Electroreduction of nitrate in water: Role of cathode and cell configuration

Jing Ding [a], Wei Li [a], Qing-Liang Zhao [a,*], Kun Wang [a], Zhen Zheng [b], Yun-Zhi Gao [c]

[a] State Key Laboratory of Urban Water Resources and Environment (SKLUWRE), School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China
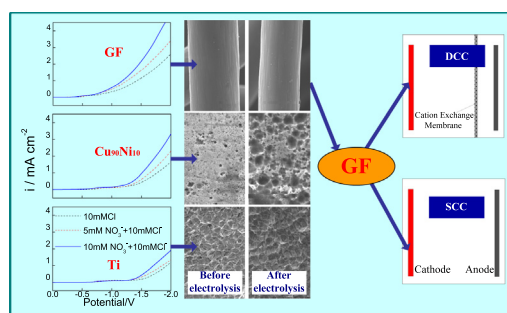[b] State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin 150090, China
[c] School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150090, China

HIGHLIGHTS

- GF cathode exhibited the best in nitrate removal (70%) and corrosion resistance.
- Much higher nitrate removal was obtained in DCC than in SCC.
- The optimal value of applied cathodic potential of −1.8 V was recommended.
- The presence of chloride ion enhanced nitrate removal in DCC.

GRAPHICAL ABSTRACT

ABSTRACT

The performance of direct electroreduction of nitrate was studied to investigate the role of different cathodes (graphite felt, GF; Cu–Ni alloy, $Cu_{90}Ni_{10}$; titanium, Ti) and cell configurations (single-chamber cell, SCC; dual-chamber cell, DCC). Experimental results indicated the performances of these electrodes for nitrate removal rate and cathodic current in linear sweep voltammograms were in the order of GF > $Cu_{90}Ni_{10}$ > Ti. The GF cathode, with the highest nitrate removal of 70%, also exhibited higher corrosion resistance than the $Cu_{90}Ni_{10}$ cathode. Nitrate removal in DCC was much higher than in SCC with GF as cathode. The cation membrane equipped in the reactor significantly improved the nitrate electroreduction. The nitrate reduction efficiency was the highest at an applied cathodic potential of −1.8 V, over which it decreased because of the impediment of hydrogen evolution at higher potential. The nitrate removal rate increased slightly with the presence of chloride ion, however, decreased with sulfate ion in the solution. Nitrate removal in DCC with GF as cathode showed broad application prospect.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Nitrate contamination in natural resources derives mainly from the excessive applications of fertilizers and the discharge of municipal effluents [1]. Nitrate pollution may cause a series of problems on human health and aquatic ecosystems, with the limiting level tolerated for drinking water 11.3 mg/L-N recommended by WHO [2] and the maximum contaminant level 10 mg/L-N set by EPA [3]. Numerous researches for nitrate removal have been performed so far such as biological denitrification, ion exchange, reverse osmosis, chemical reduction and electrodialysis [4–6]. Unfortunately, these processes show some drawbacks (e.g., the sensitivity of autotrophic or heterotrophic bacteria to environment, additional carbon substrate, continuous monitoring, slow kinetics, and generation of concentrated brine) [1,7]. These

limitations have awakened considerable interest in electroreduction of nitrate, which has advantages of convenience, no sludge production, relatively low investment costs and ability to treat highly concentrated nitrate or effluents that contain other toxic compounds [7–10].

Electrochemical reduction of nitrate has been widely studied, and the main cathodic products involved during nitrate electroreduction are NO_2, NO_2^-, NO, N_2O, N_2, NH_2OH, NH_3 and NH_2NH_2, as nitrogen has oxidation states from +5 to −3 [11]. The electrochemical transformation activity and selectivity to the desired products of nitrate are highly dependent on the cathode material, applied cathodic potential, cell configuration and the presence of other anions [8,9]. Various monometallic electrodes of transition and main group metals, such as Cu [9,10], Sn [12,13], Bi [11,13], Ni [14], Ti [15,16], Fe [15,16], and Pb [17] have been investigated before. Recently, more attention has moved to bimetallic, ternary metallic or alloy electrodes for high activity and selectivity, such as Cu–Zn [18], Cu–Ni [7,19], Rh–Ni [20], Sn–Pd [21], Ag–Pd [22], Ag–Pt–Pd [22], Pd–Co–Cu alloy [8], and stainless steel [17]. The normal and modified nonmetallic electrodes, such as graphite [17], silicon carbide [17] and Cu or Pd–Cu modified pyrolytic graphite [23], have also been used in the electrochemical reduction process. Lacasa et al. [17] reported graphite exhibited the highest electroreduction removal of nitrate compared to other materials like conductive diamond, stainless steel, silicon carbide and lead. However, titanium cathode showed higher reduction activity than graphite in Dash and Chaudhari's research [15]. Copper and Cu–Ni alloy also exhibited a catalytic effect to enhance the adsorption of nitrate through limiting the adsorption of hydrogen onto the cathode surface [7,9,19]. Dortsiou et al. [24] revealed the reduction rates of several metal electrodes (Sn, Bi, Pb, etc.) were the same when performed at a definite rational potential (Er), which was the difference between the applied potential and the potential of zero charge of each metal. To avoid the side reaction, the materials with a high overpotential for hydrogen evolution are usually preferred as cathodes for nitrate electroreduction.

