

Electrochemically-induced Reduction of Nitrate in Aqueous Solution

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In this study, we evaluated the removal of nitrate from synthetic groundwater by a cathode followed by an anode electrode sequence in the electrochemical flow-through reactor. We also tested the feasibility of the applied electrode sequence to minimize the production of ammonia during the nitrate reduction. The performance of monometallic Fe, Cu, Ni, and carbon foam cathodes was tested under different current intensities, flow rates/regimes, and the presence of Pd and Ag electrode coating. With the use of monometallic Fe and an increase in current intensity from 60 mA to 120 mA, the nitrate removal rate increased from 7.6% to 25.0%, but values above 120 mA caused a decrease in removal due to excessive gas formation at the electrodes. Among tested materials, monometallic Fe foam cathode showed the highest nitrates removal rate, which further increased from 25.0% to 39.8% in the presence of Pd catalyst. In addition, the circulation under 3 mL min⁻¹ elevated the nitrate removal by 33%, and the final nitrate concentration fell below the maximum contaminant level of 10 mg L⁻¹ nitrate–nitrogen (NO₃-N). During the treatment, the yield of ammonia production after the cathode was 92±4%, while after the anode (Ti/IrO₂/Ta₂O₅), the amount of ammonia significantly declined to 50%. The results proved that flow-through, undivided electrochemical systems with Fe cathodes can be used to remove nitrate from groundwater to safe levels with the possibility of simultaneously controlling the generation of ammonia via anodic processes.

Keywords: electrochemical; nitrates; ammonia; groundwater; cathode.

1. INTRODUCTION

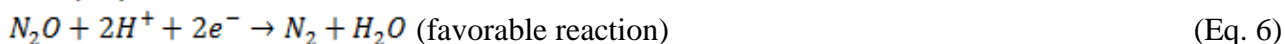
Nitrates are commonly found in groundwater at high levels due to intensive release from nitrogen fertilizers, industrial wastes, animal wastes, and septic systems, and their presence at high concentrations presents a significant environmental problem [1]. Higher levels of nitrates are found in private wells than in public water systems, in shallow wells (<100 feet below land surface) than in

deep wells, and in agricultural areas than in urban areas. About 16% of the U.S. population uses private, unregulated water systems that are usually located in areas considered more vulnerable to nitrate contamination (i.e., rural areas). The maximum contaminant level (MCL) for nitrates in drinking water is 10 mg L⁻¹ nitrate–nitrogen (NO₃–N) or 45 mg L⁻¹ nitrate (NO₃⁻), and exposure to elevated levels of nitrates are reported to cause methemoglobinemia, or "blue baby" disease [2].

The best available technologies for treatment of nitrate-contaminated water include reverse osmosis, electro-dialysis, and ion exchange [3]. However, the utility of these processes has been limited due to their expensive operation costs and the subsequent problem of disposing the generated nitrate waste brine. Alternatives methods that have a potential to be used *in situ* are biological denitrification, chemical reduction, and physical adsorption [4].

Similar to chemical reduction, electrochemically-induced reduction of nitrate is a practical approach that is influenced by the type of electrode, type of catalyst, pH, and hydrogen flow [5-11]. The main advantages of electrochemical reduction include *in situ* generation of hydrogen at the cathode via water electrolysis, the possibility of using catalysts in small amounts (as cathode coating), and low energy consumption if alternative power sources are used (e.g., solar power) [12-18], while the main challenges relate to reduction selectivity towards nitrogen gas production [7, 19-22].

The electro-reduction of nitrate at the cathode is a very complex process which starts with nitrate ion adsorption (Eq. 1) and involves the simultaneous transfer of one electron and proton from a proton donor (e.g., water molecule, hydroxonium ion) (Eq. 2) that leads to a series of reactions.



