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Self-powered denitration of landfill leachate through ammonia/nitrate coupled redox fuel cell reactor

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HIGHLIGHTS

- An ammonia/nitrate coupled redox fuel cell (CRFC) was assembled to remove nitrogen.
- Ammonia was catalytically oxidized and nitrate was reduced to produce electricity.
- Nitrifying leachate's ammonia as oxidant in CRFC and both pollutants were removed.
- Nitrate removal of 46.9% and maximum power density of 170 mW m^{-2} could be achieved.
- 46.9–91.4% nitrates removed and 170 mW m^{-2} maximum power density achieved.

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ABSTRACT

In order to explore the feasibility of energy-free denitrifying N-rich wastewater, a self-powered device was uniquely assembled, in which ammonia/nitrate coupled redox fuel cell (CRFC) reactor was served as removing nitrogen and harvesting electric energy simultaneously. Ammonia is oxidized at anodic compartment and nitrate is reduced at cathodic compartment spontaneously by electrocatalysis. In 7.14 mM ammonia + 0.2 M KOH anolyte and 4.29 mM KNO_3 + 0.1 M H_2SO_4 catholyte, the nitrate removal efficiency was 46.9% after 18 h. Meanwhile, a maximum power density of 170 mW m^{-2} was achieved when applying Pd/C cathode. When NH_4Cl/nitrate and ammonia/nitrite CRFCs were tested, 26.2% N–NH_4Cl and 91.4% N–NO_2^- were removed respectively. Nitrogen removal efficiency for real leachate at the same initial NH_3–N concentration is 22.9% and nitrification of ammonia in leachate can be used as nitrate source. This work demonstrated a new way for N-rich wastewater remediation with electricity generation.

1. Introduction

Highly concentrated ammonia nitrogen exists in the landfill leachate. For a fresh leachate, the ammonia nitrogen concentration ranges of 50–3500 mg/L (Mangimbulude et al., 2012). They are mainly from biodegradable process of the protein and other nitrogenous substances in landfill, which are very difficult to deal with (Lou et al., 2009). NH_3–N with two forms of free ammonia (NH_3) or ammonium (NH_4^+) is present in water. Both of them in the composition ratio depend on the pH value of the water. A high proportion of free ammonia exists in the high pH value water; otherwise ammonium salts occupy high proportion due to pH break the equilibrium of ammonia and ammonium. That is high concentrations of NH_3–N will increase the degree of contamination of water bodies and high N/C ratio would cause serious nutritional imbalance proportion (Wang et al., 2012). Certainly, the stability of the effective operation of biological treatment system will also be affected due to microbial activity inhibition. It will also increase the load of subsequent processing.

The treatment of leachate has become an increasing interest because of the requirements to reduce nutrient emission (Wang et al., 2012). During the past decades, variety of technologies was devoted to high ammonia concentrations removal because of its high contaminant strength (Gao et al., 2015; Lou et al., 2009), including biological modes (Chung et al., 2015; Mahmoud et al., 2014; Miao et al., 2015), ozonation (Chys et al., 2015), chemical precipitation (Camargo et al., 2014; Di Iaconi et al., 2010), reverse osmosis (Talalaj, 2015; Zhang et al., 2013a) and adsorption (Foo et al., 2013; Wang et al., 2014), and etc. Although these approaches

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are efficient to remove ammonia nitrogen, the considerable energy consumption has been critical. Instead of energy inputs, a net energy extracted from a waste for its decontamination has attracted attention nowadays (Logan and Rabaey, 2012; McCarty et al., 2011).

In fact, chemicals contain energies. One of the most effective devices to retrieve these energies is a fuel cell, which is an electrochemical device that directly converts the chemical energy in a fuel into electricity (Winter and Brodd, 2004). Inspired by fuel cells, a device termed pollutants coupled redox fuel cell (PCRFC) reactor (Yu et al., 2014; Zhang et al., 2013b) to harvest energy and to treat wastewater was proposed. Importantly, the redox potential of PCRFC anode should be lower than that of the cathode. Only in this way can the interior bias be produced to transfer the electrons of the anode through the external circuit to the cathode. Generally, a low redox potential contaminant in aqueous solution can function as fuels to be oxidized on catalytic anode to give electrons, and the high one will serve as electron acceptors to be reduced on catalytic cathode. Chemical energy in contaminants can, therefore, be converted to electricity and contaminants itself can be meantime eliminated.

Note that the NH_3–N is in a low valence state and has a tendency to be oxidized, which can be used as fuel to convert to N_2. Conventionally, nitrification and denitrification are often employed to remove nitrogen contaminants, and the microbial nitrification is a common and easy process. To be an extremely interesting, NO_3^- or NO_2^- will be right candidates as electrons acceptor instead of O_2, the N–NO_3^- or N–NO_2^- in the water may be converted to N_2, volatilizing into the atmosphere and got removed, just like the microbial denitrification (Virdis et al., 2008, 2009; Zhang and Angelidaki, 2012). This is an artificial removal of nitrogen technology simulating the biological nitration–denitrification process. To be our best knowledge, the decline of nitrogen in this ammonia/nitrate coupled redox fuel cell has been first attempted since it is difficult to be assembled.

