Electrochemical Investigation of Nitrate Reduction Mechanism Using Nano Zero Valent Iron

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Abstract: To identify the nitrate reduction mechanism and the pathways, the present work based on the electrochemical reduction of nitrate at the surface of carbon paste modified reduced graphene oxide nano zero valent iron (rGO-nZVI) composite electrode in a neutral pH electrolyte of 0.1 M NaCl + 0.4 mM $NaNO_3$. In an inert environment under three-electrode configuration, counter Pt and Ag/AgCl reference electrodes were used with working electrode. Electrochemical performance towards de-nitrification was investigated by cyclic voltammetry to identify the intermediate or final products. With 50 mVs^{-1} scan rate, the cathodic peak at -1.039 V implies the conversion of nitrate into nitrite. Nitrite ions from the initial reaction further converted into ammonia and confirmed it with the peak potential at -1.182 V. The peak at about -0.391 V implies the oxidation of nitrite into nitrate. Hydrogen desorption allows the formation of fresh surface sites therefore fresh surface with nZVI and surface bound nitrate further facilitate nitrate reduction. As a supporting material here, rGO enhances the stability of nZVI particles and their dispersion without participating the reduction pathways. However, the mechanisms for electrochemical reduction of nitrate to ammonia are highly complex due to the undesired reactions, products and stable intermediates.

Keywords: Electrochemical reduction, Groundwater, Nano zero valent iron, Nitrate

1. Introduction

Groundwater and surface water nitrate contamination due to anthropogenic activities break the natural nitrogen cycle and become a significant threat to human health at any stage of life. For this reason, the World Health Organization (WHO) guidelines specify 50 mg L^{-1} nitrate in drinking water (Ward et al., 2018) as the maximum permissible contaminant limit (MCL). With limited success, biological denitrification, ion exchange, and chemical reduction are some of the available nitrogen reduction technologies (Khoshro, Mirbagheri, & Sabbaghi, 2020; Sun, Zhou, Zhao, & Wu,

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2021) which convert nitrate into low valence state ammonia or nitrogen (N_2). However, among the various available methods, currently, there is an increasing interest in the application of micro/nano zero-valent metals like Fe, Zn, Al, Mg, etc. to reduce excessive nitrate levels in the water. Compared to these zero-valent metals, iron suitably matches this process because of the high surface area which leads to its high surface reactivity (Salam, Fageeh, Al-Thabaiti, & Obaid, 2015). Further ensuring sustainability, nZVI-based water treatment technologies are considered promising because of their easy operation, low dosage, high-cost effectiveness, and enhanced reactivity.

Effective surface area and the removal performance eventually decrease due to the strong tendency towards nZVI particle agglomeration. Easy oxidation of nZVI into iron oxide further decreases its reduction ability. Additionally, after the treatment process by separating the nZVI particles from the treated water, regeneration and reuse is also quite difficult. Therefore to overcome most of these limitations, the nZVI synthesis processes can be modified by either improving the surface of the particles or supported them on to the solid substrates (Halpegama, J.U et al., 2021).

During the nitrate reduction, ammonia is generated as the main product with little N_2 due to the poor ability of nZVI in the selective reduction of nitrate to N_2. Besides using nZVI solely, an effective denitrification process can be identified with nZVI incorporated reduced graphene oxide (RGO) due to the presence of a large number of microscopic galvanic cells (Halpegama, J.U et al., 2021). With the loss of electrons to form Fe^{2+}, nZVI act as anode while the rGO accelerate the reduction reaction as a cathode by accepting electrons or transferring them to target pollutants. The combined effects of adsorption, desorption, and reduction make the composite quite a complex system therefore identification of the reduction mechanism is challengeable (Song et al., 2020).

The present study synthesized a novel polyphenol-derived rGO-nZVI composite to remove excessive nitrate in groundwater. As the main objective, this study was based on the electrochemical investigation of the nitrate reduction mechanism further with molecular spectroscopic evidences.

2. Material and methods

2.1 Materials

To identify molecular spectroscopic evidences, polyphenol derived rGO-nZVI composite material was fabricated and denitrification process was followed up as documented in elsewhere (Halpegama, J.U et al., 2021). Sodium chloride ($NaCl \geq 99.0\%$) and sodium nitrate ($NaNO_3 \geq 99.0\%$) were in analytical grade and purchased from Sigma Aldrich (USA). For electrochemical characterization, freshly prepared composites were obtained and all the solutions were prepared with ultra pure water (0.055 µS/cm at 25 °C). Inert environment was maintained by purging high purity nitrogen gas ($N_2 \geq 95.0\%$) before initiating the electrochemical research work.

2.2 Nano zero valent iron corrosion product identification

Cold field emission scaning electron microscope (Hitachi, Japan SU8020) was used to identify the rGO-nZVI morphology and surface structures.

2.3 Electrochemical evidences for denitrification

Experiments related to the electrochemical reduction of nitrate were carried out in an undivided cell with carbon paste modified electrode (Cheng-Chi Kuo, 2014) (nafion mixed polyphenol derived rGO-nZVI composite material with 0.07 cm^2 surface area). Counter Pt and Ag/AgCl reference electrodes were further used with modified working electrode under three-electrode configuration. As an electrolyte 15 mL of 0.1 M NaCl + 0.4 mM $NaNO_3$ solution was used. Using CH instrument cyclic voltammetry analysis was performed to investigate the evidences of nitrate reduction. Before the experiment, all the solutions were kept in an inert environment after purging nitrogen. At a 50 ms^{-1} scan rate, te voltage was scanned from -2.0to 2.0.

