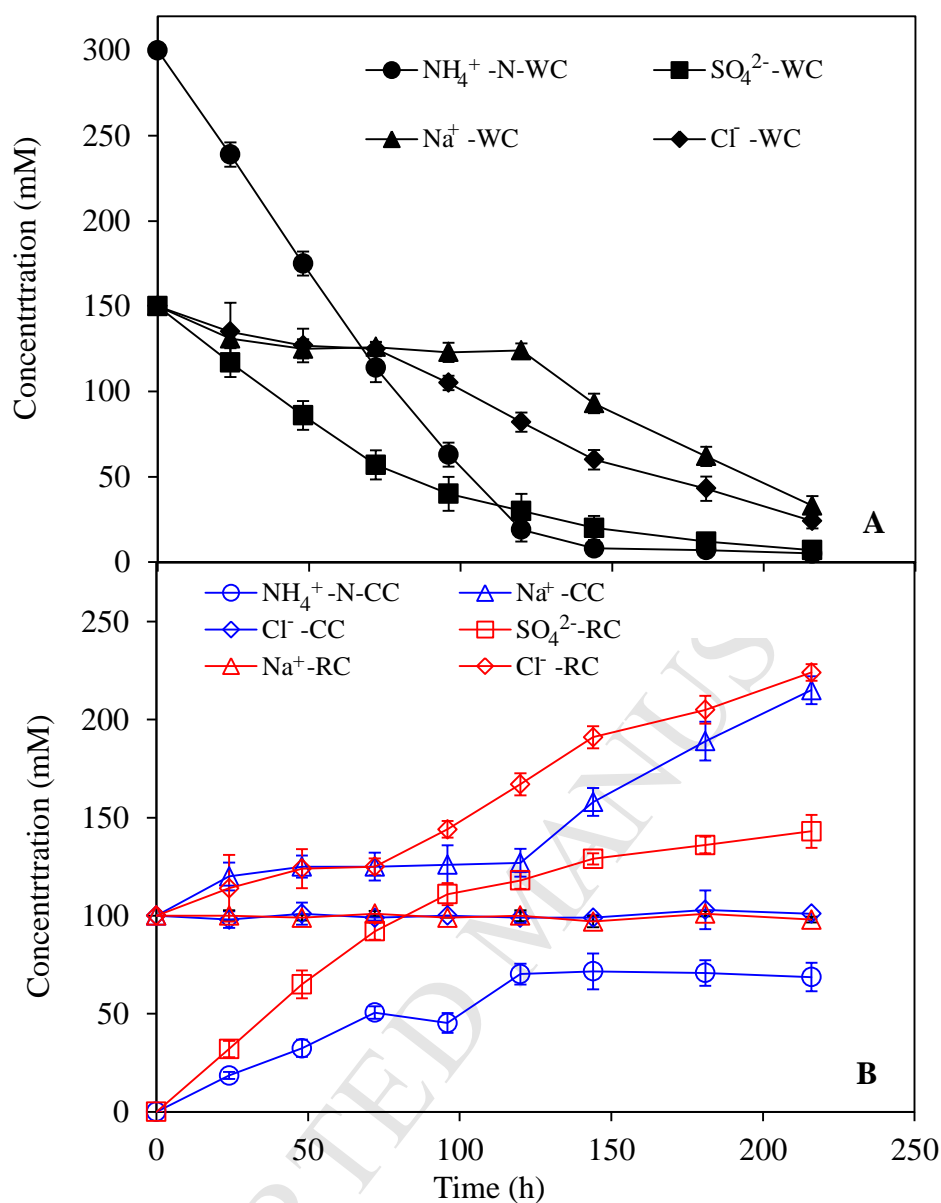
**Figure 2** Change of process performances with time. (A)  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  concentrations; (B) pH in different chambers; (C) Current and hydrogen production; (D) CE, CTE and  $\text{RH}_2$ . AC, anode chamber; RC, recovery chamber; WC, working chamber; CC, cathode chamber; OC, open circuit; R, gas recirculation in the cathode.