Among tested materials, Cu-modified Pd electrode shows a higher capacity of nitrate reduction than a monometallic Pd electrode [22]. The nitrates reduction activity and selectivity are determined by bimetallic ensembles containing Pd with Cu or Sn as promoters, at which the nitrates are adsorbed [8]. Further, nitrates are reduced to nitrites by atomic hydrogen (H_a), which is supposed to spill over from Pd sites to the bimetallic sites [9]. However, the use of expensive bulk Pt and Pd is a disadvantage from a practical viewpoint. Cost-effective materials such as graphite, Ni, and Fe are used as cathodes with promising results for nitrate removal and selectivity towards nitrogen gas production [7, 21, 23]. Catalyst-modified electrodes are used to improve the electro-reduction and enable the full scale application. For example, the Pd-modified Cu electrodes show the highest electrocatalytic capacity and stability in the nitrate-reduction process [21].

The optimization of electrochemical setup for nitrates removal has been studied for both undivided [19, 20, 24] and divided electrochemical cells [21, 23]. Although the divided cells provide

easier control of the conditions since electrolytes are split with the membrane, their use is impractical for the groundwater treatment applications [13, 15, 25-28], and the production of ammonia in catholyte increases over time [7]. The undivided cell offers a simpler design and lower energy consumption, but the water electrolysis products can adversely influence the removal of the target contaminant; oxygen formed at the anode can also be reduced at the cathode, which competes with the reduction mechanisms. A flow-through cell with the cathode placed in front of the anode, with respect to the flow direction, has been developed by our laboratory to minimize the adverse effect of oxygen on reduction processes at the cathode and allow sequential reduction and oxidation zones [29]. In undivided cells, ammonia removal can be induced via oxidation at “non-active” type anodes or via reaction with hypochlorite formed at the anode in the presence of high concentration of chlorides. However, but this approach is more applicable for wastewater treatment or possibly for the treatment of groundwater in coastal areas that is susceptible to saltwater intrusion [30].

To the best of our knowledge, the flow-through electrochemical systems, especially those using foam cathodes for the removal of nitrate in groundwater, have not been investigated so far. The main objective of this study was to investigate nitrate reduction by different commercially-available and cost-effective cathode foam materials. The goal is to evaluate the performance of a system that operates under the cathode followed by an anode sequence to sequentially reduce nitrate at the cathode and oxidize ammonia at the anode. We tested Fe, Cu, Ni, and carbon foam in the absence and presence of Pd and Ag as cathode coatings for nitrate removal under different current intensities and flow modes. The use of bimetallic Fe cathodes was not evaluated so far for the nitrate removal.

2. EXPERIMENTAL

All chemicals used in this study were analytical grade. Calcium sulfate was purchased from JT Baker. Sodium nitrate and sodium bicarbonate were purchased from Fisher Scientific. Sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) were from Sigma-Aldrich. Deionized (DI) water ($18.2 \text{ M}\Omega \cdot \text{cm}$) from a Millipore Milli-Q system was used in all the experiments.

A vertical acrylic column was used as an electrochemical undivided cell [14]. The galvanostatic experiments were conducted under the experimental conditions given in **Table 1**. Ti/mixed metal oxide (MMO) mesh (3N International) was used as the anode in all experiments. The Ti/MMO electrode consists of IrO_2 and Ta_2O_5 coating on a titanium mesh with dimensions of 36 mm diameter by 1.8 mm thickness. Fe foam (45 pores per inch, PPI, 98% iron and 2% nickel) was purchased from Aibixi Ltd., China, and Ni foam (100 PPI, Purity>99.99%) was purchased from MTI corporation. Cu foam (40 PPI, Purity>99.99%) and carbon (C) foam (45 PPI, Purity>99.99%) were purchased from Duocel®. We used Fe, Cu, C, and Ni foam as commercially available electrode materials with high reactive surface areas. Using electrodes with a high active area is of great importance for flow-through systems in order to increase the time for the reaction between target contaminant and the electrode surface. Holes (0.5 cm diameter) were drilled in the foam cathodes to prevent accumulation of gas bubbles in the cathode vicinity. Ni foam was immersed in 80 g L^{-1} sulfuric acid for 5 minutes to remove the oxide layer and then washed thoroughly with water. Fe

