Supporting Information for:

Bipolar Membrane Electrodialysis for Ammonia Recovery from Synthetic Urine: Experiments, Modeling, and Performance Analysis

Submitted to

Environmental Science & Technology

August 2021

Yujiao Li[1 a,b,c], Ruoyu Wang[1 a], Shaoyuan Shi[b,c], Hongbin Cao[b,c], Ngai Yin Yip[d,e] and Shihong Lin* [a,f]

[a] Department of Civil and Environmental Engineering, Vanderbilt University, Nashville, TN 37235-1831, USA

[b] Beijing Engineering Research Center of Process Pollution Control, Institute of Process Engineering, Innovation Academy for Green Manufacture, Chinese Academy of Sciences, Beijing, 100190, China

[c] University of Chinese Academy of Sciences, Beijing, 100049, China

[d] Department of Earth and Environmental Engineering, Columbia University, New York, 10027-6623, United States

[e] Columbia Water Center, Columbia University, New York, 10027-6623, United States

[f] Department of Chemical and Bimolecular Engineering, Vanderbilt University, Nashville, TN 37235-1831, USA

[1] These authors contribute equally to the work.

*Email: shihing.lin@vanderbilt.edu

9 pages
4 figures

2 table

1 code

S1. Figures

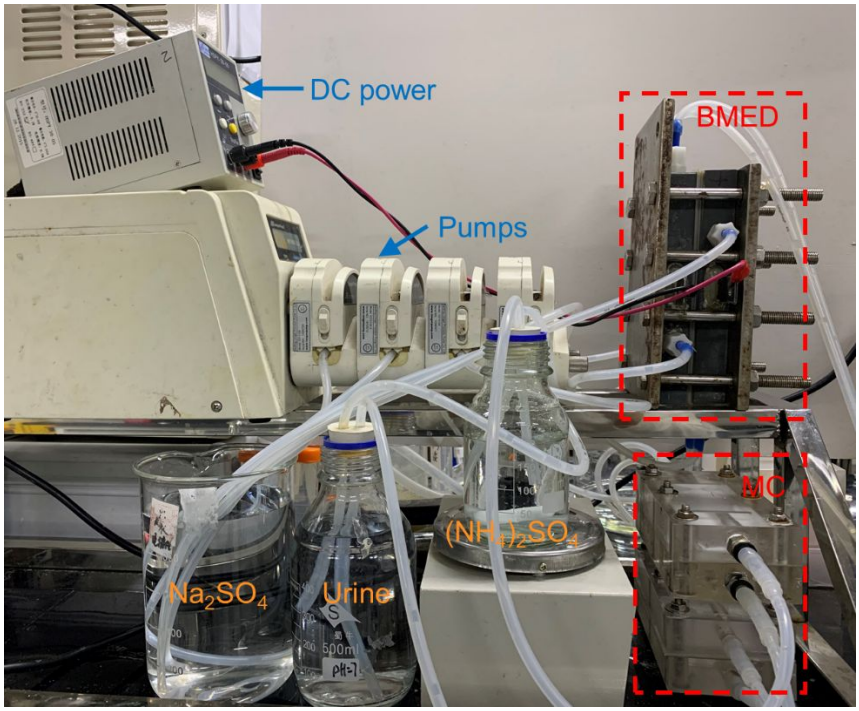

Figure S1. BMED-MC system setup in the lab.

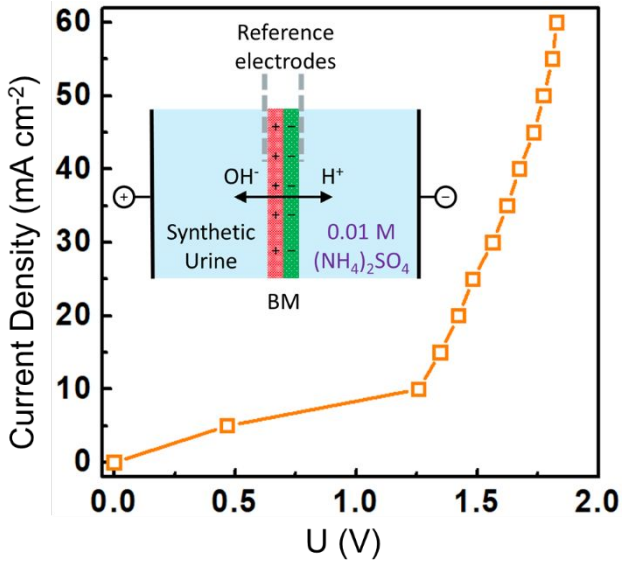

Figure S2. I-V curve of the used bipolar membrane (Neosepta BP-1, Tokuyama Co., Japan) under synthetic urine and 0.01 M $(NH_4)_2SO_4$ solution. The inset shows the electrochemical cell setup used to characterize