3. Results and discussion

3.1 Characterization of polyphenol derived rGO-nZVI composite

The SEM images of polyphenol derived rGO-nZVI composite imply the heterogeneous morphology with coarse sheet like surfaces of rGO and nZVI particles. These particles were clearly observed in spherical shapes and well dispersed on the surfaces of rGO (Figure 1). EDS further confirmed the presence of elemental iron in the structure and the possibility of presence of corrosion products of iron oxides due to the immediate exposure to the environment. By forming a core-shelled structures, these nVI particles were well preserved and inhibit the oxidation of Fe(0) as documented in elsewhere (Halpegama, J.U et al., 2021).

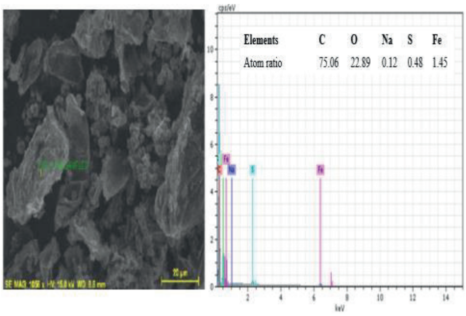

Figure 1 – SEM-EDS analyses of rGO-nZVI composite material

3.2 Electrochemical behaviors and contribution of surface oxidized nZVI on nitrate removal

Among these characterization techniques, cyclic voltammetry is used here, to identify the enhanced stability of nZVI in rGO-nZVI-P composite material compared to rGO-nZVI-B. In 0.01M NaCl, electrochemical characteristics of oxidation and reduction of iron species at the electrode can be observed only for the rGO-nZVI-B sample, but not for rGO-nZVI-P. This suggests reduced accessibility and lower electron transfer kinetics when iron was reduced by green tea catechines. At the same time, strongly increased currents are observed on both electrodes when NO_3^- is present in the solution (Figure 2). Consequently, according to our assumption, nZVI is reactive towards solution NO_3^- in both cases. Moreover, a comparison between the electrochemical signatures of green tea polyphenols to the CV of rGO-nZVI-P shows that green tea polyphenols clearly remain in the sample and are electroactive (Figure 2).

Previous research has shown that solution Fe^{2+} species can sustain NO_3^- reduction on nZVI particles through charge exchange with surface iron oxide species. Hence, Fe^{2+} in solution contributes to the overall reduction of NO_3^- by being itself oxidized, but catalysed through the oxidized nZVI particle surface. On the surface of nZVI, electron transfer between Fe^{2+} and Fe^{3+} occurs, and when the Fe^{2+} is in the solution, it will further promote the NO_3^-/NO_2^- redox conversion. This implies that, in the $NO_3^-/NaCl$ system, spontaneous electron transfer between Fe^{2+} and Fe^{3+} is crucial for promoting the NO_3^-/NO_2^- redox reactions (Han et al., 2016).

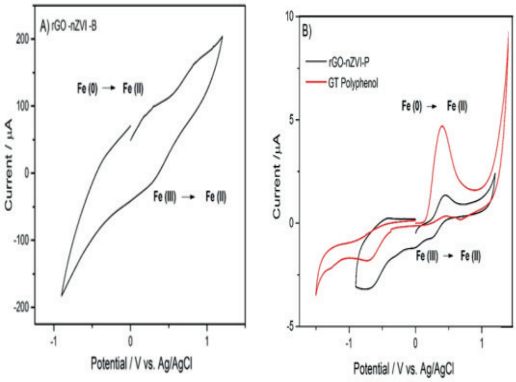

Figure 2 – A. Cyclic voltammogram of rGO- nZVI- B modified GCE in 0.0161 mM $NaNO_3$ and 0.01M NaCl under nitrogen purging. B. Cyclic voltammogram of rGO- nZVI-P modified GCE in 0.0161 mM $NaNO_3$ and 0.01 M NaCl at 25 ^{0}C under nitrogen purging and the GCE immersed in GT polyphenol extracted 0.01 M NaCl under nitrogen purging.

In rGO-nZVI-B, the anodic peak at +0.398 V occurs due to $Fe^0 \rightarrow Fe^{2+}$ oxidation. Although, polyphenols by themselves cannot reduce nitrate in solution, when the rGO-nZVI-P modified GCE is used, the enhanced anodic peak at +0.440 V is ascribed to a synergy between Fe (0)→ Fe (II) and polyphenol oxidation. The slight shift of the peak at +0.440 V signifies the enhanced stability of Fe (0) when polyphenol is present in the composite. Therefore, we ascribe the improved NO_3^- reduction efficiency in the rGO-nZVI-P sample to adsorbed polyphenols acting as electron source for the nZVI catalyst in reducing NO_3^-.

4. Conclusions

Polyphenol derived rGO-nZVI composite effectively remove nitrate in the contaminated groundwater. Ammonia is the major product accounting nitrite and nitric oxide as a byproduct. Electrochemical investigation of reduced species of nitrate is challengeable due to the complex nature of the electrode material and the combined effects of adsorption, desorption and reduction. Therefore, this work further suggest the requirement of advanced electrochemical techniques for the investigation.

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