Appendix 1 – Background Information Ammonia Recovery

Introduction:

Our wastewater' has become a source of nutrients and energy towards closing the loop for a circular economy. Amongst all the nutrients present in wastewater, nitrogen plays a vital role in plant growth. (FAO, 2019) Nitrogen (N2) amounts 78% of all gasses present in the atmosphere and it can be artificially fixated by the Haber-Bosch process into reactive nitrogen forms to be used as fertilizer (Figure 1). (Maurer et al., 2003) Two percent of the energy consumed worldwide is used uniquely to produced fertilizers by the Haber-Bosch process.

After consumption, significant amounts of nitrogen end up in our wastewater. It is important to remove this from our wastewater, otherwise an excess of nitrogen will end up in our surface and ground water. This can cause environmental effects, like eutrophication.

In order to decrease its environmental effect, nitrogen is removed via nitrification-denitrification or Anammox at wastewater treatment plants (WWTP). (Maurer et al., 2003; Sengupta et al., 2015) These aforementioned nitrogen removal processes have high energy consumption and contribute to N_2O emissions to the atmosphere.

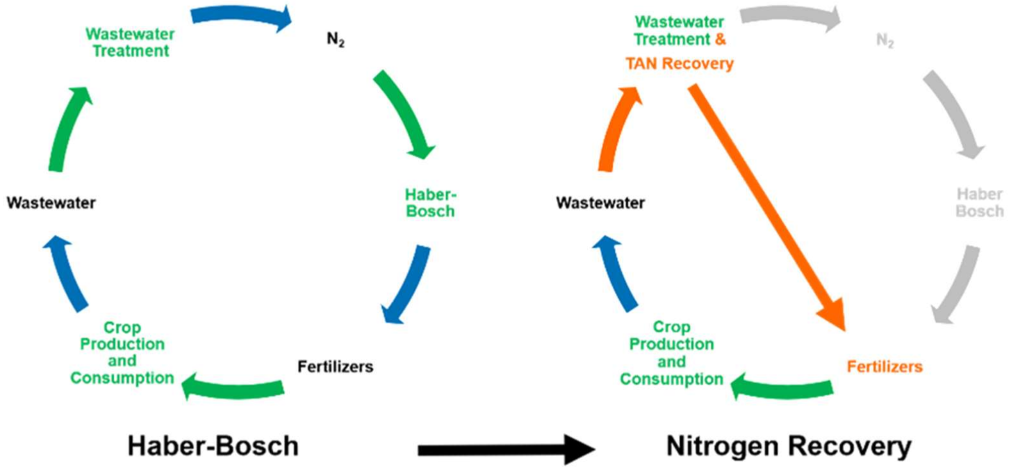

Figure 1. Short circuiting the Nitrogen Cycle using ES

In order to optimize the nitrogen removal process, so less energy is consumed and less N_2O is emitted, we research at Wetsus an Electrochemical System (ES) for the removal. This could be an option to concentrate the nitrogen in solution (ammonium/ammonia), allowing an efficiently extraction and recovery (Figure 2). (Kuntke et al., 2018; Rodrigues et al., 2020)

In the ES, Cation Exchange Membranes (CEM) and Anion Exchange Membranes (AEM) are stacked. These membranes, as the names say, only let certain ions pass through the membrane. In this way, specific ions can be removed electrochemically from one solution and concentrated in the other.

Appendix 1 – Background Information **Ammonia Recovery**

How it works

In this toolkit the system in figure 2 is at work.