electrodes were immersed in 1 M HCl to remove any foreign metals and surface oxide layers. The palladization procedures for Fe and Cu foam were performed under the conditions given in *Rajic et al., 2016* [29]. The Pd content at Fe and Cu was 0.5 mg cm^{-2} of geometric electrode surface area. The amount of Pd selected was based on our previous work and application for trichloroethylene (TCE) removal [29]. The electroplating of Ag on Fe foam was performed at -0.4 V vs SCE for 30 minutes resulting in the 68.9 mg of Ag deposited at the electrode (3.4 mg cm^{-2} of geometric electrode surface area).

Table 1. Experimental conditions

Foam Cathode	Catalyst Coating	Current Intensity (mA)	Flow (mL min^{-1})	Solution
Fe	-	60, 90, 120, 200	3	$22.5 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$
Fe	-	120	10	$22.5 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$
Fe	-	120	3	$11.25 \text{ and } 22.5 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$
Ni	-	120	3	$22.5 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$
C	-	120	3	$22.5 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$
Cu	-	120	3	$22.5 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$
Cu	Pd (0.5 mg cm^{-2})	120	3	$22.5 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$
Fe	Pd (0.5 mg cm^{-2})	120	3, 10 (circulation)	$22.5 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$
Fe	Ag (3.4 mg cm^{-2})	120	3 (circulation)	$22.5 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$

Synthetic groundwater was prepared by dissolving 413 mg L^{-1} sodium bicarbonate and 172 mg L^{-1} calcium sulfate in deionized water. The concentrations of bicarbonate ions and calcium ions are representative of groundwater from limestone aquifers, resulting in electrical conductivity of 800 to $920 \mu\text{S cm}^{-1}$. The sodium nitrate was added to the solution to achieve concentrations of 50 and 100 mg L^{-1} of nitrates ($11.25 \text{ and } 22.5 \text{ mg L}^{-1}$ as $\text{NO}_3\text{-N}$). The initial pH of the contaminated synthetic groundwater was 8.2 ± 0.3 , and the initial oxidation-reduction potential (ORP) value was $210 \pm 5 \text{ mV}$. The temperature was kept constant at 25°C . There were no changes in the solution temperature during the treatment. Synthetic groundwater flow through the column was maintained by a peristaltic pump (Cole Parmer, Masterflex C/L). Galvanostatic conditions during treatments were maintained by an Agilent E3612A DC power supply. The experiments were conducted at current intensities which support the hydrogen formation and, therefore, the reduction of nitrates. Although hydrogen formation competes with nitrates reduction, these conditions were applied as suitable for real application and possible reduction of other species that can occur in groundwater (e.g., TCE).

Analysis of nitrates and nitrites was performed by an ion chromatograph (IC) (Dionex 5000) equipped with an AS20 analytical column. A KOH solution (35 mM) was used as a mobile phase at a flow rate of 1.0 mL min^{-1} . Ammonia concentration in the samples was measured according to the phenate method.

The nitrate concentration is determined at specified times during treatment. The efficiency of the materials performance was first assessed only based on nitrates removal; the most efficient setup

was further investigated on mechanisms of removal. Results are expressed as the means of the duplicate experiments with their corresponding standard deviations being less than 2%. The control experiment (flow without the current) showed that there is no adsorption of nitrates on the reactor material, electrodes or tubing used in the experiments. Current efficiencies (CE) were calculated according to Faraday's law; it is assumed that the electrochemical reduction of nitrate involves 5 electrons for production of nitrogen gas. Energy consumption (EC) was calculated as watt hour per g of nitrate removed during treatment (Wh g^{-1}).