the I-V curve. The membrane area is 17.5 cm^2. The manufacturer reports a water splitting voltage of 1.2 V under 1 M NaOH and 1M HCl solution.

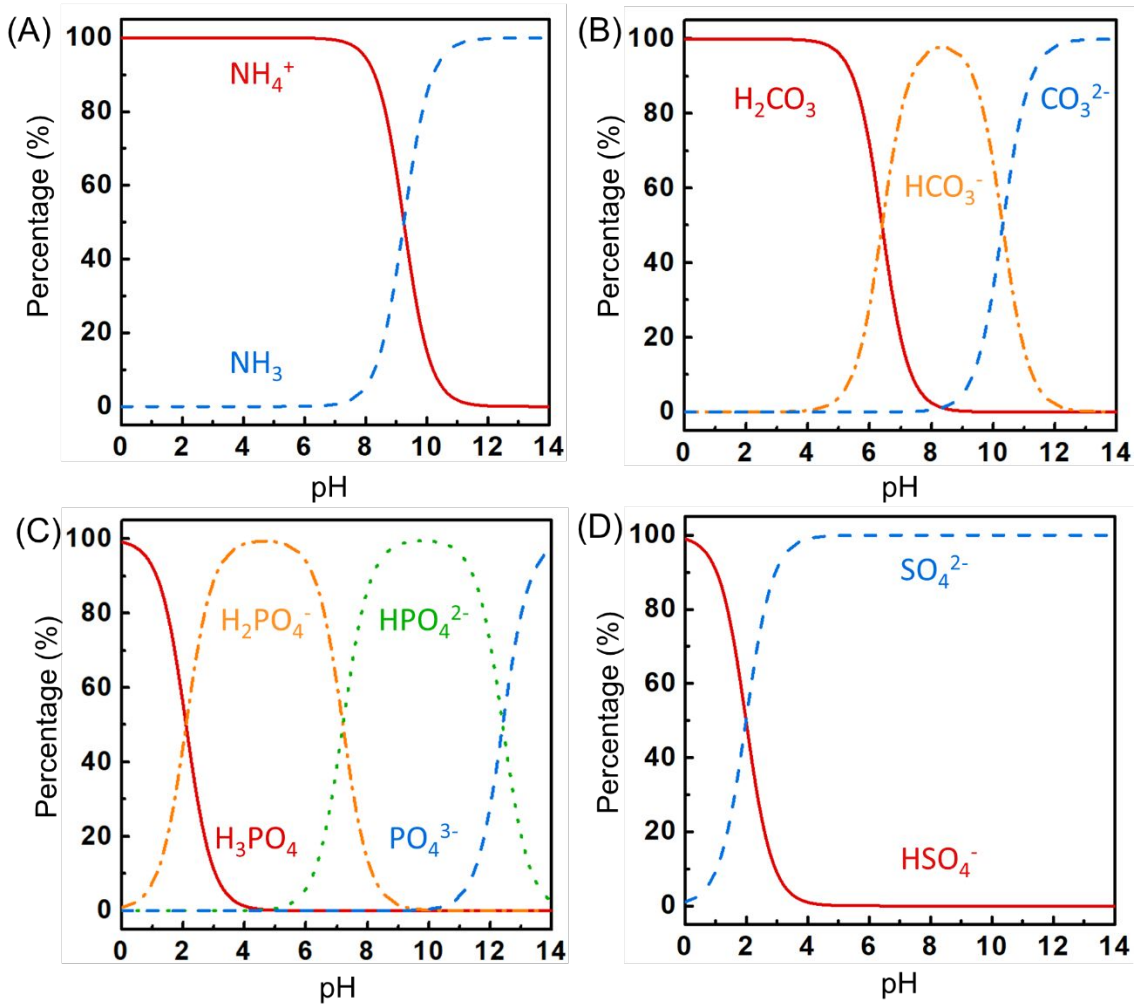

Figure S3. (A) Dissociation equilibrium between ammonia, NH_3, and ammonium, NH_4^+, as a function of pH. Ammonium has a pK_a of 9.25 at 25 ℃. (B) Dissociation equilibrium between carbonic acid, H_2CO_3, bicarbonate, HCO_3^-, and carbonate, CO_3^{2-}, as a function of pH. Carbonic acid and bicarbonate have a pK_a of 6.35 and 10.33 at 25 ℃, respectively. (C) Dissociation equilibrium between phosphoric acid, H_3PO_4, dihydrogen phosphate, $H_2PO_4^-$, monohydrogen phosphate, HPO_4^{2-}, and phosphate, PO_4^{3-}, as a function of pH. Phosphoric acid, dihydrogen phosphate and monohydrogen phosphate have a pK_a of 2.14, 7.20 and 12.37 at 25 ℃, respectively. (D) Dissociation equilibrium between sulfate, SO_4^{2-}, and bisulfate, HSO_4^-, as a function of pH. Bisulfate has a pK_a of 1.99 at 25 ℃.

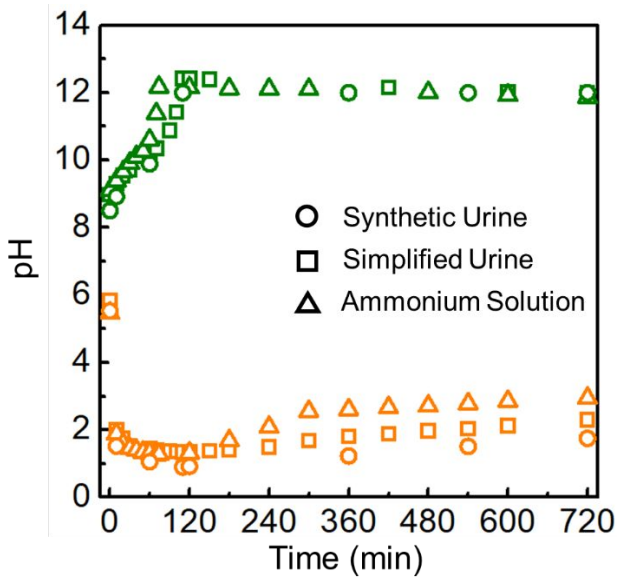