The distribution of nitrate reduction products was also widely studied, depending on the cathode materials and the cathodic potential [9]. The nitrate electroreduction was studied in alkaline solution from −0.6 to −1.4 V and different reactions occurring on copper electrode were revealed by Reyter et al. [9]. On the basis of previous studies, ammonium instead of the desired N_2 was the main product during the electrochemical reduction of nitrate on Cu or Cu–Ni alloy [25,26]. The high selectivity to N_2 (92%) during electrochemical reduction with the application of Sn electrode was reported [12], but with such serious drawbacks as very negative potential (−2.9 V) and severe cathodic corrosion resulting in pollution of the electrolyte as tin hydride was detected. via intermediate nitrite, Wang et al. [27] suggested the main final products were nitrogen and ammonium ions, and trace of NO and N_2O. The activity and selectivity to N_2 depended on the Sn content on the electrode and pH of the electrolyte. As reported [7,10], it was feasible to perform both cathodic reduction of nitrate and further anodic oxidation of the produced ammonium to nitrogen gas in a cell.

Nevertheless, most metal materials undergo corrosion in electroreduction process, especially in extreme environment. Reyter et al. [7] revealed that Ni and $Cu_{70}Ni_{30}$ electrodes demonstrated better corrosion resistance than Cu and $Cu_{90}Ni_{10}$ in the presence of chloride, nitrate and ammonium via corrosion measurements. Dash and Chaudhari [15] also gave the corrosion rates of Ti when nitrate was reduced. Conversely, nonmetallic materials such as graphite/carbon always demonstrated a strong corrosion resistance, which was commercially used in the field of fuel cell [28]. GF had the advantages of wide operating potential range, good stability and low cost, which was used for all vanadium redox flow battery [29]. There were only a few reports about applying GF to

nitrogen removal, e.g. using activated carbon fiber felt cathode for ammonium oxidation in a biofilm electrode reactor [30], modifying graphite felt electrode with neutral red for ammonium and nitrite oxidation [31], and serving as a solid electron mediator for microbial cultivation during denitrification [32]. However, there are no studies of using GF material as cathode for nitrate electroreduction, while the efficient removal of nitrate on a corrosion resistant electrode shows broad application prospect.

The objective of this study is to demonstrate the effectiveness of GF cathode for efficient nitrate reduction and corrosion resistance. Specifically, the GF cathode was compared with $Cu_{90}Ni_{10}$ (metal alloy) and Ti (monometal) electrodes for their electroreduction activity and selectivity to product. Additionally, the electrochemical characteristics and corrosion resistance of GF were evaluated. Finally, electroreduction of nitrate under different cell configuration (DCC and SCC) and applied potential with GF cathode were investigated, and the influence of chloride and sulfate ions were discussed to demonstrate the perspective of cathodic reduction of nitrate and further anodic oxidation of the produced ammonium to increase the selectivity of nitrate reduction to nitrogen gas.

2. Materials and methods

2.1. Experimental set-up

An electrolytic reactor (140 mL) with and without a cation exchange membrane (CEM, Ultrex CMI-7000) was used. Three commercial electrodes with the size of 6 cm × 6 cm × 0.2 cm were selected as cathodes: GF (Carbon Content: 99.9%), $Cu_{90}Ni_{10}$ (Cu:Ni 90:10 wt.%), and Titanium (Ti: 99.5%). The GF chosen in this study was polyacrylonitrile (PAN) based carbon fibers with bulk density of 0.12–0.14 g cm^{-3}. The metal cathodes were rinsed and polished with deionized water, while GF electrode was used as anode for 30 min to eliminate the residual pollutants of last run before each electrolysis. Commercial Ti/Ru–Ir oxide metal with the same size was used as counter electrode. The interval distance of two electrodes was 2 cm. An external saturated calomel electrode (SCE) in the cathodic compartment interlinked to the electrolyte solution via a Luggin capillary for the construction of three electrode system. All cathodic potentials reported here were against this reference electrode (+0.245 V vs. S.H.E.). All experiments were performed at room temperature and under external cathodic potentials of −1.2 to −2.0 V by applying potentiostat power supply (JPS-3005, Zhaoxin Corporation). The schematic diagram of the cell configuration was shown in Fig. 1. The electrolyte in SCC was circulated by peristaltic pump (BT100-1F, Longer Pump), while anodic and cathodic electrolytes were recycled separately in DCC. Samples taken from the reactor were stored at 4 °C, and then analyzed as soon as possible.

The neutral solution of 2 mM $NaNO_3$ was the supporting electrolyte. In order to investigate the effect of Cl^- and SO_4^{2-} on nitrate removal performance, synthetic nitrate solutions were prepared with 2.5 mM NaCl or 2.5 mM Na_2SO_4. During the corrosion resistance evaluation of the cathode, an extra amount of NaCl was added to the electrolyte. All chemicals were of analytical-reagent grade and the solution was prepared by deionized water.

2.2. Analytical methods and calculation

To evaluate the electrolytic reaction characteristics of the nitrate, the linear sweep voltammograms (LSV) in several electrolytes were measured at the GF, $Cu_{90}Ni_{10}$ alloy and Ti electrodes, using a conventional workstation, a computer interface and an ALS Software (CHI 660E, CH Instruments). The measurements were performed in solutions containing varying amounts of $NaNO_3$ and Na_2SO_4 with 10 mM NaCl as a supporting electrolyte.