3. RESULTS AND DISCUSSION

3.1. Monometallic cathodes

We tested the performance of different cathode materials for nitrate removal in an undivided flow-through electrochemical cell (Fig. 1). The nitrate removal efficiency for monometallic Ni foam was 6.57% and for C foam was 5.29%, indicating that these materials are not suitable for the nitrates removal, which is consistent with other studies [23, 24, 31]. Nitrate transformation at the cathode involves series of reactions; nitrate sorption (Eq. 1) and the chemisorption of H_a at the electrode (Eq. 2) are of great importance for the reaction rate and highly vary for different electrode materials. As given in the modern volcano plots calculated based on hydrogen adsorption energies [32, 33], materials such as Pt, Pd, Ni, and Co are good catalysts for H_a evolution. This means that their metal- H_a bond energies enable fast H_a discharge and H_a desorption from the metal surface that promote reaction with protons or other reducible species like nitrates [34]. However, Ni cathode showed limited performance under the conditions used in this study (Fig. 1). It is assumed that, as in the case of Pd catalysts/electrodes [8, 9], Ni is a good electrocatalyst for H_a discharge but has weak ability to sorb nitrate. Therefore, secondary metals are needed to promote the nitrate adsorption step (Eq. 1). This was reported for Ni-Cu alloy cathodes where the performance was related to the synergistic effect of adsorption of nitrate at Cu sites and cathodic discharge of H_a at Ni sites [24, 31].

Further, we tested the performance of Fe and Cu foam cathodes under current intensity of 120 mA and flow of 3 mL min^{-1} , and nitrate removal efficiencies after 3 h were 25.0% and 22.1%, respectively. The Fe foam showed higher efficiency for nitrate removal among tested materials (Fig. 1), and the final nitrate concentration after treatment fell below MCL ($10 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$). Although scarce, other studies on Fe cathode showed significant performance towards nitrate removal and indicated that reduction occurs via a consecutive-reaction mechanism [23, 35]. Fe and Cu are proven to promote nitrate sorption (Eq. 1) [9, 36], while based on their metal- H_a bond energies, they can sufficiently supply nitrate with H_a and promote hydrogenation [33].

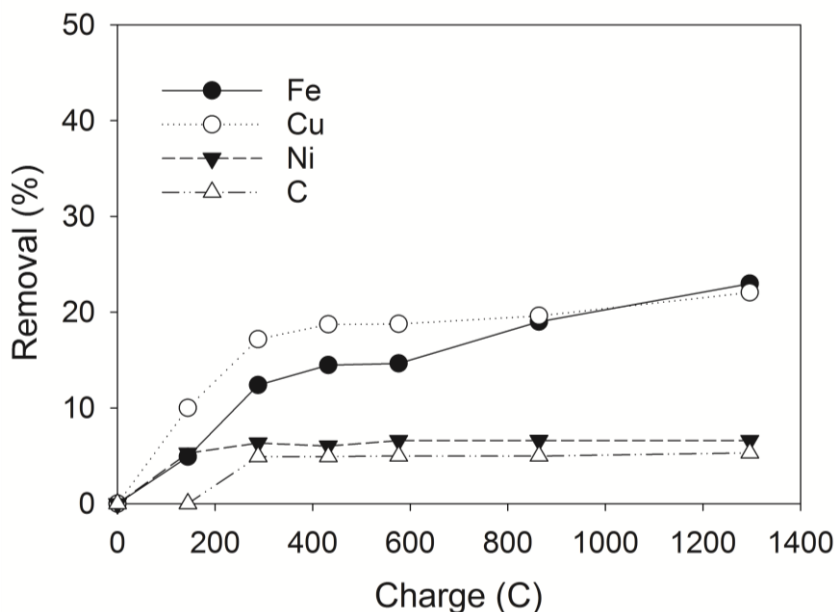


Figure 1. Nitrate removal by different cathode materials (120 mA current intensity, flow of 3 mL min⁻¹, 22.5 mg L⁻¹ NO₃-N)

However, the nitrates reduction process is compromised by a hydrogen gas evolution reaction that occurs in parallel. In addition, in the systems that operate under very negative reduction potentials, the reduction of nitrates at the cathode is suppressed by the repulsion between the anion and similarly charged electrode. These processes limit overall nitrate removal for all cathode materials tested in this study (Fig. 1). Also, the short retention time for the reaction in the flow through system and oxidation of reduction byproducts to nitrate adversely affect the reduction mechanism [7]. The repulsion between nitrate and the cathode under high negative potentials might be suppressed by the presence of Na⁺ and Ca⁺ ions, which may form ion pairs and ion bridges with the reacting ion [37]. This might influence the hydrogen evolution reaction mechanism, but the hydrogen evolution reaction through cation discharge has been investigated for Sn and Pb cathodes and was not the purpose of this study.

