Title
Electrochemically Mediated Removal of Nitrate on Granular Activated Carbon

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Publication Date
2016

UNIVERSITY OF CALIFORNIA
RIVERSIDE

Electrochemically Mediated Removal of Nitrate on Granular Activated Carbon

A Thesis submitted in partial satisfaction
of the requirements for the degree of

Master of Science

in

Chemical and Environmental Engineering

by

Katherine Rose Muller

August 2016

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Acknowledgments

This thesis would not have been possible without the extensive support, guidance, and expertise of my advisor, Dr. David Jassby. His professional and personal advice were the cornerstones of this project and of my own growth as a student and researcher. I would like to specifically thank him for guiding this project so patiently and constructively.

I am very grateful to Dr. Sharon Walker and Dr. Haizhou Liu for serving as my committee members, as well as supporting my experimental work for the past two years.

I would also like to acknowledge the other students who supported me and contributed to this work, specifically Wenyan Duan and Avner Ronen, who I thank for their extensive practical advice, support, and professional guidance. I am also thankful to Michelle Chebeir, Leo DeRita, Sarah Taylor, and Alexander Dudchenko for contributing to experimental work and design on this project, and to all of the water laboratory students. I also thank Dr. Ilkeun Lee and the Analytical Chemistry Instrumentation Facility for assisting with sample analyses.

This thesis research was financially supported by the NSF WaterSENSE IGERT research grant, the Department of Chemical and Environmental Engineering at the University of California-Riverside, and the California Space Grant Fellowship.

Dedication

I dedicate this work to my parents, for their endless support and for being shining examples of love, empathy, and conscience. This thesis is submitted in partial satisfaction of their unwavering belief in me.

ABSTRACT OF THE THESIS

Electrochemically Mediated Removal of Nitrate on Granular Activated Carbon

by

Katherine Rose Muller

Master of Science, Graduate Program in Chemical and Environmental Engineering
University of California, Riverside, August 2016
Dr. David Jassby, Chairperson

Nitrate in drinking water poses a serious public health risk which affects water sources in California and around the world. The environmental risks of nitrate are twofold: as a contaminant in drinking water it threatens the health of infants and pregnant women, and in lakes and coastal regions it contributes to algae blooms, eutrophication, and hypoxic “dead zones.” However, nitrate is an extremely stable and soluble contaminant, which makes cost-effective removal very difficult. Activated carbon adsorption of contaminants is an accessible, economical method of water purification, but activated carbon is highly inefficient at adsorbing nitrate. Electrochemical reduction of nitrate is achievable, but has excessive energy requirements and often necessitates high-pressure or high-temperature water treatment.

Electrochemically-mediated nitrate removal on granular activated carbon (GAC) provides the benefits of both adsorption and electrochemical treatment methods and produces a high-quality permeate stream under room temperature and atmospheric pressure. Application of 5V to a GAC packed-bed filter doubled nitrate removal over 24-hour filtration period with no observed generation of ammonia or nitrate. In addition, a reverse-polarity rinse of the filter system allowed for complete regeneration of the removal efficiency of the GAC.

This removal was determined to be pH-insensitive, linearly dependent on hydraulic retention time, and moderately sensitive to interference by inorganic salt species commonly observed in groundwater. As a new treatment method for nitrate-contaminated water, electrochemically-mediated removal of nitrate on GAC offers a highly efficient, green, and reusable method with significant potential for drinking water applications.

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1. Introduction

1.1 Motivation

The importance of clean, sustainable drinking water resources to global public health cannot be overstated. Severe, ongoing droughts threaten large portions of the globe, and many more regions will face water shortages as a result of climate change. Sustainable groundwater management and wastewater reuse are two core segments of most water management plans; however, both require extensive water treatment.[1][2] Groundwater supplies must be protected from contaminant leaching, while wastewater reuse is dependent on the removal of hazardous compounds.[3]

As the global demand for water increases, so does the demand for better water treatment technologies. New methods are needed that can treat drinking water efficiently and effectively despite a variety of water quality challenges. At the same time, these methods must be more environmentally benign and less centralized in order to allow widespread use.[4] Given the current state of water availability, new treatment methods that meet these requirements can offer a significant benefit to global health and sustainability.

1.2 Nitrate Contamination

Nitrate is one of the most widespread contaminants in groundwater, which is released into the environment primarily through agricultural runoff.[5] Nitrate is a public health hazard in drinking water, with the major health concern stemming from nitrate exposure being methemoglobinaemia, a form of anemia that occurs in infants due to high nitrate exposure.[6] Furthermore, nitrate has been linked to a higher incidence of several cancers, including gastric cancer, as it may serve as a precursor to carcinogenic N-nitroso compounds.[7][8] Nitrate contamination of surface waterways has also led to severe environmental degradation; nitrate has been shown to be a major contributor to eutrophication in rivers, lakes, and coastal regions.[9] Algal blooms fed by nitrate releases also pose a direct threat to human health and water supplies.[10]

Unfortunately, elevated nitrate concentrations occur in water supplies worldwide, and groundwater nitrate contamination is a threat to public health in regions ranging from Southern California to China and India.[11][12] Nitrate is of specific concern in rural, agricultural, and low-income areas where agricultural runoff management is limited.[13][14] Regions that lack the economic resources to manage nitrate using traditional treatment methods are in need of accessible solutions to prevent long-term health consequences.[15]

Nitrate is a particularly concerning contaminant due to its extreme stability and solubility. Nitrate does not form low-solubility compounds that can be easily removed via sedimentation, is slow to degrade over time, is difficult to convert to nitrogen gas, and is soluble in water up to nearly 1 kg/L at room temperature.[16][17] While a variety of methods for removing nitrate do exist, they are limited by both energy consumption and infrastructure requirements.[18] As a result, nitrate contamination in groundwater is a serious, intractable limitation on the provision of safe drinking water and the protection of existing groundwater supplies.

1.3 Nitrate Removal

Nitrate is extremely difficult to treat in water; the methods that are applicable are often energy-intensive, infrastructure-intensive, or both.[16] The most common method of nitrate treatment is biological denitrification, where nitrate is converted to nitrogen gas (N_2) via a biological treatment process.[19] While this method is very effective, its applicability is typically limited to wastewater treatment due to the lack of carbon sources in groundwater.[20] Biological denitrification also requires significant infrastructure and includes disinfection steps to remove bacteria.[21] As a result, biological denitrification is primarily used in large-scale centralized wastewater treatment, where other biological treatment such as nitrification is already performed, and operators can afford to install and monitor the necessary infrastructure.[22][23] In addition, there are concerns with using biological processes to treat drinking water due to the potential bacterial contamination of the treated water, as well as the addition of microbial carbonaceous and nitrogenous products, whose presence in drinking water can lead to the formation of disinfection byproducts.[21][24]