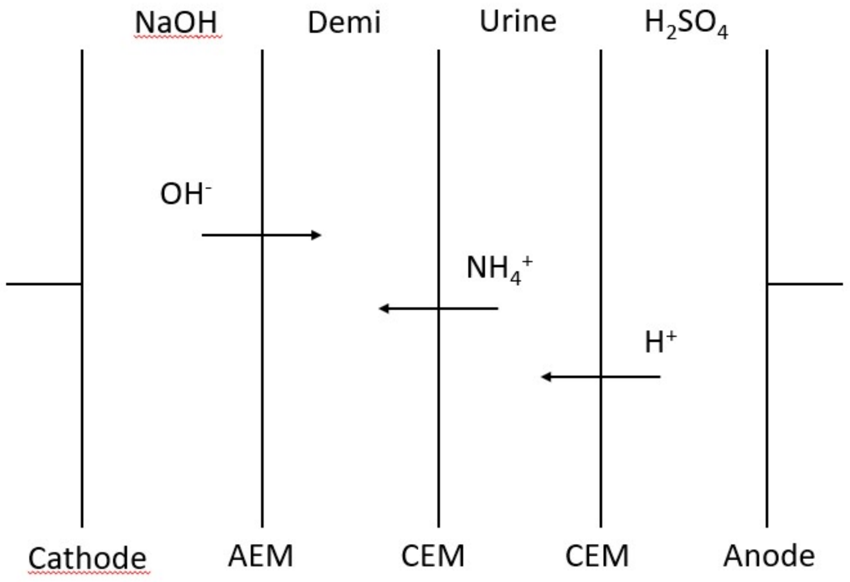

Figure 2. Schematic view of the mechanism of the ES

The supply of current drives ammonium and other positive ions (H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}) through a cation exchange membrane towards the cathode (Figure 2). The ammonium concentrates in the demiwater stream, together with OH^-. The pH increases and so the ammonium is converted to ammonia NH_3.

In an ES, all the reactions are uniquely electro-chemical, meaning an easily operation of the system. Additionally, ESs can support higher current densities then bio-electrochemical systems and work with streams at an extreme pH. An ESs including compartments (anode, feed, concentrate and cathode) can be used for ammonia recovery. At the anode and cathode occur water splitting forming protons and hydroxide, respectively. The electrons are moving from the anode through an external circuit towards the cathode, where the reduction of water occurs. The reduction reaction produces hydroxide ions and hydrogen. Since the feed is acidified by the protons formed at the anode, the oxidized NH_4^+ moves through the CEM to the concentrate. Ammonium and other cations in solution are therefore separated from undesired species in solution such as anions (Cl^-) or micropollutants. If a pure ammonium is fertilizer is required, the catholyte stream can be supplied to a gas permeable membrane (TMCS, stripping unit), where the ammonia can be recovered. This is possible since ammonia is an amphoteric specie, unlike sodium or potassium. It can be found in solution as soluble gas (NH_3) or protonated (NH_4^+), depending on the pH. (Kuntke et al., 2017; Rodríguez Arredondo et al., 2017)

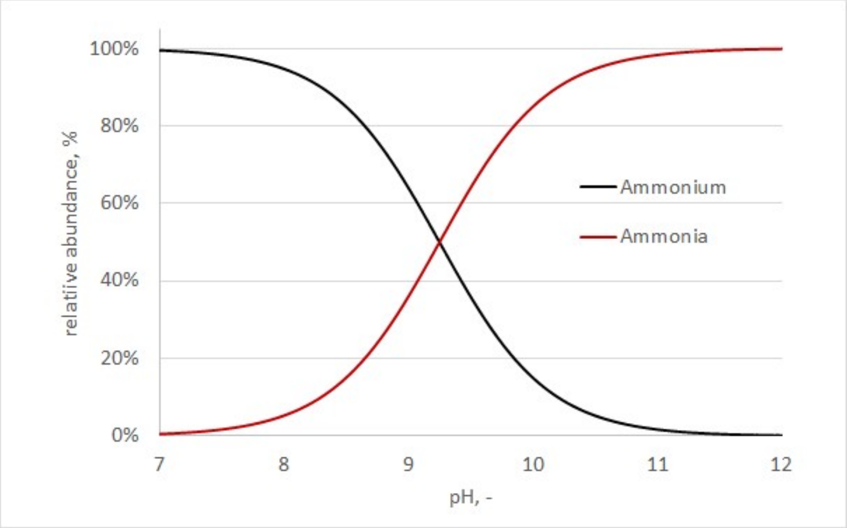

Figure 3. Relative abundance of NH_3 and NH_4^+ in solution

Objectives

The main objective of the proposed project is to recover/concentrate the nitrogen in solution electrochemically from different wastewaters.

Lab procedure:

See Student Card Model 1 for how to build the electrochemical cell and prepare solutions

See Student Card Model 2 for performing the experiment and analysing the results via titration.

Calculations

a. Load Ratio (L_N) is the ratio of applied current density to the nitrogen loading. The Load Ratio determines to a large extent the performance of the ES system (removal and energy consumption). (Rodríguez Arredondo et al., 2017) A Load Ratio of one means the amount of current applied to the system is equal to the total charge supplied as TAN. When $L_N<1$ more TAN is present than the electrons supplied to the cell, conversely when $L_N>1$ the system is supplied with an excess of current. Load Ratio can be determined using the following formula:

$$L_N = \frac{j \times A_m}{C_{TAN,influent} \times Q_{influent} \times F}$$

Where, j is the current density (A m^{-2}), $C_{influent}$ is the nitrogen concentration (mol L^{-1}) in the influent, V is the volume (L), F is the Faraday constant (C mol^{-1}) and A_m is the surface area of CEM (m^2).