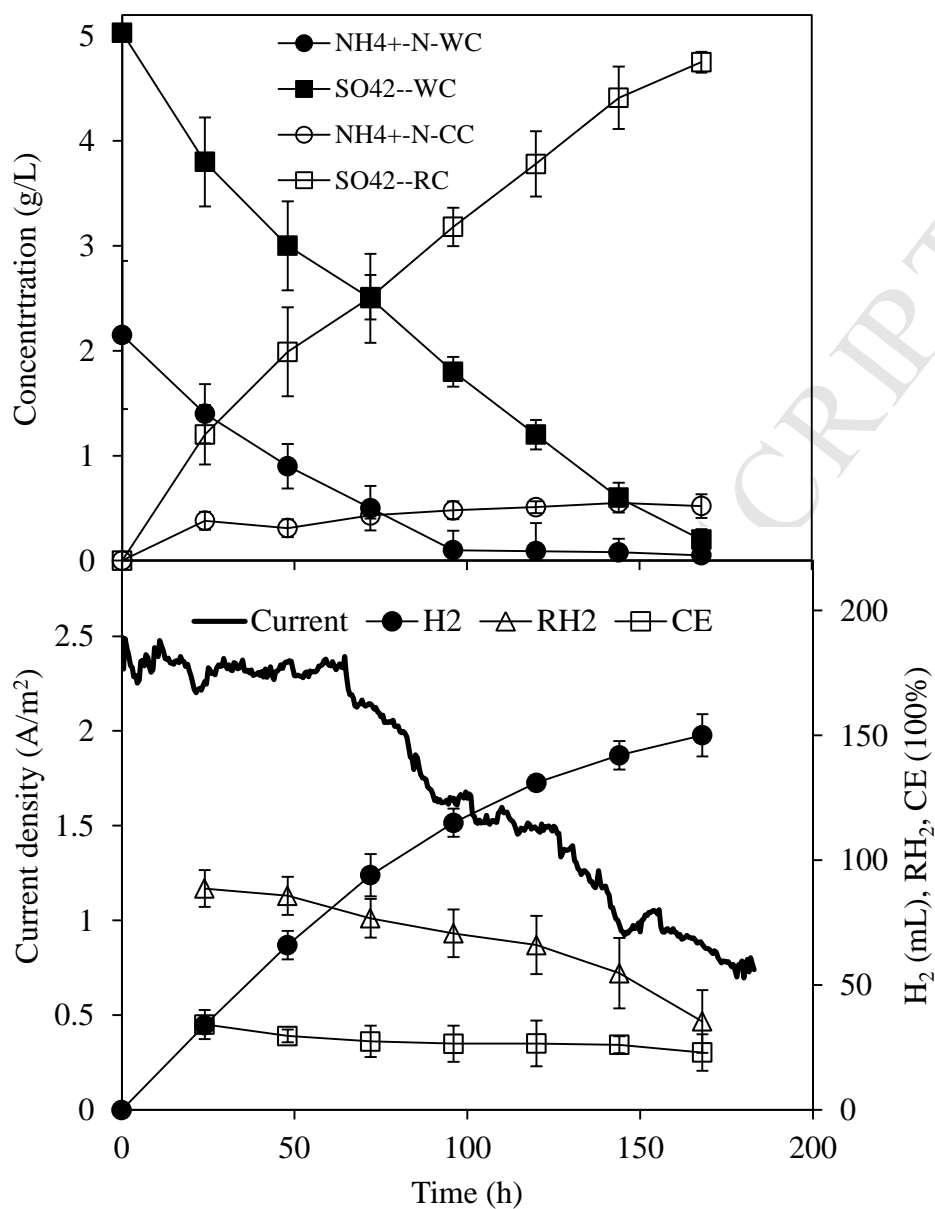
**Figure 3** Process performances at different applied voltages. The initial NH<sub>4</sub><sup>+</sup>-N and SO<sub>4</sub><sup>2-</sup> concentration in the WC was 4 and 13.7 g/L (mole ratio of 2:1).



**Figure 4** Process performances at different initial  $(\text{NH}_4)_2\text{SO}_4$  concentration. The applied voltage was 1.2 V.



