

# Retrieval of Ammonia as Energy Source from Municipal Wastes by Electrochemical Deionizing and Ingathering Method

Xiao Feng<sup>1</sup>, Xu Yang<sup>2</sup>, Binbin Yu<sup>3</sup>, Zucheng Wu<sup>2\*</sup>, Wen Liao<sup>2</sup>, Qiong Ren<sup>2</sup>

1 School of Environmental and Municipal Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450046, China

2 Department of Environmental Engineering, Laboratory for Electrochemistry & Energy Storage, Zhejiang University, Hangzhou 310058, China

3 College of Pharmaceutical and Chemical Engineering, Taizhou University, Taizhou 318000, Zhejiang, China

\*Corresponding Author: wuzc@zju.edu.cn

## ABSTRACT

Ammonia as energy carrier has been recognized and is a hot research topic in recent years.  $\text{NH}_3\text{-N}$  often contaminated in municipal wastewater and caused eutrophication of water body. The use of an electrochemical deionizing and ingathering (EDI) method exhibits the ability to segregate targeted ions absorbed in a dilute solution. Through multistage experiment, we demonstrated a concentration of  $\text{NH}_4^+$  of 836.3 mg/L and 1734.8 mg/L, 1032 and 953 times of magnitude respectively in the multistage process. Besides, we analyzed the possibility of separation of these ions by increasing applied voltage. This technology provides a feasibility of retrieving ammonia from a very low concentration in wastewater to be as energy resources.

**Keywords:** electrochemical deionizing and ingathering, ammonia ions, segregation

## 1. INTRODUCTION

Research topics about nitrogen removal from water body has been the top priority to scientists in this field [1, 2]. Ammonia is the main contaminant in domestic wastewater and since it is toxic to organism, it is quite difficult to treat this type of wastewater. One process to remove  $\text{NH}_3\text{-N}$  is nitrification and its denitrification technology, in which parts of  $\text{NH}_3\text{-N}$  was biologically oxidized to nitrite or nitrate and then reacted with  $\text{NH}_3\text{-N}$

to form  $\text{N}_2$  [3]. However, this biological denitrification process needs a restrict condition, i.e. the concentration of  $\text{NH}_3\text{-N}$ /organic carbons should be kept at ratio of around 1/30. That means it needs additional chemicals and energy consumptive. In addition, the removal of  $\text{NH}_3\text{-N}$  by metal precipitation can also lead to secondary pollution, which is not a sustainable way [4]. More advanced methods like electrodialysis (ED) technology and ion exchange (IE) technology can achieve the extraction of ammonium ions to purify water, which has a prospect for application. However, the high costs obstruct the development of both techniques due to the energy consumption of ED [5] and resin regeneration of IE [6]. Another alternative technology is electrodeionization method, which is developed on the basis of the advantages of ED and IE, has a trustworthy reputation in the production of ultra-pure water [7]. It is superior to many methods, due to the electric-regeneration of resin without chemicals and the ability to remove metal ions [8-10].

Previous works of the electrodeionization have been focused on the removal of salts to purify water instead of retrieval of those salts as resources. All the researches provide evidence for the ability of this technology to retrieve useful ions and purify the water simultaneously [11], thus this technology can be considered as a promising approach for the retrieval of ammonia in domestic and municipal wastes especially a landfill leachate containing higher concentration of ammonia [12-15]. However, there still are some

imperfections according to previous studies, e.g. the concentration of NH<sub>3</sub>-N in the concentrated solution was only 80~100 mg/L, not high enough to retrieve them.

Herein, we made attempt to solve the problems mentioned above by employing the electrochemical deionizing and ingathering (EDI) method. First, we ameliorated the conventional EDI set-up, which had been in application of the metal ions recovery [16, 17] with no precipitation on the surface of the ion exchange membrane. Second, in order to increase the enrichment factor, and to improve the utilization of electrical energy, a multi-stage EDI process was adopted in this paper. After enrichment of 3-stages EDI process, a 3-orders magnitude of NH<sub>3</sub>-N from mg/L ingathered to be as g/L has been achieved to identify the possibility and applicability of ammonia retrieval. As it noticed that ammonia as energy and hydrogen carrier (17.6 w/w% H<sub>2</sub>) has become a hot research topic in recent years [18]. This technology provides an alternative option for energy retrieval from a waste.