In this work, a novel ammonia/nitrate CRFC is presented that can operate for simultaneous ammonia wastewater treatment and electricity generation by using ammonia as a fuel in the anode and nitrate as an electron acceptor in the cathode. NH_3/N_2, NH_4^+/N_2 have been identified as reasonable fuels with a redox potential of −0.74 V vs SHE (Standard Hydrogen Electrode, SHE) and +0.27 V vs SHE, respectively, corresponding to NO_3^-/N_2 with +0.74 V vs SHE standard potential. The reaction mechanism of NH_3, NH_4^+/NO_3^- coupled redox cell can be described below.

$$\text{Anode}: \quad 2NH_3 + 6OH^- \rightarrow 2N_2 + 6H_2O + 6e^- \quad E^0 = -0.74V \tag{1}$$

$$\text{Cathode}: \quad 2NO_3^- + 10e^- + 12H^+ \rightarrow N_2 + 6H_2O \quad E^0 = +0.74V \tag{2}$$

$$\text{Overall}: \quad 2NH_3 + 2NO_3^- + 6H^+ \rightarrow 2N_2 + 6H_2O \quad E^0 = +1.48V \tag{3}$$

Eq. (3) shows that the theoretical electromotive force of NH_3/NO_3^- cell is higher than that of H_2/O_2 cell (1.23 V), which means that this type of coupled redox cell is accessible in thermodynamics. However, ammonia can hardly react with nitrate without external energy due to the sluggish reaction kinetics of nitrate reduction. Catalysts are vital to accelerate reactions. Platinum and its bi-metal annoy has been identified as an effective candidate to catalyze the oxidation of ammonia (Assumpcao et al., 2014). Palladium catalyst is reported to be crucial for the selectivity of generating N_2 (Duca and Koper, 2012).

Thus, the nitrification (bacteria)|nitrate||ammonia CRFC device was designed and assembled to examine the N removal efficiency and to measure the cell performance, which is helpful for understanding of mechanism. Besides, real landfill leachate, containing ammonia of about 800 mg L^{-1}, was possibly used both as fuel and oxidant (nitrification of the leachate) in CRFC for its applicability study.

2. Methods

2.1. Cell fabrication and measurements

Fig. 1 shows assembly of ammonia||nitrate fuel cell configuration with nitrification device. Two glass tubes (14 cm length, 15 mm diameter) were used as anode and cathode chambers respectively. Both of the anolyte and the catholyte volumes were 11.0 mL. They are separated by a saturated KCl agar-gel (4 mm diameter). Electrode was connected with Ti wire to collect current. An external resistor (1000 Ω) was loaded between the anode and cathode (Fig. 1). Two types of cells were fabricated, cell A and cell B. For cell A, the cathode was coated with Pd/C. For cell B, the cathode was without catalyst, the rest of the cell is the same with cell A. All cells anode was coated with Pt/C.

The cell voltage was recorded every 1 min by a data acquisition system (PISO-813, ICP DAS). Polarization test was performed by changing external resistance from 10,000 Ω to 300 Ω. The levels of nitrogen ranging from 50 to 120 mg L^{-1} were chosen as the anolyte and catholyte in cell A and B to testify the CRFC performance for nitrogen removal in 2 days. To investigate the applicable possibility, the real landfill leachate was diluted to the required approximate level. Then the synthesized nitrogen was replaced by the above resulted solution.

2.2. Nitrification of landfill leachate

Ammonia in landfill leachate was used as nitrate source, which was biologically nitrified and was employed to serve as electron's acceptor. A packed-bed reactor with 1.0 L culture volume was used in this experiment (Fig. 1). Porous ceramic ring was chosen as nitrifying bacteria carriers, which were about 10 mm long and have external and inner diameter of 10 and 6 mm respectively. The volumetric surface available for bacterial growth was assumed to be 200 m^2/m^3. The filling volume percentage of ceramic rings to the total volume (1.5 L) was about 30%.

During the whole nitrification process, temperature was kept at 27 °C. Aeration of air (0.5 L/min) was done to keep the aerobic condition within the bioreactor. pH was adjusted to 8 daily by addition of 1.0 M Na_2CO_3 solution. When starting the nitrification process, nitrifying culture medium was firstly used to accumulate nitrifying bacteria and form biofilm on the ceramic ring surface. Subsequently, diluted ammonia and landfill leachate were added into the bioreactor to be nitrified.

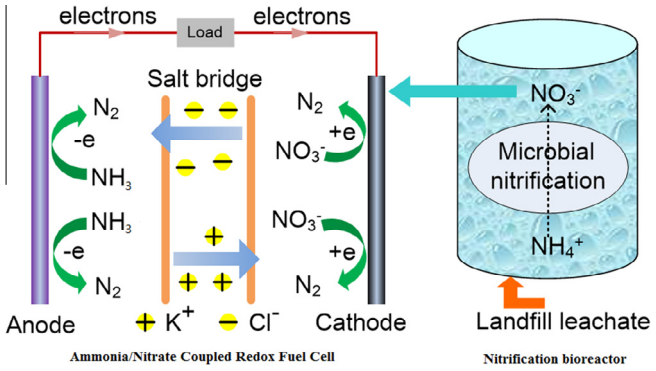

Fig. 1. Schematic of ammonia/nitrate fuel cell configuration with nitrification.