In addition, we tested the nitrates removal with a Fe foam cathode under different current intensities (Fig. 2). The increase in the current intensity from 60 mA to 120 mA resulted in a removal increase from 7.6% to 25.0%, respectively. However, further increase in current intensity (200 mA) resulted in the 23% of removal efficiency. The intensive hydrogen gas production at the cathode due to water electrolysis competes with nitrate hydrogenation while bubbles formation minimizes the sorption of nitrate ions on the cathode [38, 39]. The CEs for 60 mA, 90 mA, 120 mA, and 200 mA are: 4.33%, 1.77%, 6.19% and 2.78%, respectively. ECs per g of nitrates removed are (kWh g⁻¹): 1.25, 3.05, 0.87, and 1.94. Both CE and EC indicate that 120 mA is the optimum current intensity under tested conditions.

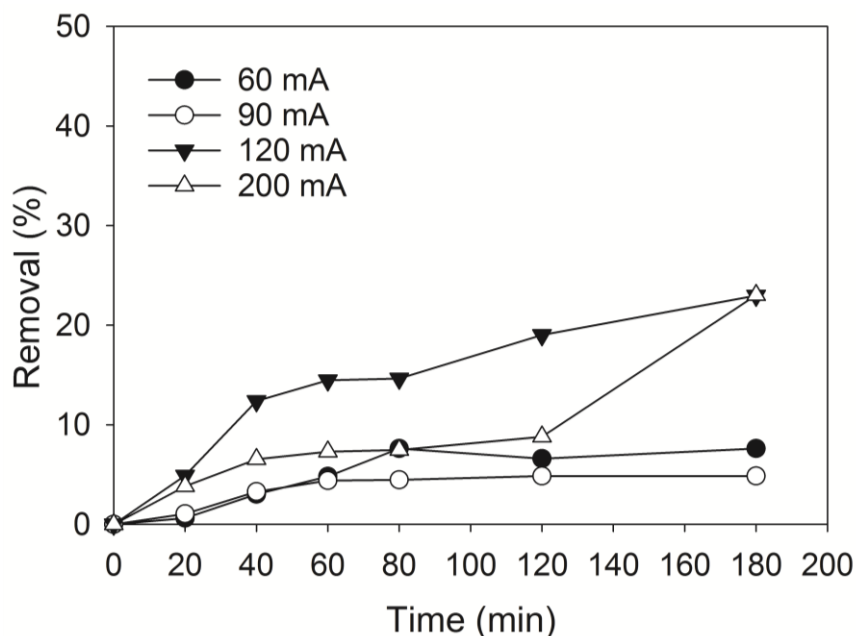


Figure 2. Nitrate removal under different current intensities (Fe foam cathode, flow of 3 mL min^{-1} , $22.5 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$, 180 min)

3.2. Bimetallic cathodes

As mentioned, bimetallic electrodes and catalysts showed superior performance for the nitrate reduction compared to monometallic forms and have been mostly investigated for Cu and Pd modified Cu materials [7, 21, 22, 24]. In this study, the removal of nitrate by palladized Cu foam electrodes (0.5 mgPd cm^{-2} geometric area) increased by 25%. The proposed mechanism for bimetallic Pd/Cu materials rely on high ability of Cu to sorb nitrates (Eq. 1) as well as good electrocatalytic capability of Pd for fast formation of H_a and catalysis of the nitrites reduction [8]. However, the overall low performance of palladized Cu foam under tested conditions is due to the small amount of Pd used; it was previously reported that the Pd:Cu as weight ratio should be equal to 4:1 or 6:1 depending on the preparation procedure for Pd–Cu catalysts [9]. This ratio suggests a high amount of Pd, which due to its cost, would be a disadvantage for the real system application. In addition, the tested bimetallic cathode showed low overall removal, therefore, no further investigation was performed on the nitrate removal mechanism.