## 2. EXPERIMENTAL

### 2.1 Materials

The experimental set-up was illustrated in our previous works [19, 20]. The EDI device consisting of five separate compartments was the most important part of the experiment. The five compartments were: anode compartment, cation resin-loaded compartment, concentrated compartment, anion resin-loaded compartment and cathode compartment, respectively from left to right in the EDI device. It is worth mentioning that the resin-loaded compartment was placed between two resin membranes thus the five compartments were separated one from each other by the membranes, to achieve the retrieval and purification without secondary pollution and precipitation.

### 2.2 Analysis

Ion chromatographic method was adopted to analyze NH<sub>4</sub><sup>+</sup> and coexisted ions. Enrichment degree (*ed*) and removal efficiency (*re*) were adopted to determine the performance of the EDI in removing low concentration nutrient anions. Equations were as follows [21]:

$$ed = \frac{C_c}{C_i} \quad (1)$$

$$re = \frac{C_i - C_o}{C_i} \times 100\% \quad (2)$$

where, *C<sub>c</sub>*, *C<sub>i</sub>* and *C<sub>o</sub>* represents concentration of *i* in the concentrate compartment, influent and effluent, respectively.

## 3. RESULTS AND DISCUSSION

### 3.1 Electrical force for ion's migration

Table 1 listed the enrichment degree of ammonia against different applied voltage, it was obvious that with the increase of applied voltage. The concentration of NH<sub>4</sub><sup>+</sup> in concentrate compartment increased and the retrieval of the ammonia as *ed* were 9.5, 10.6 and 12.1 after 11 hours corresponding to the applied voltage of 2.5 V/cm, 3.8 V/cm and 5.0 V/cm, respectively.

Table 1. The enrichment degree (*ed*) of ammonia against applied voltage (The initial concentration of ammonia was 100 mg/L.)

Applied voltage V/cm	2.5	3.8	5.0
Enrichment degree <i>ed</i> (times)	9.5	10.6	12.1

The *ed* increased under a higher applied voltage, mainly because ions transported through ion exchange membranes under the driving force of applied voltage, and higher voltage had an positive effect on the anions diffusion and transfer.

Under electrical forces, the migration of ion *i* corresponds with valence state of *z<sub>i</sub>* and mobility of  $\bar{u}_i$ . The transport of ions through ion exchange membranes can be determined by three contributions as electrical migration, ion diffusion and convective term, respectively. At higher applied voltage, the electro-migration dominated the ion transport. In this case, the diffusion and the convection terms could be ignored, and the electrical migration can be described by the simplified Nernst-Planck relationship of Eq. (3):

$$N_i = z_i \bar{C}_i \bar{u}_i \text{grad}\phi \quad (3)$$

Here, *gradφ* depicts potential gradient, and higher electric energy would make the *gradφ* value increase, thus more NH<sub>4</sub><sup>+</sup> transferred to the concentrated compartment at a higher voltage.

### 3.2 Metal hydroxide precipitation

In Table 2, the pH values were less than 7.00 after 30min and decreased gradually during the whole operation process. When the time was 660min, the pH values were 1.97-3.21. This was mainly because that the migration velocity of  $H^+$  was higher than that of the  $OH^-$ . Thus this acidic solution was effective to avoid the precipitation phenomenon in the concentrated solution [17].

Table 2. pH value in the concentrated compartment under different applied voltage

Time (min)	2.5 V/cm	3.8 V/cm	5.0 V/cm
0	7.21	7.21	7.21
30	6.88	6.83	6.71
60	6.29	5.21	4.96
90	5.00	4.50	3.54
120	4.13	4.08	2.50
150	3.58	3.50	2.38
180	3.42	3.21	2.33
210	3.25	3.04	2.29
240	3.26	2.92	2.25
300	3.25	2.79	2.25
360	3.25	2.67	2.13
420	3.25	2.58	2.04
540	3.21	2.58	1.98
660	3.21	2.54	1.97

