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# Integrated experimental and modeling evaluation of energy consumption for ammonia recovery in bioelectrochemical systems

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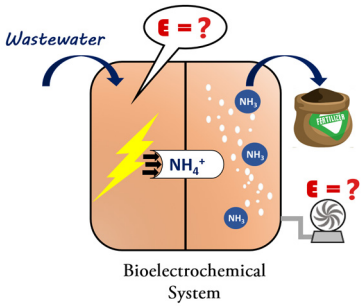
## HIGHLIGHTS

- Energy consumption for recovering ammonia in BES is systematically quantified.
- There is a trade-off between energy consumption and ammonia recovery efficiency.
- The major energy consumers are the catholyte aeration and external power supply.
- High current output and moderate aeration rate help reduce energy consumption.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Bioelectrochemical systems (BES) can recover ammonia from wastewater driven by electricity generation. However, energy consumption of such an approach has not been well evaluated. In this study, the effects of several key operating factors including catholyte aeration rate, external voltage, and external resistance on both ammonia recovery and energy consumption were systematically investigated. A mathematical model developed for ammonia removal/recovery in BES was applied to help interpret the experimental results. It was found that a high aeration rate in the catholyte could facilitate ammonia recovery. An aeration rate of 100 mL $min^{-1}$ resulted in the lowest energy consumption of 4.9 kWh $kg^{-1}$ N recovery among the tested aeration rates. A low external resistance facilitated the ammonia recovery via higher current generation, while a moderate external voltage (e.g., 0.5 V) helped to achieve low energy consumption. The highest ammonia recovery rate of 7.1 g N $m^{-2}$ $d^{-1}$ was obtained with energy consumption of 5.7 kWh $kg^{-1}$ N recovery. Therefore, there is a trade-off between energy consumption and ammonia recovery.



## 1. Introduction

Nitrogen is a key inorganic contaminant, and excessive discharge of nitrogen, for example via incomplete wastewater treatment, can amplify the nitrogen transfer to aquatic ecosystems and result in eutrophication that deteriorates ecosystem and decreases the supply of drinking water source [1]. The annual cost due to eutrophication in the United States is about $2200 million [2]. Thus, removal of nitrogen from wastewater is necessary to limit nitrogen discharge. In wastewater, the primary form of nitrogen is ammonium [3], which can be removed by either biological or physicochemical methods [4,5]. In biological ammonium removal processes such as nitrification, denitrification and anaerobic ammonium oxidation (anammox), ammonium is converted to nitrogen gas microbiologically. The physicochemical ammonium

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removal processes like ion exchange, air stripping and high gravity technologies can separate ammonia from liquid at the expense of chemical or energy consumption [6–8].

Sustainable wastewater management aims to recover valuable resources from wastewater, such as energy, nutrients and water. The concentration of ammonium in some wastewaters such as digester centrate, livestock wastewater, and landfill leachate can be over 500 mg $L^{-1}$ [9]. Thus, ammonia recovery, instead of removal, will be of strong interest. Ammonia nitrogen is a key fertilizer component for agricultural applications, and >90% of the world ammonia production is currently based on the Haber-Bosch synthesis process, which consumes 1–2% of world energy [10]. The demand for fertilizer is increasing at 3–4% per year along with the steadily growing global demand for food to feed additional 2.3 billion people by 2050 [11,12]. About 30% of ammonia in fertilizers ends up in wastewater as ammonium ions [13]. Therefore, recovering ammonia from wastewater may provide a promising approach for supplying ammonia to sustain fertilizer and food production, and avoid energy-intensive synthesizing processes [14].

An emerging technology for ammonia recovery from wastewater is bioelectrochemical system (BES) [15,16]. In a BES, organic compounds in wastewater are oxidized by the exoelectrogens growing on an anode electrode and the generated electrons spontaneously flow from the anode electrode to a cathode electrode [17]. During electricity generation, ammonium ions are driven to transport from the anode to the cathode to maintain charge neutrality [18]. The high pH of the catholyte due to reduction reactions converts ammonium ions to ammonia, which can be driven off the catholyte with mechanical mixing or aeration for recovery. Various BES including microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) have been studied to achieve ammonia recovery [19,20]. Because higher current generation would greatly enhance ammonium transport towards recovery [17], MECs with external power exhibit a better performance for ammonia recovery than MFCs [21]. Ammonium nitrogen has been successfully recovered as ammonia from ammonium-rich wastewater, such as synthetic wastewater, urine, landfill leachate, and swine wastewater [22–27]. Mathematical models have also been developed to improve our understanding of ion transport mechanism during ammonia recovery and the BES operation [28–30].