Figure S4. pH variation in the base (green dots) and acid (orange dots) compartments as a function of time over the duration of 12-hour operation. Square, triangle and round symbols represent simplified urine, simplified ammonium solution and synthetic urine experiments, respectively. A constant current density of 60 mA cm^{-2} was applied at the beginning and was cut off after base compartment pH exceeded 12.

S2. Table

Table S1. Initial compositions of the synthetic urine, simplified urine and ammonium solution

	Synthetic Urine	Simplified Urine	Ammonium Solution
pH	8.0~9.0	8.0~9.0	8.0~9.0
Total Ammonia Nitrogen (mg N L^{-1})	3772	3360	3360
Sodium (mg Na L^{-1})	1610	1610	0
Potassium (mg K L^{-1})	1447	1447	0
Chloride (mg Cl L^{-1})	3080	4142	1775
Total Sulfate (mg SO_4^{2-} L^{-1})	1680	1680	7200
Total Phosphate (mg P L^{-1})	169	0	0
Total Inorganic Carbon (mg C L^{-1})	1860	1860	0
COD (mg O_2 L^{-1})	3460 (as acetate)	0	0

Table S2. Key parameters in BMED-MC performance modelling

Parameter	Value	Parameter	Value

k_H (Pa M^{-1})	1631.3	R_{AEM} (Ω cm^2)	3.0
L_p (mol $m^{-2}h^{-1}Pa^{-1}$)	0.013	R_{CEM} (Ω cm^2)	3.2
h (L A^{-1} h^{-1})	0.005	R_{BM} (Ω cm^2)	16.0