Reverse osmosis (RO) and ion-exchange (IX) resins have also been demonstrated to be effective nitrate removal methods, but have significant drawbacks in the form of brine production, energy consumption, and complexity. Brine generation is a serious environmental issue and is an inherent part of both RO and IX.[25] This brine is usually disposed of in the ocean, making safe brine management difficult outside of coastal regions.[26] Both of these methods are also dependent on complex, sensitive systems that require expensive resins and membranes. IX nitrate removal methods also produce brine, which necessitates extensive post-treatment for disposal.[11][18] In addition, the most common IX resins preferentially bind to chloride and bicarbonate over nitrate, limiting the possible application of IX in groundwater treatment.[27]

Electrochemical reduction of nitrate is a possible alternative method for nitrate removal, due to its wide applicability to contaminants and its structural simplicity.[22][28] However, many current electrochemical methods have limited feasibility due to their over-reduction of nitrate, high energy consumption, extreme conditions, or the need for chemical additives.[4][7][29] Generally, a metal species must be present to catalyze the reaction, with copper, nickel, and iron being common choices, although they may over-reduce nitrate to ammonia, limiting their effectiveness.[4][16][30] Bockris and Kim (1997) reported a method for a relatively low-energy nitrate reduction on a nickel-based packed bed column, which also offered the possibility of treating other salts and metals.[31] The reduction of nitrate to ammonia by zero-valent iron has been shown to achieve complete nitrate removal, but requires the constant addition of buffers and iron to the treatment water.[29] Graphite electrodes have been proposed as an alternative to metal species, but Dash and Chaudari (2005) reported that these electrode have only an 8% reduction effectiveness.[32]

A promising technique for cost-effective removal of nitrate is adsorption. In addition to being inexpensive and easily scalable, adsorption techniques are generally environmentally benign and pose little risk to drinking water safety.[10] However, the widespread use of adsorption methods for nitrate removal is limited by the availability of effective adsorption substrates.[6] Commercially available granular activated carbon (GAC) is one of the most economical and widely used substrates available, but GAC has a relatively low maximum room temperature adsorption effectiveness of 1.2 x10^{-3} mg NO_3-N/m^2 GAC area.[30][33] In addition, the adsorption of nitrate onto GAC is extremely slow, requiring multiple days of exposure to relatively high nitrate concentrations to reach maximum adsorption.[13] Work has been done to increase the adsorption capacity of activated carbon, e.g. using a variety of highly-efficient activated carbon sources, such as bamboo, or by functionalizing the GAC surface. [10][33] Additionally, GAC is a potentially effective treatment method for an enormous variety of contaminants; an improvement in the adsorption potential of GAC could have significant implications for water treatment. [34][35]

One method of improving adsorption efficiency is capacitive deionization (CDI), which removes soluble ionic species effectively and at relatively low cost.[36] CDI systems apply low electrical potentials to porous, and the charged electrodes attract dissolved ions of opposite charges from the bulk solution, creating highly concentrated electrical double layers (EDLs) on the porous surface of the electrodes.[37][38] As a result, this electrosorption has a saturation point: the EDL will eventually grow sufficiently large to fully neutralize the applied potential and sorption will cease.[37] However, if electrochemical reactions can be induced on the CDI electrode, both the efficiency and filter lifetime can be significantly increased.[36][39]

1.4 Project Overview

The goal of this work was to determine and optimize the effectiveness of an electrochemically-mediated GAC filtration system for nitrate removal. The application of a surface potential to the GAC was proposed to induce the electrosorption of nitrate on the GAC and potentially lead to electrochemical transformation of the nitrate. In addition to probing the general behavior of this nitrate removal process, this project investigates the feasibility of this technique for realistic groundwater treatment in terms of filter recoverability and reusability, energy efficiency, and sensitivity to environmental conditions.

We found that the removal efficiency was voltage dependent; when 5V was applied to the GAC filter, the removal efficiency was doubled over a 24-hour period. The nitrogen balance within the GAC filter system indicated that both significant electrochemical nitrate removal and enhanced adsorption occurred. In addition, this electrochemically-mediated removal was shown to be completely recoverable. Following a reverse-polarity rinse, the removal efficiency completely recovered for three repeated uses of a single GAC filter. Nitrate removal was also demonstrated to be dependent on the presence of chloride and the hydraulic retention time (HRT), independent of pH at environmentally relevant values, and moderately sensitive to interference by common ionic species present in groundwater (CO_3^{2-}, SO_4^{2-}). In addition, the energy consumption of the removal process is relatively low, even without optimization, requiring less than 1 kWH/m^3. The simplicity, efficiency, and reusability of this method may offer an enormous improvement in GAC-based nitrate removal that would be both practical and effective for drinking water treatment.

2. Materials and Methods

2.1 Flowthrough Packed-Bed Column System

A flowthrough packed-bed column system was built as shown in Figure 1. The column body was impact-resistant polycarbonate tubing (McMaster-Carr, OD=0.75” ID =0.625”) with spacers cut from polyester mesh (20.3 x 20.3). Tubing was laboratory grade Tygon PVC tubing (McMaster) and MFlex norprene tubing (Cole-Parmer, #13). All tubing connectors were nylon (McMaster-Carr). The counterelectrode was titanium wire (Malin, D=0.025”) and titanium foil; the electrode was stainless steel wire (McMaster-Carr, D=0.064”). The columns were sealed with polypropylene compression tube fittings (McMaster-Carr, ID=0.75”).

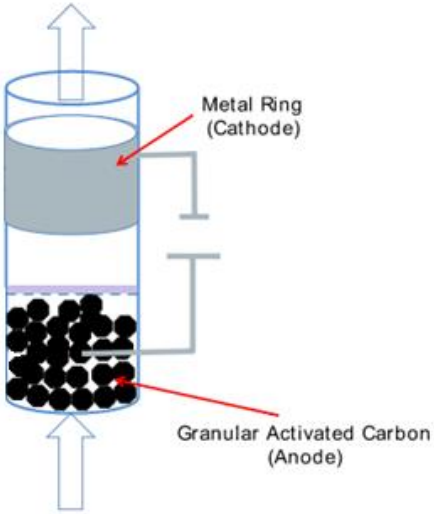

Figure 1. Schematic and image of the flowthrough packed-bed column system.

The column was operated using a peristaltic pump (Cole-Parmer, 1-100 RPM #7553-80). Prior to use, the column and its components were rinsed with deionized water and air-dried overnight. 4.00 g of pre-washed GAC was added to the column, then held in place by mesh and Tygon spacers. The total bed volume between the spacers was measured to be 5.35 mL. All samples were collected from the column outflow. The experimental conditions tested are listed in Table 1.

Table 1. Standard operating conditions for GAC filter system operation.

Condition	**Range Tested**
Hydraulic Retention Time (min)	1 – 9
pH	4 – 10
Applied Voltage (V)	0 – 7.5
Electrolyte Solution	See Table 3
Nitrate Initial Concentration (ppm)	10 – 100

The voltage in the system was generated by a DC power supply (BK Precision, #1660) with voltages confirmed by a voltmeter (Extech, #IP67) and current continuously monitored using a multimeter (BK Precision, #5491B) inserted between the voltage source and the counterelectrode. The column was operated in continuous single-pass mode.