### 3.3 Multistage experiment

Wastewater Example 1<sup>-</sup> with  $NH_4^+$  concentration of 82.0 mg/L and Example 2<sup>-</sup> with  $NH_4^+$  concentration of 180.5 mg/L were applied respectively to multistage experiments, with the applied voltage of 3.8 V/cm, the flow rate of 20 mL/min and the time of 11h. The dilute effluent of the first stage was taken as inflow of the second stage, and the dilute effluent of the second stage as inflow of the third stage. The experimental results were shown in Table 3. It could be seen from Table 3 that  $NH_4^+$  could be retrieved from the wastewater to the recovery concentration. As to Example 1<sup>-</sup>, after 11h, concentration of  $NH_4^+$  in the concentrated compartment was 836.3 mg/L and 8.0 mg/L in the dilute effluent, with the *ed* of 10.2 and *re* of 90.2%. For Example 2<sup>-</sup>, after 11h, concentration of  $NH_4^+$  in the concentrated compartment was 1735.0 mg/L and

17.9 mg/L in the dilute effluent, with the *ed* of 9.6 and *re* of 90.1%.

It can be seen from the table after three stages of enrichment, 3-orders of magnitudes was achieved, that is the concentration of ammonia from mg/L to g/L. In Example 1,  $NH_4^+$  concentrations in the effluent were 0.81mg/L and 1.82mg/L respectively, which were far below the discharge criteria. The enrichment degrees of  $NH_4^+$  reached 1032 and 953 times of magnitude, respectively.

Table 3. Multistage enrichment at the applied voltage of 3.8 V/cm, with the flow rate of 20 mL/min and the initial concentration of 82.0 mg/L and 180.5 mg/L in the first stage.

	Concentration (mg/L)	
	Example 1 <sup>-</sup>	Example 2 <sup>-</sup>
Initial concentration	82.0	180.5
First stage (concentrated)	836.3	1735.0
Second stage (influent)	8.0	17.9
Third stage (effluent)	0.81	1.82

### 3.4 Applicability

With reference to leachate in municipal solid waste of Hangzhou, China, we testified the practicality of the EDI device. The initial concentration of ammonia were as follows:  $NO_3^-$  2.6 mg/L,  $NH_4^+$  82.0 mg/L, and  $PO_4^{3-}$  5.58 mg/L. The retrieval of N was operated as described in Table 3. the applied voltage was 3.8 V/cm, flow rate was 20 mL/min. The discharge standard and concentration of  $NO_3^-$ ,  $NH_4^+$ , and  $PO_4^{3-}$  in the effluent treated by EDI process were listed in Table 4.

Table 4. The mean concentration of purified water by EDI process in contrast with the discharge standard

	Concentration (mg/L)		
	$NO_3^-$	$NH_4^+$	$PO_4^{3-}$ (P)
Discharge standard	10.0	5.0	0.5
Purified water	0.18	0.81	0.46

As is shown from Table 4,  $NH_3$ -N from the wastewater could be removed and retrieved before entering into  $A^2O$  of municipal sewage plant. Furthermore,  $NO_3^-$ -N  $PO_4^{3-}$  (P) could also be removed, thus the nitrification and denitrification process can be omitted and make the process more simple.

## ACKNOWLEDGEMENT

The authors are grateful for the financial support of the National Natural Science Foundation of China (Grant No. 21173188).