b. The students can further calculate the operation time. What happens with time (t0, t1 and t2 – observe if the system operates at different rates and why)

Safety:

1. General lab safety rules
2. Gloves for the wastewater and acid
3. Make changes in the system when the current is off

Measurements:

1. pH of all solutions
2. NH_3 in solution by titration (indicate the relation between ammonia and ammonium to determine the total nitrogen in solution)
3. Cell voltage and Cell current
4. Volumes of all solutions at t0 and tf (ideally constant)

Questions:

1. What are the consequences of discharging wastewater with high nitrogen content in the environment?
2. How much nitrogen (NH_4^+ and NH_3) was removed from the solution (g)? Use the results from the titration method combined with the Table in Supplementary information.
3. How much energy was consumed to recover that nitrogen (kwh/gN)? Use the equation below.

$$Energy\ consumption = \frac{E_{cell}\, I_{cell} t}{(C_{inf} - C_{eff})V}$$

Where E_{cell} is cell voltage (V), I_{cell} is applied current (A), t is the number of hours of the experiment (h), C_{inf} is the influent ammonium concentration ($g_N\ L^{-1}$), Q_{inf} is the influent flow rate ($L\ d^{-1}$), C_{eff} is the effluent ammonium concentration ($g_N\ L^{-1}$) and Q_{eff} is the effluent flow rate ($L\ d^{-1}$).

4. Give 3 benefits of recovering the nutrients from wastewater instead of applying directly in the soil as fertilizer?
5. Conclude about the use of wastewater with different salinity, and/or ammonium concentration. Discuss the effect of operating at higher or lower current.

References

FAO, 2019. World fertilizer trends and outlook to 2022, Society.

Kuntke, P., Rodríguez Arredondo, M., Widyakristi, L., ter Heijne, A., Sleutels, T.H.J.A., Hamelers, H.V.M., Buisman, C.J.N., 2017. Hydrogen Gas Recycling for Energy Efficient Ammonia Recovery in Electrochemical Systems. Environ. Sci. Technol. 51, 3110–3116. https://doi.org/10.1021/acs.est.6b06097

Appendix 1 – Background Information Ammonia Recovery

Kuntke, P., Sleutels, T.H.J.A., Rodríguez Arredondo, M., Georg, S., Barbosa, S.G., ter Heijne, A., Hamelers, H.V.M., Buisman, C.J.N., 2018. (Bio)electrochemical ammonia recovery: progress and perspectives. Appl. Microbiol. Biotechnol. 102, 3865–3878. https://doi.org/10.1007/s00253-018-8888-6

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/10.1017/S000748530002229X

Rodrigues, M., De Mattos, T.T., Sleutels, T., Ter Heijne, A., Hamelers, H.V.M., Buisman, C.J.N., Kuntke, P., 2020. Minimal Bipolar Membrane Cell Configuration for Scaling up Ammonium Recovery. ACS Sustain. Chem. Eng. 8, 17359–17367. https://doi.org/10.1021/acssuschemeng.0c05043

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

Sengupta, S., Nawaz, T., Beaudry, J., 2015. Nitrogen and Phosphorus Recovery from Wastewater. Curr. Pollut. Reports 1, 155–166. https://doi.org/10.1007/s40726-015-0013-1