2.2 Chemicals

Chemicals used were of reagent grades and all solutions were prepared in Millipore water (Milli-Q, Q-Gard 2). Unless otherwise specified, all chemicals were ACS Certified reagents from Fisher Scientific. Stock nitrate/chloride solutions and calibration solutions were prepared from sodium nitrate and sodium chloride (Fisher Bioreagents). Interfering ion solutions were prepared using sodium sulfate, sodium carbonate, and sodium persulfate. Eluent solutions were prepared using sodium bicarbonate and sodium carbonate. GAC (Foxwest, 6-12 Mesh) was washed with deionized water to remove carbon dust, then dried in an oven at 90 °C.

2.3 Ion Chromatography

Ion chromatography analyses were performed on a Dionex DX-120 Ion Chromatograph, using a Dionex IonPac AS22 4 x 250 mm analytical column for anion analysis. Samples were prepared by performing a 1:5 dilution of sample : Millipore water and were analyzed in triplicate. The eluent used was a helium-degassed solution of 4.5 mM sodium carbonate and 1.4 mM sodium bicarbonate. Total elution time was 11.0 minutes at a flow rate of 0.86 mL/min. Chloride eluted at 5.0 minutes, and nitrate eluted at 7.8 minutes.

2.4 Total Nitrogen and Carbon Analysis

Total nitrogen (TN) and total organic carbon (TOC) analyses were performed on an OI Analytical Aurora 1030C TOC Analyzer. Samples were prepared by performing a 1:10 dilution of sample : Millipore water and were analyzed in triplicate. TOC analyses were performed in 1088 configuration (Acid Volume: 0.100 mL, Dilution Factor: 1, Pre-Acid Volume: 0.100 mL, Sparge Time: 02:00, Sample Volume: 1.000 mL, System Pressure: 16 psi, Rinse Volume: 15.000 mL, Chase Volume: 0.100 mL, Calibration Curve Range: 0 - 2 ppm carbon). TN analyses were performed in TNb configuration (Acid Volume: 0.100 mL, Dilution Factor: 1, Pre-Acid Volume: 0.100 mL, Sparge Time: 02:00, Sample Volume: 0.800 mL, System Pressure: 16 psi, Rinse Volume: 15.000 mL, Chase Volume: 0.100 mL, Calibration Curve Range: 0 – 10 ppm nitrogen).

2.5 Carbon Characterization

GAC surface area was determined via BET surface area analysis (Micrometrics Surface Area and Porosity Analyzer, ASAP 2020). Approximately 500 mg of dried GAC was degassed at 500 μmHg for 240 min, then analyzed with a maximum manifold pressure of 925 mmHg.

Fourier-transform infrared spectroscopy analysis was performed using a Thermo Scientific FTIR-ATR system. Samples were prepared by finely grinding 500 mg KBr and 1 mg GAC and packing the powder into a sample cup. Samples were analyzed in transmission mode from 400 cm^{-1} to 4000 cm^{-1}.

X-ray photoelectron spectroscopy (XPS) characterization was performed using a Kratos AXIS ULTRADLD XPS system equipped with an Al Kα monochromated X-ray source and a 165-mm mean radius electron energy hemispherical analyzer. Vacuum pressure was kept below 3×10^{-9} torr during the acquisition. Carbon (300 eV – 275 eV, 200 ms, sweep 5, sensitivity: 0.278) and nitrogen (410 eV – 390 eV, 200 ms, sweep 20, sensitivity: 0.477) were analyzed for samples prepared by fine grinding 5 mg of dried activated carbon.

3. Results

3.1 Nitrate Removal

Three columns, each containing 4g of packed GAC, were operated in parallel to treat a supply of nitrate-containing water. The column effluent was sampled hourly, with nitrate concentration determined by ion chromatography (IC) and compared to total nitrogen (TN) to determine if ammonia or nitrite were formed. In this system, nitrate breakthrough occurred almost instantaneously due to the large grain size of the GAC and the short hydraulic retention times. The removal efficiency for the first 200 bed volumes treated was highly variable and increased steadily. After approximately 300 bed volumes treated, the removal efficiency stabilized and increased extremely slowly.

Nitrate removal via commercial GAC was first tested to determine its dependence on voltage. A solution of 40 ppm nitrate/50 ppm chloride was prepared from sodium nitrate and sodium chloride as an electrolyte, and was run through the GAC column system with a hydraulic retention time (HRT) of 2 minutes under several voltage conditions (Figure 2). When no GAC was present, regardless of the applied voltage, no nitrate removal was observed. In the presence of GAC the removal of nitrate varied significantly during early column operation, when adsorption onto the GAC was occurring rapidly. As more of the adsorption sites on the GAC are filled, the rate of nitrate removal slows. From this figure, we see that 90% nitrate breakthrough, or a removal efficiency of only 10%, occurred within 300 bed volumes under the application of 0V and -5V. When 5V was applied, a similar rapid adsorption curve was observed at first, but the removal efficiency remained consistently high ($\geq$ 60%) for the duration of the experiment.

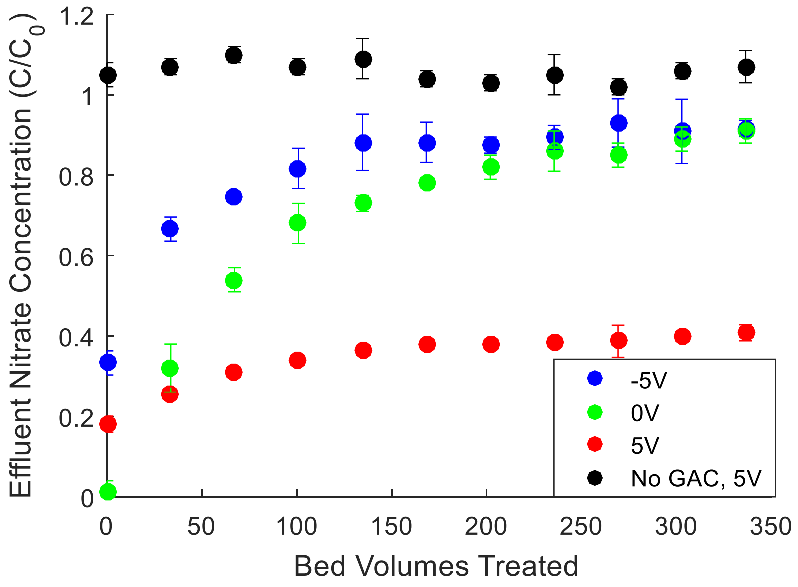

Figure 2. Nitrate concentration (given as C/C$_0$) as a function of bed volumes treated for different voltage conditions. HRT 2 min, pH 7, 40 ppm NO_3^-/50 ppm Cl^-.