## REFERENCE

- [1] Schmadel NM, Harvey JW, Alexander RB, Schwarz GE, Moore RB, Eng K, Gomez-Velez JD, Boyer EW, Scott D. Thresholds of lake and reservoir connectivity in river networks control nitrogen removal. *Nat Commun* 2018;9:2779.
- [2] Conley DJ, Paerl HW, Howarth RW, Boesch DF, Seitzinger SP, Havens KE, Lancelot C, Likens GE. *ECOLOGY* Controlling Eutrophication: Nitrogen and Phosphorus. *Science* 2009;323:1014-5.
- [3] Thakur IS, Medhi K. Nitrification and denitrification processes for mitigation of nitrous oxide from waste water treatment plants for biovalorization: Challenges and opportunities. *Bioresour Technol* 2019;282:502-13.
- [4] Xiang SY, Liu YH, Zhang GM, Ruan R, Wang YP, Wu XD, Zheng HL, Zhang Q, Cao LP. New progress of ammonia recovery during ammonia nitrogen removal from various wastewaters. *World J Microbiol Biotechnol* 2020;36:144.
- [5] Xiong JH, Guo SC, Hou YP, Dai Z, Zhu HX, Wang SF, Chen GN. Using the modified sugarcane bagasse cellulose cation membrane as a separator in the electro dialysis device for ammonia nitrogen removal. *J Biobased Mater Bio* 2019;13:475-83.
- [6] Kavvada O, Tarpeh WA, Horvath A, Nelson KL. Life-cycle cost and environmental assessment of decentralized nitrogen recovery using ion exchange from source-separated urine through spatial modeling. *Environ Sci Technol* 2017;51:12061-71.
- [7] Wood J, Gifford J, Arba J, Shaw M. Production of ultrapure water by continuous electrodeionization. *Desalination* 2010;250:973-6.
- [8] Shen XL, Chen XM. Membrane-free electrodeionization using phosphonic acid resin for nickel containing wastewater purification. *Sep Purif Technol* 2019;223:88-95.
- [9] Lee D, Lee JY, Kim Y, Moon SH. Investigation of the performance determinants in the treatment of arsenic-contaminated water by continuous electrodeionization. *Sep Purif Technol* 2017;179:381-92.
- [10] Zahakifar F, Keshtkar AR, Souderjani EZ, Moosavian MA. Use of response surface methodology for optimization of thorium(IV) removal from aqueous solutions by electrodeionization (EDI). *Prog Nucl Energy* 2020;124:103335.
- [11] Rathi BS, Kumar PS. Electrodeionization theory, mechanism and environmental applications. A review. *Environ Chem Lett* 2020;18:1209-27.
- [12] Xu LJ, Dong F, Zhuang HC, He W, Ni M, Feng SP, Lee PH. Energy upcycle in anaerobic treatment: Ammonium, methane, and carbon dioxide reformation through a hybrid electrodeionization-solid oxide fuel cell system. *Energy Convers Manage* 2017;140:157-66.
- [13] Xu LJ, Pang YS, Huang DZ, Zhuang HC, Luo TF, Lee PH, Liu WZ, Zhang S, Feng L. Increasing ammonia recovery from high-level ammonium wastewater via adding sodium sulfate to prevent nitrogen generation in the cathode. *Environ Res* 2020;186:109521.
- [14] Wang HY, Zhou Q, Zhang GM, Yan GK, Lu HF, Sun LY. A novel PSB-EDI system for high ammonia wastewater treatment, biomass production and nitrogen resource recovery: PSB system. *Water Sci Technol* 2016;74:616-24.
- [15] Grasham O, Dupont V, Camargo-Valero MA, Garcia-Gutierrez P, Cockerill T. Combined ammonia recovery and solid oxide fuel cell use at wastewater treatment plants for energy and greenhouse gas emission improvements. *Appl Energy* 2019;240:698-708.
- [16] Chen XF, Wu ZC. A new configuration of membrane stack for retrieval of nickel absorbed in resins. *J Zhejiang Univ Sci B* 2005;6:543-5.
- [17] Feng X, Wu ZC, Chen XF. Removal of metal ions from electroplating effluent by EDI process and recycle of purified water. *Sep Purif Technol* 2007;57:257-63.
- [18] Lan R, Irvine JTS, Tao SW. Ammonia and related chemicals as potential indirect hydrogen storage materials. *Int J Hydrogen Energy* 2012;37:1482-94.
- [19] Feng X, Liu YZ, Chen XF, Wu ZC. Treatment of electroplating wastewater containing copper ions by EDI process. *Technol Water Treatment* 2011;37:96-8,122.
- [20] Feng X, Xue ZK, Chen XF, Wu ZC. Effect of applied voltage on the EDI electro-regeneration of cation exchange resins loaded with nickel ions. *J Henan Normal Univ Nat Sci* 2011;39:86-8.
- [21] Meyer N, Parker WJ, Van Geel PJ, Adiga A. Development of an electrodeionization process for removal of nitrate from drinking water - Part 2: Multi-species testing. *Desalination* 2005;175:167-77.