Further, the addition of Pd on Fe foam cathode was investigated to promote nitrate removal by creating sufficient amount of H_a , while Ag coating was used to promote the nitrate adsorption step (Eq. 1) [40]. The bimetallic Pd and Ag-modified Fe cathode were not investigated for nitrate removal so far. In our system, the use of palladized Fe foam compared to monometallic Fe caused an increase in nitrate removal from 25% to 39.8%. Due to similar performances of monometallic Fe and Cu cathodes (Fig. 1), known promoters for nitrate removal, and similar metal- H_a bond energies for these two metals, it is assumed that Fe and Cu used in this study have similar promoting abilities. Pd is known to have low affinity to adsorb nitrate, while Fe (as chemical catalyst in presence of hydrogen gas) was reported to achieve high efficiencies of nitrate reduction, even without the presence of promoting

metals such as Cu [36, 41]. This indicates that the removal mechanism most likely relies on a synergistic effect of Fe ability to promote nitrate adsorption (Eq. 1) and an extensive cathodic discharge of H_a from Pd sites.

On the contrary, only 11% of the nitrate was removed by Ag coated Fe foam. The decrease in the removal efficiency of Ag coated Fe foam compared to the monometallic Fe foam cathode (25%) is due to the foam coverage with Ag sites (much higher than Pd), which pose weaker promoter activity than Fe. However, some studies reported that Ag activity depends on the preparation method [40].

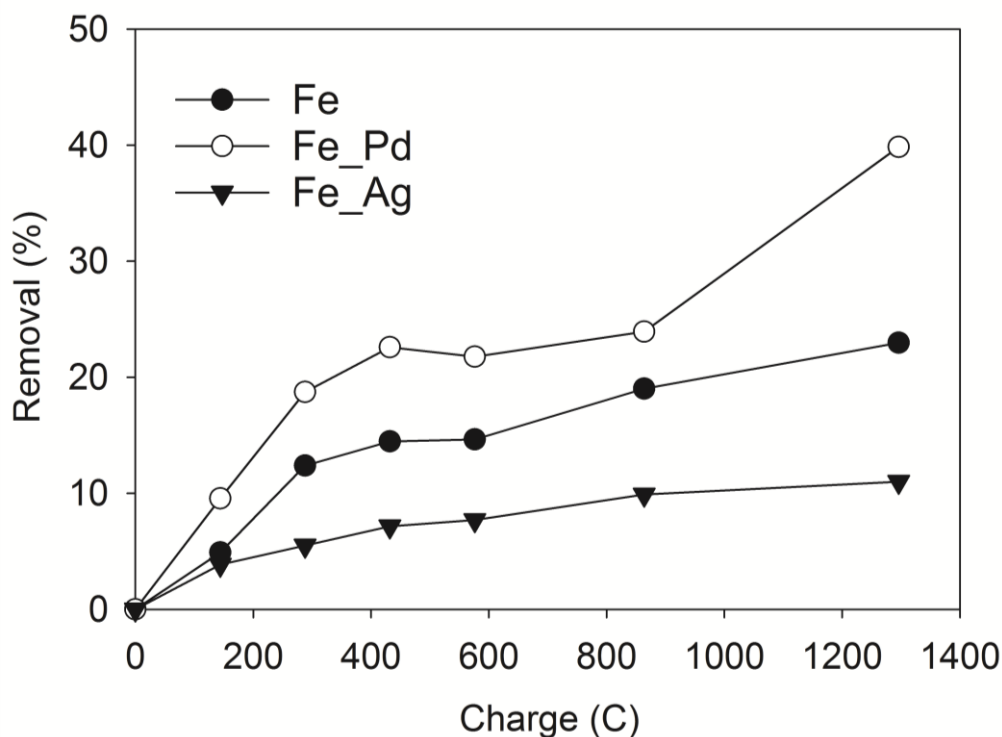


Figure 3. Nitrate removal in the presence of different catalysts and support materials (120 mA current intensity, flow-through under 3 mL min^{-1} , $22.5\text{ mg L}^{-1}\text{ NO}_3\text{-N}$)

