Kinetics of nitrate reduction with the packed bed iron bipolar electrode

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ABSTRACT

This study investigated the kinetics of nitrate reduction with the zero-valent iron bipolar (ZVI-BP) electrode. The kinetics of the nitrate reduction was considered with respect to the initial concentration of nitrate and the flow rate. Increasing the initial concentration of nitrate enhanced the nitrate reduction rate and there was the proper flow rate (20 mL/min) to achieve the highest nitrate reduction rate (6.2 h^{-1}). But increasing the initial nitrate concentration rather decreased conversion ratio of nitrate to ammonia from 54.5% to 45.9% because of the ammonia oxidation to nitrogen gas as electro-catalytic oxidation. The highest reaction rate was obtained when the experimental hydraulic retention time (HRT) was analogous to the theoretical HRT. The current efficiency was over 100% because of low current density and the redox reaction with Fe^{2+}/Fe^{3+} redox couple. The corrosion of the ZVI-BP electrodes was characterized by using the X-ray Diffraction (XRD) and the field emission scanning electron microscope (FE-SEM). Magnetite was the major corrosion product and it had potential to enhance the nitrate reduction. The modeling of nitrate reduction had similar trend with experimental data and the verification of the modeling parameter will help the up-scale design of the system.

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1. Introduction

Nitrate is the stable anionic contaminant that is in the most oxidized state. The natural nitrate reduction mainly depended on the biological processes is far slower than anthropogenic oxidation of nitrogen hence the nitrogen cycle in nature has been perturbed on the short time [1]. The overloaded nitrate in nature provokes the environmental and human health problems such as cancers with chronic exposures by drinking water [2]. In 1990s, total nitrogen deposition on the Earth's surface was 100 million metric tons and they were introduced from excessive fertilizers in agriculture, animal wastes from intensive farming, leachate from urban waste dump and untreated industrial wastewater [35,36]. Liquid nuclear waste also contains high concentration of nitrate (2–7 M) in high-level nuclear waste (HLW) and relatively low concentrations of nitrate (1.6–2.2 M) in low-level nuclear waste (LLW) [33,37].

Various technologies were introduced for efficient nitrate reduction including biological, physicochemical and electrochemical processes. Among these technologies, biological technologies are the mature process to remove nitrate but the biological processes are limited to operating conditions (e.g. temperature, pH) and additional treatments for shedding suspended solids are

needed for drinking water usage [1,3]. Physicochemical processes, including reverse osmosis, ion exchange and adsorption are only dissipated the nitrate from the sources thus the physicochemical processes need regeneration steps and additional processes for secondary waste treatments. Furthermore, the physicochemical processes have low efficient to the low concentration of nitrate [1,4,5]. On the contrary, electrochemical nitrate treatment processes are emerged owing to the convenience of the operation, cost effectiveness, high removal ratio with regardless of the concentration and small installation area. Moreover, various renewable energy sources are the candidates for green electrochemical treatments [1,6].

There are two types of the electrochemical systems with respect to the polarity of electrodes. At the monopolar (MP) system, all installed electrodes are connected with the power source and the electrodes have same polarity with the connected electrode at the power source. Hence the electrodes have only one polarity. On the contrary, installed electrodes in the bipolar (BP) system have two polarities at one electrode, simultaneously. The installed electrodes without feeder electrodes are disconnected with the power source but potential difference between the BP electrode and electrolyte induced electric potential on the BP electrode. The potential difference across the BP electrode triggers the electrochemical reaction [7]. The primary advantage of the BP system is convenience of cell construction. The BP system only needs to

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connect two feeder electrodes thus the BP system has far larger active area in a given volume than conventional MP systems. Moreover, the BP system has high efficiency with low concentrations and high limiting current density owing to the high mass transfer rate [7,8]. In a few decades, the BP systems were adapted to remove inorganic and organic contaminants in drinking water and wastewater [9–11]. For instance, the BP system was introduced to remove low concentrations of fluoride (10 mg/L) in drinking water and the removal ratio of the BP system (83%) was higher than MP system (78%) [9]. The aluminum bipolar electrode was introduced to remove COD, phosphate and surfactant in the laundry wastewater, simultaneously. In this study, the removal ratio of COD and the other contaminants was over 70% and 90%, respectively [10]. The BP trickle tower used boron-doped diamond (BDD) electrodes to remove phenol and petroleum refinery wastewater. This study showed high removal ratio of phenol (99.85%) and COD (96.04%) [11].

The application of BP system to the environmental section is poorly introduced for electro-oxidation. However, in the previous study, our group introduced the novel zero-valent iron bipolar electrode, briefly ZVI-BP electrode to remove nitrate in the drinking water. The ZVI was the best candidate among the typical electrode materials such as Fe, Cu, Ti, Ni, carbon (graphite) and Pt. At the MP system, Fe electrode showed the best removal ratio (93%) for nitrate reduction [12,13]. In this study, we newly introduced the kinetics of electrochemical nitrate reduction on the ZVI-BP electrode system. The kinetics was elucidated in detail using the mass transfer model and the reaction mechanism with the ZVI-BP electrode was also considered. The corrosion of ZVI-BP electrode was characterized by using the field emission scanning electron microscope (FE-SEM) and X-ray diffraction (XRD).