S3. Matlab Code

```
% This code is developed for modeling BMED-MC batch mode experiment with
synthetic urine

% Chemical constants
F = 96487; % C/mol, Faradaic constant
Vt = 0.0256; % V, thermal voltage
pKa = 9.25; % dissociation constant of NH4+
kH = 1631.3; % Pa/M, Henry constant of NH3
D_salt = [1.33, 1.07]*1e-9; % m2/s, diffusion coefficient of Na+, SO42-, in salt solution
D_base = [1.98, 0.955, 1.18, 0.612, 0.69, 0.846, 1.96, 1.33, 2.03, 1.07, 1.089, 9.31,
5.27]*1e-9; % m2/s, diffusion coefficient of ions in base stream
D_acid = [1.98, 1.07, 1.39, 9.31, 5.27]*1e-9; % m2/s, diffusion coefficient of ions in acid
stream
z_salt = [1,-2]; % charge, Na+, SO42-
z_base = [1, -2, -1, -3, -2, -1, 1, 1,-1,-2, -1,1,-1]; % charge, NH4+, CO32-, HCO3-, TP,
PO43-, HPO32-, H2PO4-, K+, Na+, Cl-, SO42-, Ac-, H+, OH-
z_acid = [1,-2,-1, 1,-1]; % charge, NH4+, SO42-, HSO4-, H+, OH-

% System constants
Lp = 0.013/3600; % mol/m2/s/Pa, vapor permeability in MC
A_ED = 50/1e4; % m2, area of BMED
A_MC = 60/1e4; % m2, area of MC
R_AEM = 3.0; % ohm.cm2, resistance of AEM
R_CEM = 3.2; % ohm.cm2, resistance of CEM
```

```
R_BM = 16; % ohm.cm^2, resistance of BM
L1 = 0.10/100; % m, thickness of acid base chamber
L2 = 0.6/100; % m, thickness of salt chamber
V_salt = 1; % L volume of electrode loop
V_base = 0.5; % L, volume of base loop
V_acid = 0.2; % L, volume of acid loop

% Initial conditions
I1 = 100; % A/m2, current density of phase 1 (before cut-off)
I2 = 0; % A/m2, current density of phase 2 (after cut-off)
c_salt = 0.4; % mol/L concentration of Na2SO4 in electrode solution
c_base = [0.26945, 0.04, 0.22945, 0.155, 0, 0.155, 0.00545, 0, 0.00545, 0, 0.037, 0.07,
0.087, 0.0175, 0.054, 8, 0];
% mol/L, TAN, NH3, NH4+, TC, CO3 2-, HCO3-, TP, PO4 3-, HPO3 2-, H2PO4-, K+, Na+, Cl-,
SO4 2-, Ac-, pH, pOH
c_base = calB(c_base, pKa); % dissociation equilibrium calculation of base
c_acid = [0.02, 0, 0.02, 0.01, 0.01, 0, 7, 0]; % mol/L, TAN, NH3, NH4+, TSO4, SO4 2-,
HSO4-, pH, pOH
c_acid = calA(c_acid, pKa); % dissociation equilibrium calculation of acid

% Iteration over time
dt = 10; % s, time step size
t_break = 420*60; % s, BMED duration
t_end = 420*60; % s, overall duration
t = 0; % initialize t
n = 0; % step count

% Create list to put values
J_list = zeros(1,t_end/dt);
pf_list = zeros(1,t_end/dt);
pd_list = zeros(1,t_end/dt);
```

```
pH_base = zeros(1,t_end/dt);
pH_acid = zeros(1,t_end/dt);
salt_list = zeros(1,t_end/dt);
TAN_base = zeros(1,t_end/dt);
TAN_acid = zeros(1,t_end/dt);
V_list = zeros(1,t_end/dt);
amm_base = zeros(1,t_end/dt);
amm_acid = zeros(1,t_end/dt);

% Main loop before cut-off
while t < t_break
    n = n + 1;
    pf = kH*c_base(2); % Pa, vapor pressure of feed side
    pd = kH*c_acid(2); % Pa, vapor pressure of draw side
    J = Lp*(pf-pd); % mol/m2/s, ammonia flux in MC

    % Voltages
    U_salt = I1*L2/F*Vt/sum(abs(z_salt).*D_salt.*[2*c_salt, c_salt]*1e3); % V, voltage
drop of the electrode solution
    ion_base = [c_base(3), c_base(5:6), c_base(8:15), 10.^(-c_base(16:17))]*1e3; %
mol/m3, NH4+, CO32-, HCO3-, TP, PO43-, HPO32-, H2PO4-, K+, Na+, Cl-, SO42-, Ac-, H+, OH-
    U_base = I1*L1/F*Vt/sum(abs(z_base).*D_base.*ion_base); % V, voltage drop of
base
    ion_acid = [c_acid(3), c_acid(5:6), 10.^(-c_acid(7:8))]*1e3; % mol/m3, NH4+, SO42-, H+,
OH-
    U_acid = I1*L1/F*Vt/sum(abs(z_acid).*D_acid.*ion_acid); % V, voltage drop of acid
    V_D = 0.0591*(c_base(16)-c_acid(7)); % V, Donnan potential drop across BM
    V_ele = 2.4613 + 1.8339*asinh(I1/1e4/2/0.0073); % V, electrode voltage
    V_mem = I1/1e4*(R_AEM + R_CEM + R_BM); % V, poential drop due to membranes
    V_cell = U_salt*2 + U_base + U_acid + V_mem + V_D + V_ele; % V, cell voltage