Supplementary information

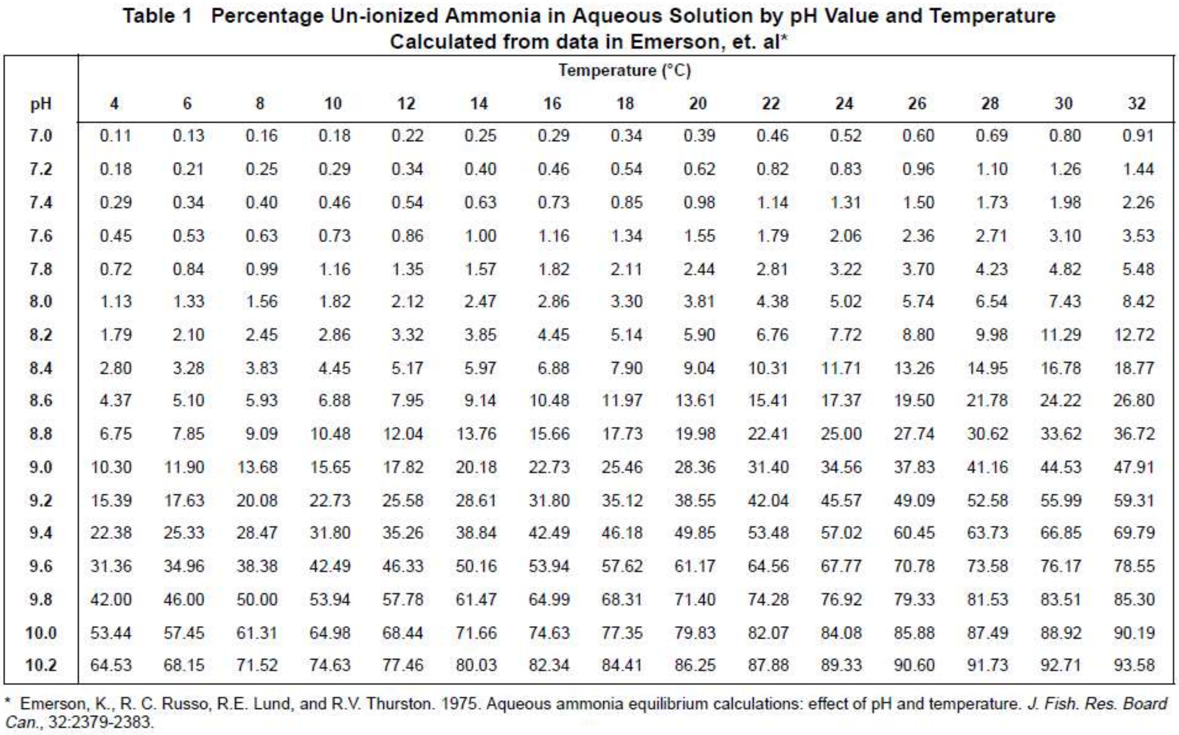

Table 1 Percentage Un-ionized Ammonia in Aqueous Solution by pH Value and Temperature Calculated from data in Emerson, et. al*

pH	Temperature (°C)														
	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32
7.0	0.11	0.13	0.16	0.18	0.22	0.25	0.29	0.34	0.39	0.46	0.52	0.60	0.69	0.80	0.91
7.2	0.18	0.21	0.25	0.29	0.34	0.40	0.46	0.54	0.62	0.82	0.83	0.96	1.10	1.26	1.44
7.4	0.29	0.34	0.40	0.46	0.54	0.63	0.73	0.85	0.98	1.14	1.31	1.50	1.73	1.98	2.26
7.6	0.45	0.53	0.63	0.73	0.86	1.00	1.16	1.34	1.55	1.79	2.06	2.36	2.71	3.10	3.53
7.8	0.72	0.84	0.99	1.16	1.35	1.57	1.82	2.11	2.44	2.81	3.22	3.70	4.23	4.82	5.48
8.0	1.13	1.33	1.56	1.82	2.12	2.47	2.86	3.30	3.81	4.38	5.02	5.74	6.54	7.43	8.42
8.2	1.79	2.10	2.45	2.86	3.32	3.85	4.45	5.14	5.90	6.76	7.72	8.80	9.98	11.29	12.72
8.4	2.80	3.28	3.83	4.45	5.17	5.97	6.88	7.90	9.04	10.31	11.71	13.26	14.95	16.78	18.77
8.6	4.37	5.10	5.93	6.88	7.95	9.14	10.48	11.97	13.61	15.41	17.37	19.50	21.78	24.22	26.80
8.8	6.75	7.85	9.09	10.48	12.04	13.76	15.66	17.73	19.98	22.41	25.00	27.74	30.62	33.62	36.72
9.0	10.30	11.90	13.68	15.65	17.82	20.18	22.73	25.46	28.36	31.40	34.56	37.83	41.16	44.53	47.91
9.2	15.39	17.63	20.08	22.73	25.58	28.61	31.80	35.12	38.55	42.04	45.57	49.09	52.58	55.99	59.31
9.4	22.38	25.33	28.47	31.80	35.26	38.84	42.49	46.18	49.85	53.48	57.02	60.45	63.73	66.85	69.79
9.6	31.36	34.96	38.38	42.49	46.33	50.16	53.94	57.62	61.17	64.56	67.77	70.78	73.58	76.17	78.55
9.8	42.00	46.00	50.00	53.94	57.78	61.47	64.99	68.31	71.40	74.28	76.92	79.33	81.53	83.51	85.30
10.0	53.44	57.45	61.31	64.98	68.44	71.66	74.63	77.35	79.83	82.07	84.08	85.88	87.49	88.92	90.19
10.2	64.53	68.15	71.52	74.63	77.46	80.03	82.34	84.41	86.25	87.88	89.33	90.60	91.73	92.71	93.58

* Emerson, K., R. C. Russo, R.E. Lund, and R.V. Thurston. 1975. Aqueous ammonia equilibrium calculations: effect of pH and temperature. *J. Fish. Res. Board Can.*, 32:2379-2383.