3.3. Influence of flow modes

Further, we circulated the solution under 3 mL min^{-1} and 10 mL min^{-1} flow velocities in order to improve the removal efficiency of palladized Fe foam by increasing the reaction time (Fig. 4). We tested different flow velocities to evaluate the influence of the mass flux. The circulation under 3 mL min^{-1} increased the removal from 39.8% under flow-through conditions to 53.2%. The circulation of the solution allows an increase in time for the reaction at the cathode, but since the initial concentration decreases, the removal rate decreases during the course of treatment. An increase in the circulation flow rate from 3 mL min^{-1} to 10 mL min^{-1} significantly decreased the removal from 53.2% to 34.3%, respectively. The increase in flow increases the mass flux but decreases the time needed for the reactions.

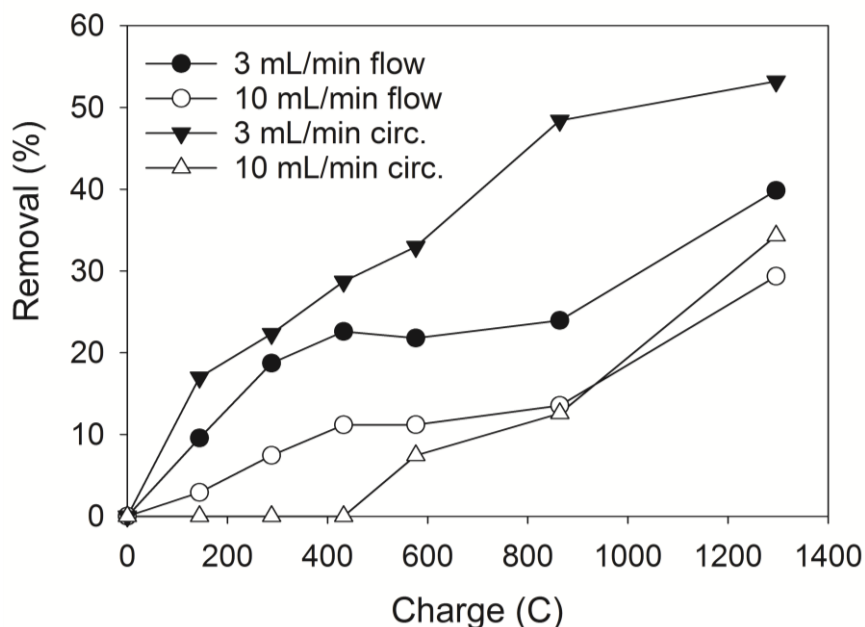


Figure 4. Nitrate removal under flow modes and flow values (Fe/Pd foam cathode, 120 mA current intensity, $22.5 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$)

3.4. Nitrate removal mechanism

The removal mechanism in the electrochemical cell used in the study was tested by measuring the amount of nitrates, nitrites, and ammonia at different sampling ports (initial, after cathode and after anode) for the palladized Fe cathode under 3 mL min^{-1} circulation; Fig. 5 shows the nitrate removal at each sampling port. The results show that the nitrate reduction occurs after the cathode and that there are no changes of removal after the anode (as nitrates are not subject to oxidation). A slight increase in nitrate concentration after anode during the first 60 minutes of treatment indicates that some of the reduction byproducts oxidize to the original nitrate, similarly noticed in [20]. Nitrites were not detected in the samples at each sampling port. The ammonia produced after the cathode had a yield of $92 \pm 4\%$. However, at the steady state after the anode, the amount of ammonia decreased significantly to 50%. This implies that the cathode followed by an anode sequence can be optimized for high removal efficiency with decreased formation rate for ammonia. Ammonia oxidizes to nitrogen gas by the oxygen produced at the anode; the Ti/MMO electrode used in this study is an “active” anode which has low oxygen overpotentials and produces oxygen due to water electrolysis [42]. Since there is no increase in nitrite and nitrate concentration after the anode, the ammonia most likely oxidizes to nitrogen gas.