2. Materials and methods

2.1. Materials

The artificial nitrate solution was prepared using sodium nitrate ($NaNO_3$, >99%, Junsei chemical, Tokyo, Japan) with deionized water. The electrodes were made of ZVI (D = 0.6 mm, Fe $\geqslant$ 98.4%, Sang-A Corporation, Seoul, Republic of Korea) and the insulators were made of silica sands ($D \leqslant$ 0.3 mm, Jumunjin Corporation, Korea). Pt-coated Nb mesh electrode (coating thickness 3.175 μm, Sun Wing Technology Company, Hong Kong, China) was used as the anode to prevent the corrosion and carbon steel (SUS304) mesh electrode was used as the cathode.

2.2. Analytical methods

Samples were gathered at the weir of the reactor. Nitrate and ammonia concentrations of all samples were measured by using a UV–VIS spectrophotometer (DR-2800™, Hach company, Loveland, CO). Nitrate concentrations were measured as chromotropic acid method and ammonia concentrations were measured as salicylate method. All methods were referred to manual from manufacturer, method No. 10020 and 10031, respectively. Nitrite concentrations were merely trace in all samples and they are highly reactive as intermediate, hence nitrite concentrations were ignored. Conductivity and pH were measured with the benchtop multi parameter meter (Orion 720A plus, Thermo Fisher Scientific) with the conductometer (Model: 013010MD, Thermo Fisher Scientific) and the pH electrode (Model: 8156BNUWP, Thermo Fisher Scientific), respectively. The initial concentration of nitrate (C_0) was increased from 30 mg/L as N to 90 mg/L as N and the flow rate was increased from 10 mL/min to 30 mL/min. morphology of the surface of ZVI-BP electrode and

the corrosion product were analyzed by using the FE-SEM (SU70, Hitachi) and the powder XRD (New D8 advance, Bruker AXS) with Cu Kα radiation at room temperature with the scan rate of 2°/min from 5° to 80°.

2.3. Set-up of the reactor

Fig. 1 shows the illustration of the BP reactor. The reactor was made of cylindrical shaped acrylic resin and the reactor was comprised of three compartments; the inlet, body, and outlet parts. The inlet part was conically shaped and packed with a number of glass beads for uniform flow through the reactor. The body part was randomly packed with a number of ZVI-BP electrodes and insulators. The packing volume ratio between ZVI-BP electrode and insulator was 1:2. The effective reactor volume of BP reactor was about 1 L (height: 20 cm × inner diameter: 8 cm). Total surface area of the packed bed BP electrodes was 0.85 m^2 when the cathode area was only considered. The surface area ratio of BP electrode and given volume was 853 m^{-1}. The outlet part had weir to evaporate gas that produced from the reaction and all samples were gathered in the outlet compartment.

A power supply (XG600-2.8, Maximum capacity: 600 V/2.8 A, Sorensen, San Diego, CA) was installed to apply external electric potential across the reactor. The applied electric potential to the BP system was fixed as 600 V that is 0.36 V to the BP electrode. Flow rate was controlled by using the peristaltic pump (Easyload® II, Cole-Parmer, Vernon Hills, IL) with the silicon tube (I.D. 4.8 mm, Masterflex®, Vernon Hills, IL). The solution in the reactor was flowed upward.

3. Results and discussion

3.1. Nitrate reduction mechanism on ZVI-BP electrode

Nitrate reduction to ammonium without any substance needs 8 electrons and pH is spontaneously increased by generation of OH^- (Eq. (1)) [6,14,15]. Meanwhile, nitrate reduction with hydrogen, namely nitrate hydrogenation is one of the nitrate reduction pathway and it is mainly occurred on the metallic catalysts [16–19]. The ZVI is one of the efficient monometallic catalysts because of low toxicity and price [2]. Nitrate reduction on the ZVI has several pathways according to the experimental conditions. Generally, nitrate oxidizes the ZVI to ferrous ion (Fe^{2+}) and nitrate was deoxidized to ammonium (Eq. (2)). This is the reversible redox reaction of the ZVI hence produced iron oxide is not easily allowed to go back to the metallic iron. But previous studies reported that acidic condition was better to increase the removal ratio of nitrate on the ZVI even the ZVI is not reproducible catalysts [2]. In this reason, repetitive supplements of the ZVI and the additional chemical substance to maintain low pH are essential on chemical reduction of nitrate with ZVI. On the contrary, electrochemical nitrate reduction with ZVI electrode is the electro-catalytic reaction and this reaction mainly occurred on the electrode surface with adsorbed nitrate [20]. Theoretically, no chemical reagent is needed in the electrochemical nitrate reduction [1]. By the water electrolysis, hydrogen ions are generated on the anode side of the ZVI-BP electrode and the hydrogen ions are participated in the nitrate reduction as the nitrate hydrogenation (Fig. 2). These consecutive reactions, namely Langmuir–Hinshelwood reactions are limited by the condition on the electrode and the electrochemical reactor [1]. If the reactions are limited by the mass transfer, the nitrate reduction steps followed in Eqs. (3)–(6) [21]. In the multi-step reactions, the number of utilized electron is estimated as one. In this study, the reaction rate was depended on the mass transfer rate of nitrate and the BP system had low current density because of low conductivity.