The removal efficiency of the electrically-mediated GAC filtration method, measured after 350 bed volumes, showed a clear correlation with increasing applied potential (Figure 3). Minimal removal was observed for 0V, and 1V, but at 2.5V, a statistically significant increase in removal occurred, continuing up to 5V. However, no improvement in performance was observed from 5V to 7.5V. As a result, 5V was chosen as an optimal setting for further investigation of the removal. No statistically significant difference between nitrate concentration (IC) and total nitrogen (TN) was observed, indicating that minimal ammonia and nitrite formation occurred.

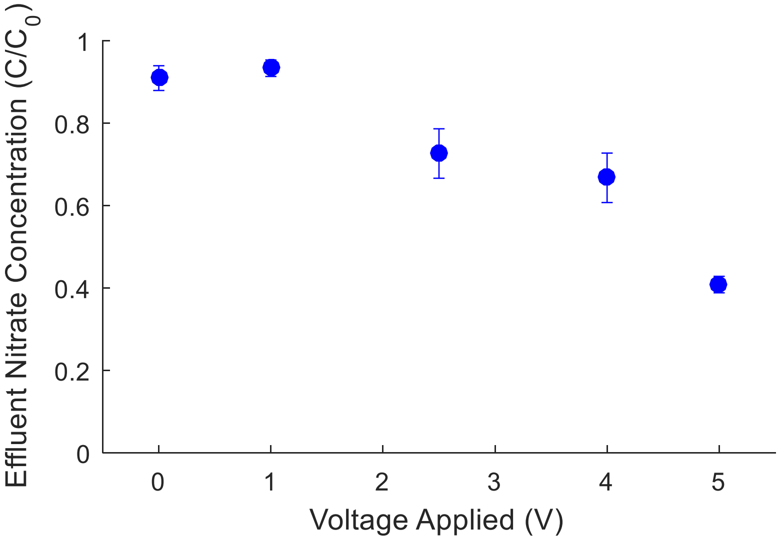

Figure 3. Nitrate concentration (given as C/C_0) after 350 bed volumes as a function of applied potentials. HRT 2 min, pH 7, 40 ppm NO_3^-/50 ppm Cl^-.

To assess the long-term performance of the system, the column was continuously operated for five days (2200 bed volumes) with an HRT of 4 minutes and an influent nitrate concentration of 40 ppm (Figure 4). The removal efficiency was still 20% after four days of operation (1600 bed volumes). Furthermore, at the end of the five day test (2100 bed volumes), the removal efficiency had not dropped further and remained consistent at 20%.

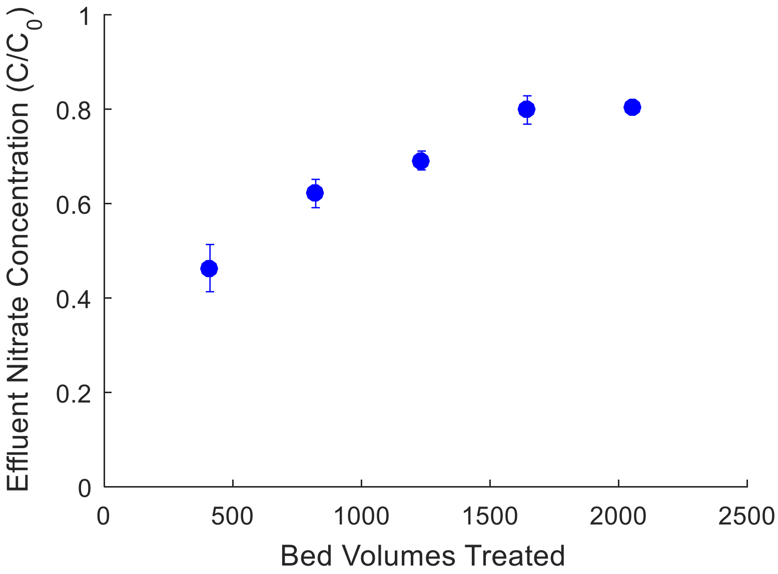

Figure 4. Nitrate concentration (given as C/C$_0$) as a function of bed volumes treated. 5V, HRT 4 min, pH 7, 40 ppm NO_3^-/50 ppm Cl^-.

To further probe this removal behavior, the experimental conditions were varied to determine which hydrodynamic conditions altered system functions. The hydraulic retention time (HRT) of the GAC column was varied between 1 and 9 minutes, and the nitrate concentration was measured after the columns had treated 125 bed volumes (Figure 5). The lowest HRT resulted in only 18% removal, while a 9 minute HRT resulted in 88%. This removal of nitrate after 125 bed volumes treated varied linearly with HRT ($R^2 = 0.94$).

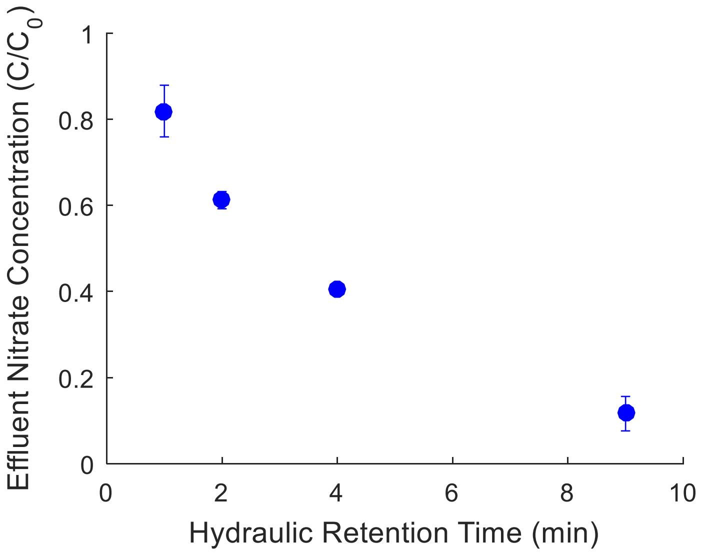

Figure 5. Nitrate concentration (given as C/C_0) after 125 bed volumes treated as a function of hydraulic retention time (HRT). 5V, pH 7, 40 ppm NO_3^-/50 ppm Cl^-.

Varying influent pH within an environmentally relevant range (4 – 10) had no effect on removal efficiency (Figure 6). However, regardless of influent pH, the effluent pH was consistently measured at 10 ± 0.1. While OH^- production is expected at the cathode, corresponding formation of H^+ at the anode should result in no overall pH shift in the effluent. This may indicate that H^+ is participating in an electrochemical transformation of NO_3^-.