Despite the great progress in ammonia recovery by using BES, energy consumption of such a process has not been fully investigated before. This information is critically important to evaluate whether ammonia recovery by using BES will be energy efficient (and cost effective). An energy-efficient treatment and recovery system will benefit our environment with contaminant removal, reduced demand for energy (and thus a lower carbon footprint), and reduced demand for raw materials through resource recovery. The major energy consumers in a BES include power supply, recirculation pumps, and catholyte aeration [31]. Energy consumption by power supply can be affected by both voltage and external resistance via current generation, which then influences ammonium ion transport. Electrolyte recirculation helps with substrate distribution that will affect current generation and electrolyte resistance. Catholyte aeration is to provide electron acceptors for cathode reactions, and to strip ammonia off the liquid for subsequent recovery. To improve our understanding of energy consumption of ammonia recovery by using BES, in this study, we have systematically investigated the effects of catholyte aeration rate, external voltage, and external resistance on both ammonia recovery and energy consumption. A mathematical model was applied to verify and further explain the effects of the operation parameters on the BES performance and energy consumption. The energy consumption by the BES was normalized to per kg N removal or recovery.

## 2. Materials and methods

### 2.1. BES setup and operation

A bench-scale cubic shape BES was used in this study. Both the anode and the cathode chambers had the same dimension of 9 cm × 4.7 cm × 1 cm. A piece of cation exchange membrane (CEM, CMI-7000, Membrane International Inc., Glen Rock, NJ, USA) with a sectional area of 42.3 $cm^2$ was used to separate the anode and cathode chambers. The anode electrode was a carbon brush (Gordon Brush Mfg. Co., Inc., CA, USA), which was pretreated by being soaked in pure acetone overnight and heat-treated in a muffle furnace (Model 550 Isotemp Series, Fisher Scientific, Pittsburgh, PA, USA) at 450 °C for 30 min. The cathode electrode was a piece of 32-$cm^2$ carbon cloth (Zoltek Companies, Inc., MO, USA) that was coated with 5 mg $cm^{-2}$ of Pt/C (10% wt Pt on Carbon Vulcan, Fuel Cell Earth LLC, USA). The BES was operated in a batch mode at room temperature (~20 °C).

The anode was inoculated with the anaerobic sludge from a local wastewater treatment plant (Peppers Ferry, Radford, VA, USA). To mimic the digestion effluent of livestock wastewater [32], the anode influent solution was prepared containing (per liter of deionized water – DI water): sodium acetate, 1.5 g; $NH_4Cl$, 3.0 g; $NaHCO_3$, 2.0 g; NaCl, 0.15 g; $MgSO_4$, 0.005 g; $CaCl_2$, 0.006 g; and trace elements solution, 1 mL [33]. The anolyte volume was 100 mL, while the cathode chamber was initially filled with 180 mL of DI water. An external voltage of 0.5 or 0.8 V was applied to the circuit by a power supply (CSI3644A, Circuit Specialists, Inc., Mesa, AZ, USA) according to a previous study [34]. When current generation dropped to lower than 0.2 A $m^2$, one batch cycle ended and the anolyte was partially replaced (75% of the anode volume), while the catholyte was remained unchanged. Both the anolyte and catholyte were recirculated at a flow rate of 20 mL $min^{-1}$, respectively. Samples (1 mL) were collected every 4 h from both chambers for measurement. The stripped $NH_3$ gas from the catholyte was absorbed by 1 M $H_2SO_4$. To study the effect of aeration rate, the catholyte aeration rate was adjusted to 300, 100, 50 and 30 mL $min^{-1}$ (1.7, 0.6, 0.3 and 0.2 vvm; vvm:gas volume (L) per liquid volume (L) per minute). In the study of current generation, two experiments were performed: in the test of external voltage effect, three external voltages 0 V, 0.5 V, and 0.8 V, were examined across external resistance of 1 Ω and with the catholyte aeration rate of 100 mL $min^{-1}$ (0.6 vvm); in the experiment of external resistance, the external resistance was manipulated at three levels, 1 Ω, 10 Ω, and 100 Ω, under the applied voltage of 0.8 V and with the catholyte aeration rate of 100 mL $min^{-1}$.

### 2.2. Measurement and analysis

The voltage across the external resistor was recorded every 2 min by a digital multimeter (2700, Keithley Instruments Inc., Cleveland, OH, USA). The pH was measured by two pH meters (Oakton Instruments, Vernon Hills, IL, USA and Accumet AB250, Fisher Scientific, Pittsburgh, PA, USA), installed in the anode and the cathode chambers, respectively. The concentrations of chemical oxygen demand (COD) and ammonium nitrogen ($NH_4^+$-N) were measured using a DR/890 colorimeter (HACH Co., Ltd., USA) according to the manufacturer's instruction. Energy consumption by the BES included the external power source, the aeration, and the recirculation of the anolyte and catholyte. The power input by the external power supply was calculated as [35]:

$$P_{power} = \frac{IU}{1000} \quad (1)$$

where $P_{power}$ is external power requirement by the power supply (kW); $I$ is the current (A); and $U$ is the external voltage (V).