```

```
164     % Record variable values for plot
165     pf_list(n) = pf;
166     pd_list(n) = pd;
167     J_list(n) = J;
168     pH_base(n) = c_base(16);
169     pH_acid(n) = c_acid(7);
170     salt_list(n) = c_salt;
171     TAN_base(n) = c_base(1);
172     TAN_acid(n) = c_acid(1);
173     V_list(n) = V_cell;
174     amm_base(n) = c_base(2)/c_base(1);
175     amm_acid(n) = c_acid(2)/c_acid(1);
176
177     n_f = J*dt*A_MC; % mol, ammonia transferred in dt
178     c_base(1) = c_base(1) - n_f/V_base; % update TAN in base
179     c_acid(1) = c_acid(1) + n_f/V_acid; % update TAN in acid
180     r_lk = 0.005/3600; % L/A/s, leakage rate of IEMs
181     eta = 1 - r_lk*10^-c_acid(7)*I1*A_ED/(I1*A_ED/F); % current efficiency
182     c_base(12) = c_base(12) + eta*I1*A_ED/F*dt/V_base; % Na+ enters into base
183     c_acid(4) = c_acid(4) + eta*I1*A_ED/F/2*dt/V_acid; % SO4 2- enters into acid
184     c_salt = c_salt - eta*I1*A_ED/F/2*dt/V_salt; % electrolyte concentration reduces
185     c_base = calB(c_base, pKa); % dissociation equilibrium calculation of base
186     c_acid = calA(c_acid, pKa); % dissociation equilibrium calculation of acid
187
188     t = n * dt; % update t
189 end
190
191 % Main loop after cut-off
192 while t < t_end && t >= t_break
193     n = n + 1;
194     pf = kH*c_base(2); % Pa, vapor pressure of feed side
```

```
195     pd = kH*c_acid(2); % Pa, vapor pressure of draw side
196     J = Lp*(pf-pd); % mol/m2/s, ammonia flux in MC
197
198     % Voltages
199     V_cell = 0;
200
201     % Record variable values for plot
202     pf_list(n) = pf;
203     pd_list(n) = pd;
204     J_list(n) = J;
205     pH_base(n) = c_base(16);
206     pH_acid(n) = c_acid(7);
207     salt_list(n) = c_salt;
208     TAN_base(n) = c_base(1);
209     TAN_acid(n) = c_acid(1);
210     V_list(n) = V_cell;
211     amm_base(n) = c_base(2)/c_base(1);
212     amm_acid(n) = c_acid(2)/c_acid(1);
213
214     n_f = J*dt*A_MC; % mol, ammonia transferred in dt
215     c_base(1) = c_base(1) - n_f/V_base; % update TAN in base
216     c_acid(1) = c_acid(1) + n_f/V_acid; % update TAN in acid
217     c_base(12) = c_base(12) + I2*A_ED/F*dt/V_base; % Na+ enters into base
218     c_acid(4) = c_acid(4) + I2*A_ED/F/2*dt/V_acid; % SO4 2- enters into acid
219     c_salt = c_salt - I2*A_ED/F/2*dt/V_salt; % electrolyte concentration reduces
220     c_base = calB06(c_base, pKa); % dissociation equilibrium calculation of base