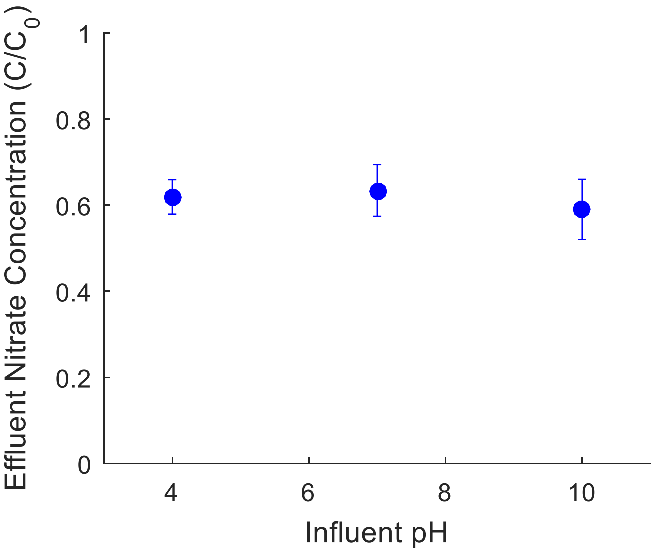

Figure 6. Nitrate concentration (given as C/C_0) after 125 bed volumes treated as a function of influent pH. 5V, HRT 2 min, 40 ppm NO_3^-/50 ppm Cl^-.

The initial concentration of nitrate was varied from 10 to 100 ppm (Figure 7). Relative removal after 125 bed volumes treated was higher for lower-concentration nitrate solutions, with 67% removal for an initial concentration of 10 ppm, where only 16% removal was achieved at an initial concentration of 100 ppm. As the relative removal efficiency dropped when nitrate concentration increased, this indicates that the system is predominantly reaction-limited. For a mass-transfer limited system, an increase in available NO_3^- would have allowed for greater removal. This result is consistent with the linear HRT relationship observed in Figure 5.

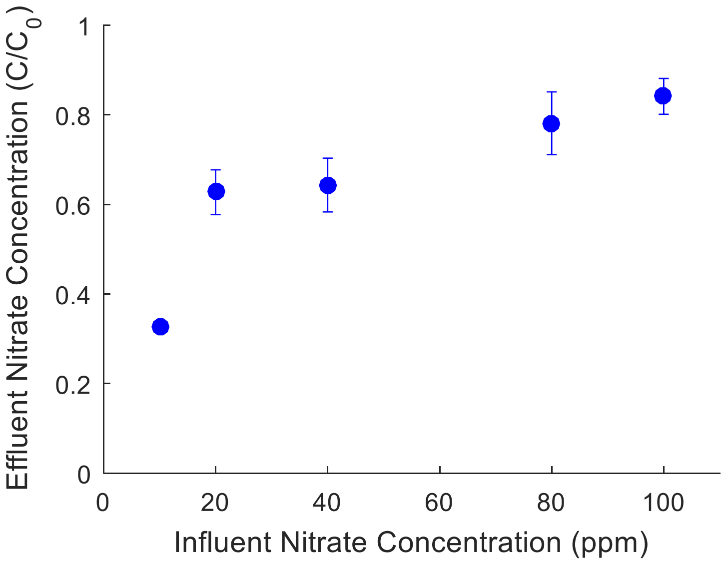

Figure 7. Nitrate concentration (given as C/C_0) after 125 bed volumes treated as a function of influent nitrate concentration. 5V, HRT 4 min, pH 7.

To determine the feasibility of this technique for use on contaminated groundwater, the sensitivity of the GAC system to several ionic species was tested. For groundwater treatment, the impact of interfering mineral ions such as CO_3^{2-} and SO_4^{2-} can dictate the usability of a water treatment method; these ions are usually present in concentrations of 0 – 300 ppm in drinking water.[8] Nitrate removal efficiency after 125 bed volumes treated was determined for four electrolyte solution variants to determine if the ions interfered with nitrate removal (Figure 8). The addition of 40 ppm of sulfate and carbonate disrupted the removal process, with removal dropping from 39% for chloride only to 29 and 30%, respectively. This interference was also determined to be concentration-dependent: increasing carbonate concentration to 80 ppm dropped the removal even further, to 20%.

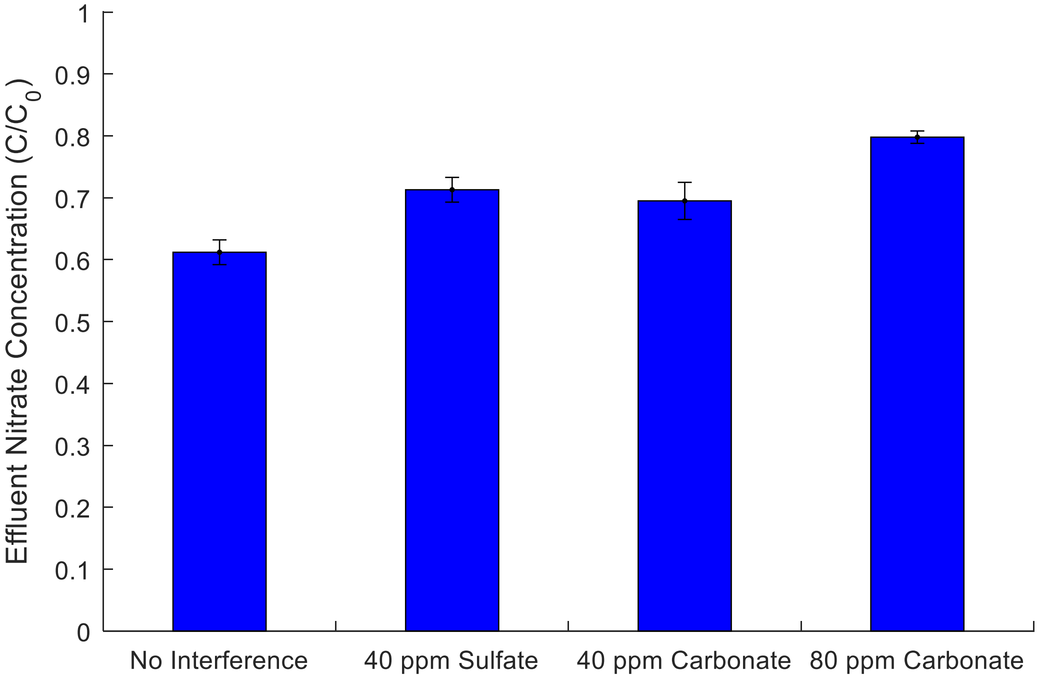

Figure 8. Nitrate concentration (given as C/C_0) after 125 bed volumes treated as a function of electrolyte solution. 5V, HRT 2 min, pH 7.