**Figure 5** The change of main ions with time in the different chambers. (A) Working chamber; (B) Recovery chamber and cathode chamber. The applied voltage was 1.2 V. The initial concentration of NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> and Na<sup>+</sup> in the synthetic wastewater was 300, 150, 150 and 150 M, respectively.



**Figure 6** The system performance with cattle manure. The applied voltage was 1.2 V.



- Novel bipolar bioelectrodialysis for ammonia and sulfate recovery from wastes.
- Hydrogen production and wastewater treatment were accomplished along with recovery.
- Cathodic gas recirculation increased the nitrogen and sulfate fluxes by 2.3 times.
- The system was affected by the voltage, other ions,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  concentrations.
- Net energy was produced at all the applied voltages between 0.8 and 1.4 V.

**Supplementary data**

Page: 3; Figure: 1

**Recovery of ammonia and sulfate from waste streams and bioenergy production  
via bipolar bioelectrodialysis**

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## Calculations

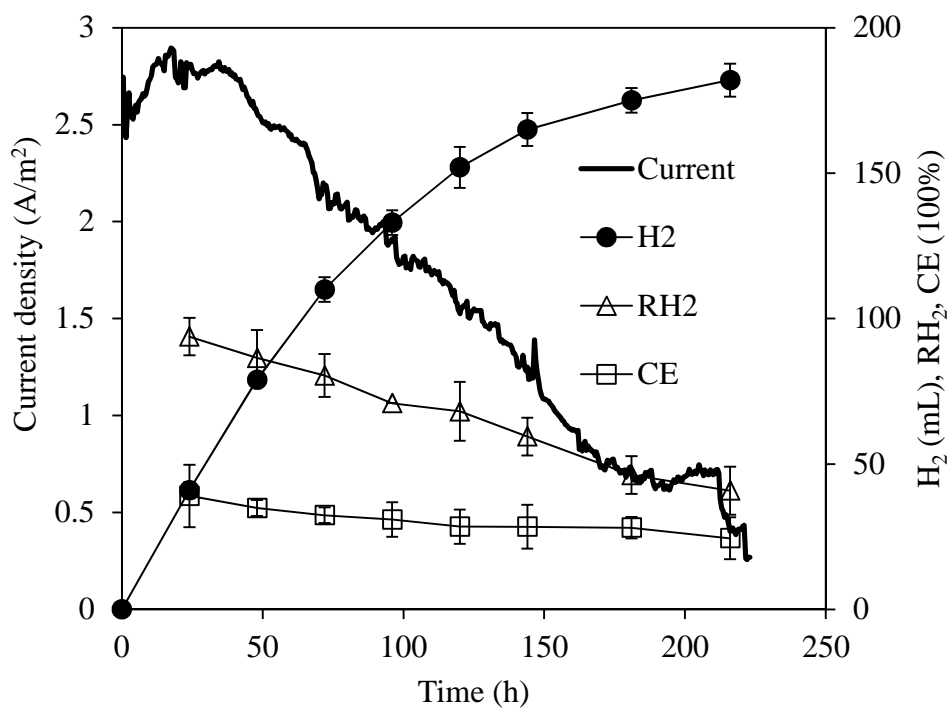
Power requirement by the pump was estimated as<sup>1</sup>:

$$P = \frac{Q\gamma E}{1000}$$

where P is power requirement (kW), Q is flow rate (m<sup>3</sup>/s),  $\gamma$  is 9800 N/m<sup>3</sup>, and E is the hydraulic pressure head (m). For the anolyte recirculation, Q was 8.3×10<sup>-7</sup> m<sup>3</sup>/s (50 mL/min). The measured hydraulic pressure head loss was 0.025 m. Therefore, the power required was 2.03×10<sup>-7</sup> kW for the anolyte recirculation pump. The energy required over the batch test (94 h) was 1.91×10<sup>-5</sup> kWh.

## Reference

1. Xiao, L.; Young, E. B.; Berges, J. A.; He, Z. *Environ. Sci. Technol.* **2012**, *46*, 11459-11466.



**Figure S1** Process performance with the appearance of other ions in the synthetic wastewater. The applied voltage is 1.2 V. The initial concentration of  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  in the synthetic wastewater was 300, 150, 150 and 150 M, respectively.