After the cathode, pH value increases due to water electrolysis (Eq. 2) and nitrate reduction to nitrite (Eq. 3). The pH changes in the effluent during the treatment are negligible; the pH value of the effluent after 180 minutes of treatment is 7.5. Since H^+ ions form at the anode as the result of water electrolysis, the neutralization of hydroxyl ions takes place. The ability to automatically regulate pH during the treatment without any additional equipment is of great importance for the field application.

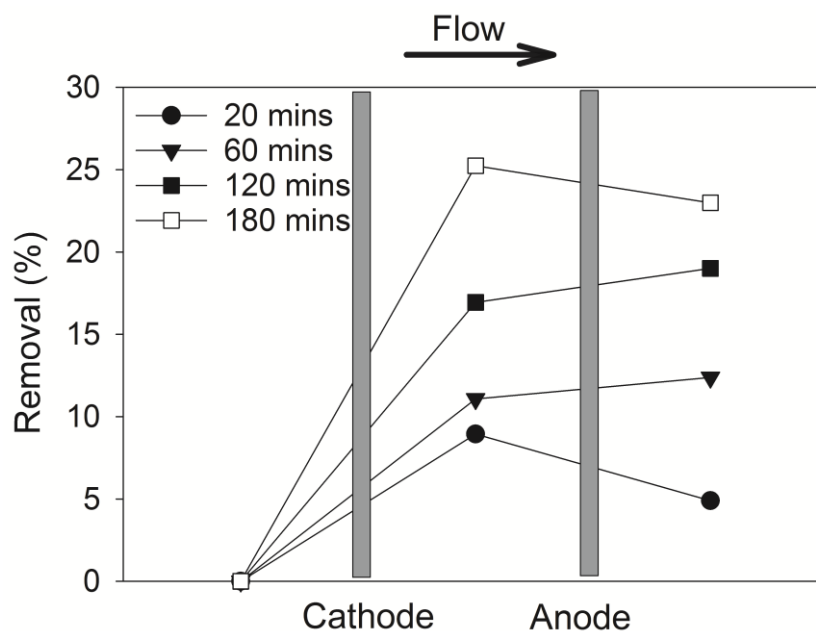


Figure 5. Nitrate removal at different sampling ports (Fe foam cathode, 120 mA current intensity, flow of 3 mL min^{-1} , $22.5\text{ mg L}^{-1}\text{ NO}_3\text{-N}$)

4. CONCLUSIONS

In this study, we evaluated the removal of nitrates in the electrochemical flow-through reactor that utilized the cathode followed by an anode electrode sequence. The performance of various cathode materials was tested under different current intensities, flow rates/regimes, and the presence of catalysts. Among tested materials, monometallic Fe foam cathode showed the highest nitrates removal rate. In the presence of Pd catalyst coating, Fe foam showed significant increase in nitrates removal compared to the monometallic Fe foam cathode: from 25.0% to 39.8% of nitrates removed, respectively. The increase in current intensity showed an increase in the nitrate removal rate. However, values above 120 mA caused a decrease in removal due to excessive gas formation at the cathode. The increase in flow rate from 3 mL min^{-1} to 10 mL min^{-1} decreased nitrate removal rate by 36%, while the circulation under 3 mL min^{-1} increased the removal from 39.8% under flow-through conditions to 53.2%. The results prove that the palladized Fe cathode followed by Ti/MMO anode sequence in the flow-through electrochemical cells can be used for sequential nitrate reduction and ammonia production control at the anode, but further optimization of the anode material is needed to achieve lower levels of ammonia in the effluent.

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