To further analyze the applicability of this technique to large-scale water treatment, the power consumption of the removal process was analyzed. The average current draw of the process was monitored and used to calculate the energy consumption per cubic meter of treated water (Figure 9). The energy consumption per cubic meter increases with increasing HRT, and therefore removal efficiency (Table 2). Reverse osmosis, for comparison, requires approximately 0.5 - 3 kWH/m^3 to treat groundwater, depending on its mineral content.[36][40]

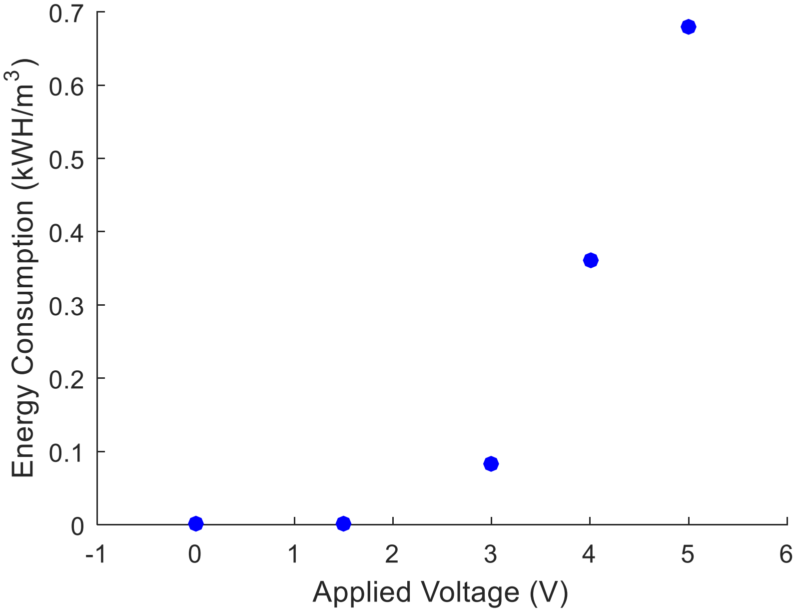

Figure 9. Average energy consumption per cubic meter of treated water as a function of voltage. HRT 4 min, pH 7, 40 ppm NO_3^-/50 ppm Cl^-.

Table 2. Average energy consumption per cubic meter as a function of HRT. 5V, pH 7, 40 ppm NO_3^-/50 ppm Cl^-.

HRT (min)	**Energy Use (kWH/m^3)**
2	0.68
4	1.62

3.2 Nitrate Fate

In order to determine whether this removal was due to sorption on the carbon surface or electrochemical transformation, a nitrate mass balance was performed on the GAC filter column. The total removal of nitrate was calculated by weight, based on influent and effluent nitrate concentrations, while the total recovery of nitrate by weight was calculated based on the column rinse effluent nitrate concentrations, total nitrogen concentrations, and the post-filtration GAC weight. The total amount of nitrate recovered in the course of a 48-hour 4L reverse-polarity desorption rinses for three consecutive cycles of nitrate removal and rinsing was between 61 and 67% of the nitrate removed (Figure 10).

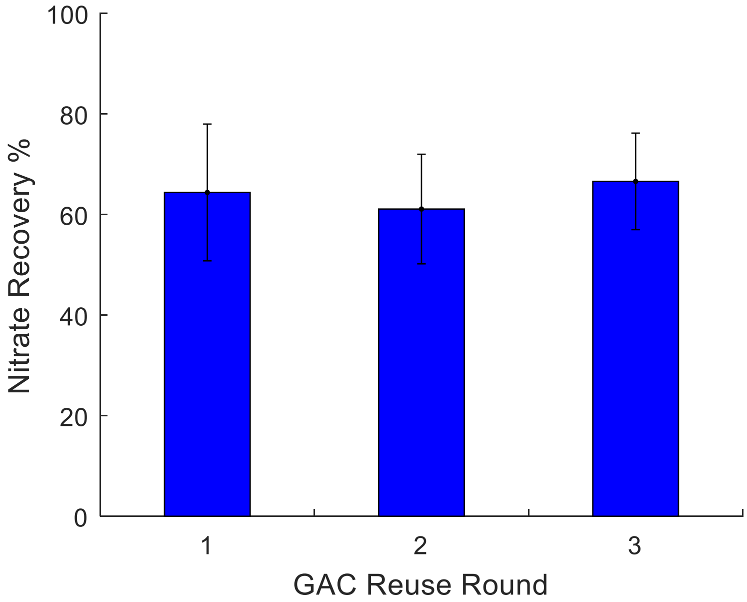

Figure 10. Nitrate recovery % after 48-hour 4 L reverse polarity rinse.

If electrosorption was the only process contributing to nitrate removal, complete recovery of the nitrate would have been observed.[36] After the reverse-polarity rinse, the weight of the GAC was unchanged, indicating that no significant permanent sorption occurred. In addition, nitrate and total nitrogen levels were not statistically different, indicating that no transformation to other aqueous species occurred. To determine if nitrate was being transformed to NO_x, overall NO_x concentrations in fume hood air were monitored during the experiment; no increase in NO_x was observed (Table 3).

Table 3. NOx concentrations observed in fume hood air prior to and during operation.

Sample	**NO_x (ppb)**
Ambient	30.0 ± 0.5
During Column Operation	29 ± 3

Based on these results, the most likely fate of the remaining nitrate is conversion to nitrogen gas (N_2). Unfortunately, detecting a small volume of N_2 is not feasible in a nitrogen-based atmosphere. In addition, while the evolution of N_2 (g) should result in visible bubble formation, this would not be visible due to the large amount of hydrogen and oxygen gas being produced by water-splitting in the system. N_2 (g) generation from nitrate in aqueous environments has previously been observed only in reductive systems, although these experiments resulted in similar nitrogen balance gaps. [31] However, in high-temperature gas reactions, oxidative decomposition of nitrate to N2 (g) has previously been reported by Li et al. (2005).[15]

Supporting this theory, the reverse-polarity rinse completely regenerated the column. If significant permanent sorption, degradation of the GAC, or transformation of nitrate onto the GAC surface occurred, the removal efficiency of the GAC would have been impacted. However, no loss of removal efficiency was observed, even after three rounds of removal and rinsing (Figure 11). After 24 hours, the 5V GAC system nitrate removal was 1.42 ± 0.01 $x10^{-3}$ mg NO_3-N/m^2 GAC. After 5 days, the nitrate loading increased to

$3.8 \pm 0.6 \times 10^{-3}$ mg NO_3-N/m^2 GAC area, which more than triples the reported maximum adsorption limit of GAC, 1.2×10^{-3} mg NO_3-N/m^2 GAC area.