221     c_acid = calA(c_acid, pKa); % dissociation equilibrium calculation of acid
222
223     t = n * dt; % update t
224 end
225
```

```
% Define a function to calculate dissociation equilibrium in acid stream

% c is [TAN, NH3, NH4+, TSO4, SO4 2-, HSO4-, pH, pOH]
function y=calA(c, pk)
    Fun2 = @(x) [pk+x(1)-x(2); % dissociation equilibrium
                 1.99+x(3)-x(2); % HSO4
                c(1)/(10^x(1)+1)-2*(c(4)-c(4)/(10^x(3)+1))-c(4)/(10^x(3)+1)+10^(-x(2))-
10^(x(2)-14)]; % electroneutrality
    x0 = [log10((c(2)+1e-10)/c(3)); c(7); log10(c(5)/(c(6)+1e-10))]; % initial guess
    options  = optimoptions(@fsolve, 'MaxFunEvals', 5000, 'Maxiter', 1000, 'Display',
'off');
    [x,fval] = fsolve(Fun2,x0,options);

    c(2) = c(1)-c(1)/(10^x(1)+1);
    c(3) = c(1)/(10^x(1)+1);
    c(5) = c(4)-c(4)/(10^x(3)+1);
    c(6) = c(4)/(10^x(3)+1);
    c(7) = x(2);
    c(8) = 14-x(2);
    y = c;
end

% Define a function to calculate dissociation equilibrium in base stream

% c is [TAN, NH3, NH4+, TC, CO3 2-, HCO3-, TP, PO4 3-, HPO3 2-, H2PO4-, K+, Na+, Cl-,
SO4 2-, Ac-, pH, pOH]

function y=calB(c, pk)
    Fun1 = @(x) [pk+x(1)-x(5); % dissociation equilibrium of NH4+
                 10.33+x(2)-x(5); % dissociation equilibrium of HCO3-
                 7.2+x(3)-x(5); % dissociation equilibrium of H2PO4-
```

```
257                 12.37+x(4)-x(5); % dissociation equilibrium of HPO4^2-
258
259                 c(1)/(10^x(1)+1)-2*(c(4)-c(4)/(10^x(2)+1))-c(4)/(10^x(2)+1)-
260 3*(c(7)/(10^x(3)+10^(x(3)+x(4))+1)*10^(x(3)+x(4)))-
261 2*(c(7)/(10^x(3)+10^(x(3)+x(4))+1)*10^x(3))-
262 (c(7)/(10^x(3)+10^(x(3)+x(4))+1))+c(11)+c(12)-c(13)-2*c(14)-c(15)+10^(-x(5))-10^(x(5)-
263 14)]; % electroneutrality
264
265     x0 = [log10((c(2)+1e-10)/c(3)); log10((c(5)+1e-10)/c(6)); log10((c(8)+1e-10)/c(9));
266 log10(c(9)/(c(10)+1e-10)); c(16)]; % initial guess
267     options  = optimoptions(@fsolve, 'MaxFunEvals', 5000, 'Maxiter', 1000, 'Display',
268 'off');
269     [x,fval] = fsolve(Fun1,x0,options);
270
271     % NH3/NH4+
272     c(2) = c(1)-c(1)/(10^x(1)+1);
273     c(3) = c(1)/(10^x(1)+1);
274     % CO3^2-/HCO3-
275     c(5) = c(4)-c(4)/(10^x(2)+1);
276     c(6) = c(4)/(10^x(2)+1);
277     % PO4^3-/HPO4^2-/H2PO4-
278     c(10) = c(7)/(10^x(3)+10^(x(3)+x(4))+1);
279     c(9) = c(10)*10^x(3);
280     c(8) = c(9)*10^x(4);
281     % pH/pOH
282     c(16) = x(5);
283     c(17) = 14-x(5);
284     y = c;
285 end
286
```