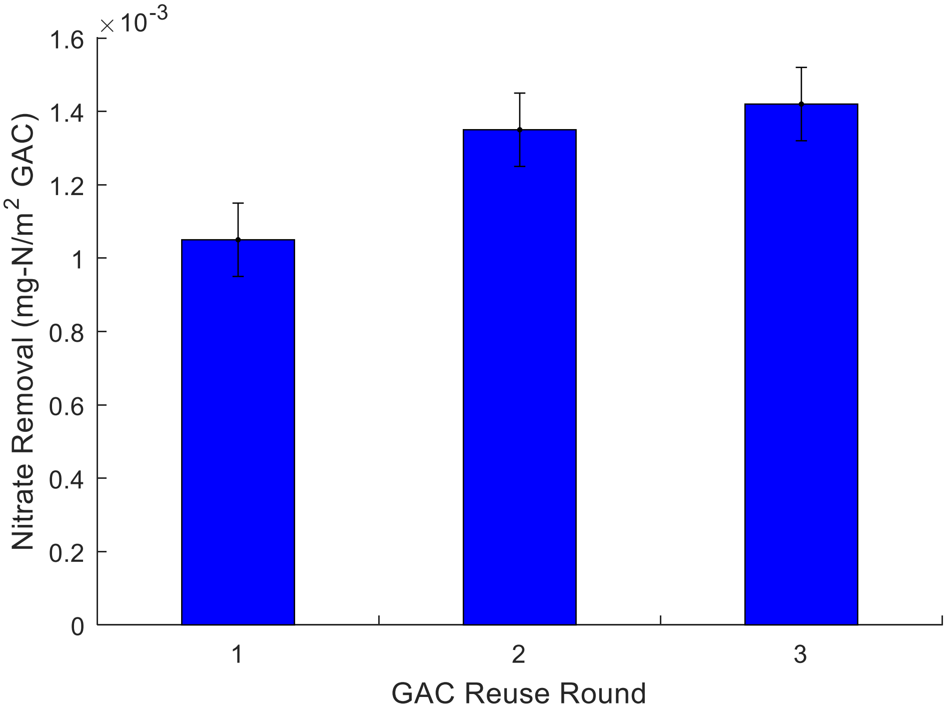

Figure 11. Total nitrate removal by the GAC filter after treating 400 bed volumes. A 48-hr 4-L reverse-polarity rinse was performed on the GAC between repetitions.

To better demonstrate the effect of the applied voltage, nitrate removal and recovery were measured over the same period for 0V (Figure 12). In addition to having a far lower total removal of nitrate, the total recovery of nitrate from the 0V GAC over a 24-hour 2L Millipore water rinse was only 9%. In addition to doubling the overall removal of nitrate, applying a voltage during the treatment process appears to modify the adsorption and desorption behavior of nitrate on the GAC.

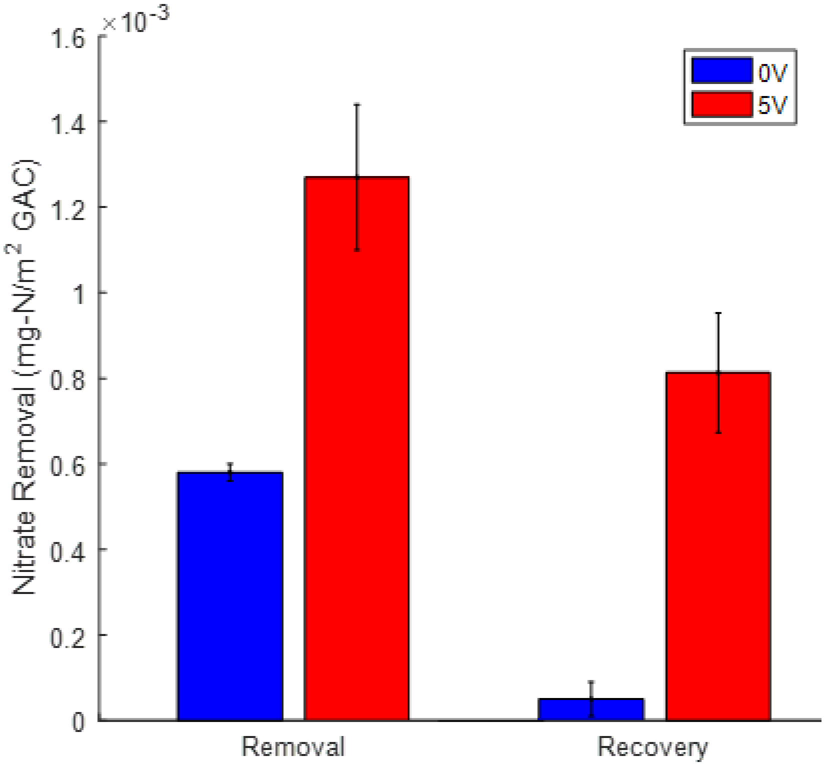

Figure 12. Removal of nitrate over 400 bed volumes and recovery of nitrate from a 24-hr 2-L rinse for applied voltages of 0 and 5V.

In order to determine if the presence of chloride enabled this removal, the nitrate removal and reverse-polarity rinse steps were performed after substituting sodium perchlorate for sodium chloride as the electrolyte solution (Figure 13). In the absence of chloride, the total removal of nitrate was halved, with removal efficiency comparable to that of GAC with no applied voltage. However, the nitrate could still be recovered, as it was, in the 5V experiments, with 76% recovery in the perchlorate test. This indicates that chloride directly mediates the removal of nitrate beyond serving as an electrolyte. Although it has only been observed in reductive electrochemical environments, chloride-dependent nitrogen removal on GAC has previously been reported during gas phase NO_2 sorption.[34]

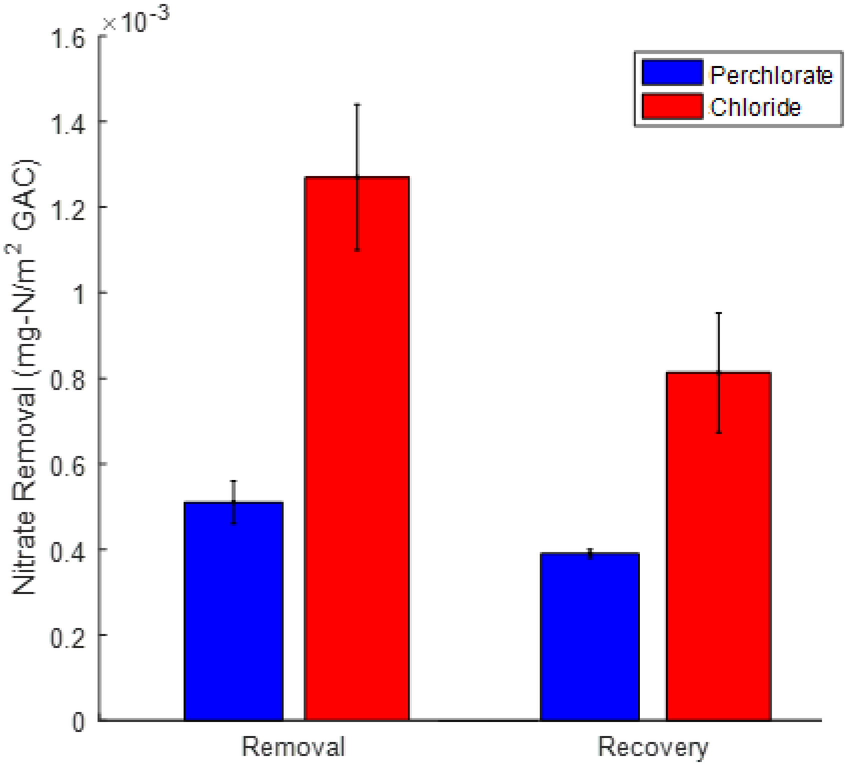

Figure 13. Removal of nitrate over 400 bed volumes and recovery of nitrate from a 48-hr 4-L rinse for electrolyte solutions of chloride and perchlorate.

3.3 GAC Analysis

In order to determine if any degradation or modification of the GAC surface occurred, characterization of the GAC was carried out before and after the nitrate removal and rinse process. BET analysis was used to determine if the surface area was altered by usage, which would impact both its properties as an adsorbent and the reported values of carbon adsorption. However, no statistically significant change in surface area was observed (Table 4).

Table 4. BET surface area analysis results for GAC before and after being used for nitrate removal and receiving a reverse-polarity rinse.

Sample	**Surface Area (m^2/g GAC)**
Before Use	800 ± 40
After Removal/Rinse	810 ± 40

FTIR analysis was also performed to detect any covalent addition of nitrogen species onto the carbon surface. Characteristic peaks for C-N bonds occur at 1200, 1650, and 2200 cm^{-1}, but no visible change occurred in those regions (Figure 14).[41]

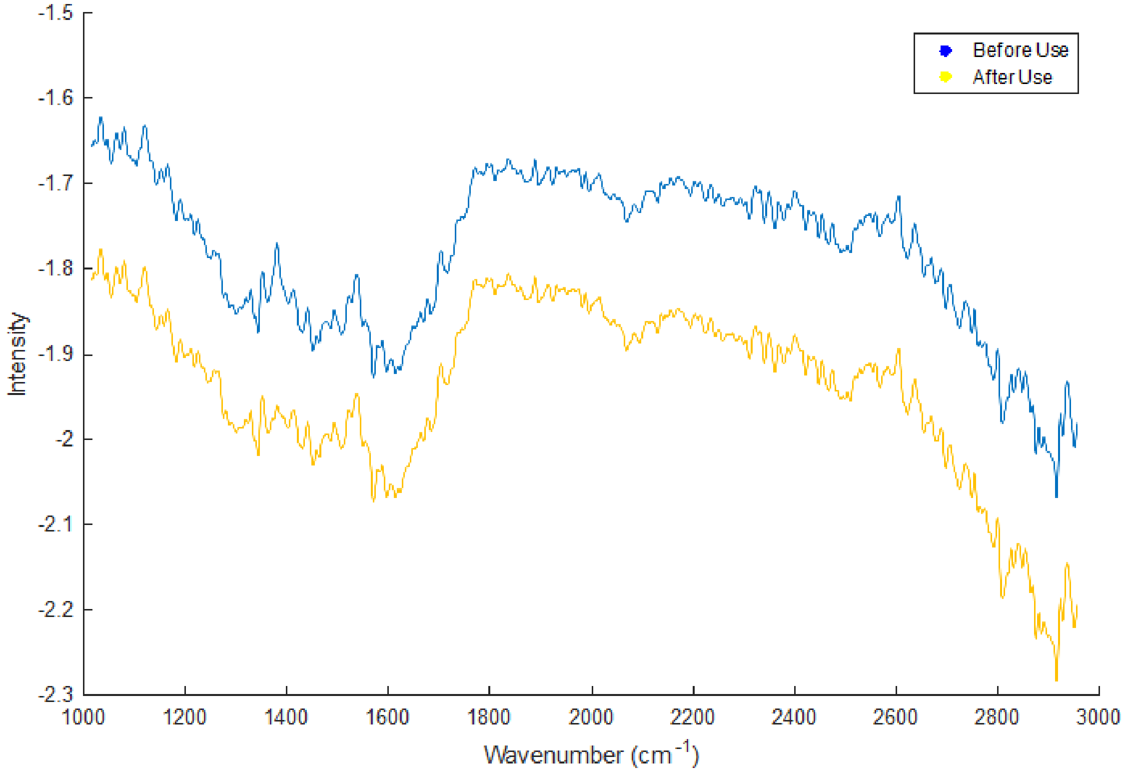

Figure 14. FTIR spectra for GAC before and after use in the nitrate removal system.

For a more sensitive analysis of the carbon, XPS elemental analysis was performed to determine if residual nitrogen species were present on the GAC. The relative prevalence of carbon and nitrogen were unchanged, with a nitrogen/carbon ratio of 0.082 (Table 5).

Table 5. XPS analysis results for GAC before and after use in the nitrate removal system

Sample	**Carbon Peak Intensity (cps)**	**Nitrogen Peak Intensity (cps)**	**Carbon/Nitrogen Ratio**
Before Use	4100	336	0.0820
After Removal/Rinse	3700	303	0.0819

Effluent from the GAC column was also analyzed for total organic carbon content to determine if degraded GAC was present. The TOC results were below the level of detection, approximately 0.05 ppm, indicating that no significant degradation occurred *in situ*. These results, combined, confirm the previous conclusion that the nitrogen removal not accounted for by electrochemically-mediated adsorption can be most likely attributed to the evolution of N_2 gas.

4. Conclusions and Future Work

The electrochemically-mediated removal of nitrate on GAC was investigated, quantified, and tested to determine its feasibility. Analysis of the removal indicated that the removal could be attributed to a combination of enhanced electrosorption and electrochemical transformation, both of which were influenced by the application of voltage. Overall, the performance of this system indicates that it could be an extremely promising water treatment technique, and would be particularly valuable in areas where nitrate contamination is the major water quality issue.

The effectiveness of this GAC-based system was shown to be voltage dependent, with an optimum nitrate removal setting of 5V. The electrochemical mediation of the removal had three major effects: first, the overall adsorption was increased; second, a significant portion of the nitrate was electrochemically transformed to N_2 gas; third, the adsorption of the carbon proceeded in a reversible manner. A removal efficiency of 20% could be maintained for continuous treatment of 2000 bed volumes, and possibly longer. Furthermore, the decline in removal efficiency during the removal experiments could be completely regenerated by a reverse-polarity rinse of the column system. Three consecutive removal-rinse cycles were performed on a single GAC filter, and no permanent loss of effectiveness was observed. In addition, no degradation or modification of the GAC was observed.

The mass balance of nitrate in the system, along with extensive testing of the effluent and the GAC itself, indicates that about 20% of the removal can be attributed to nitrogen gas evolution. The possible alternatives of NO_x production, GAC polymerization, permanent sorption, ammonia formation, and nitrite formation were eliminated.

The behavior of the system was further investigated to determine both its mechanism and its practicality as a water treatment system. The removal was dependent on the HRT, but not the influent concentration above 40 ppm, indicating a reaction-limited process. The removal efficiency was independent of pH within environmentally relevant limits. However, one of the major limitations of this method is its sensitivity to interfering groundwater ions. The inhibitory effect of moderate levels of carbonate is particularly concerning for groundwater applications. The presence of 80 ppm carbonate reduced the efficiency after treating 125 bed volumes from 40% to 20%, halving the treatment effectiveness. As a result, this technique would be most useful in areas with low TDS that are specifically experiencing high levels of nitrate contamination.

The major practical advantages of this new technique is its relative energy efficiency, simple operation, minimal environmental impact, and ease of modification. As the effluent nitrate concentration and energy consumption are linearly related to HRT, the removal efficiency and energy use can be directly controlled via the flow rate. For example, a water source that exceeded the legal nitrate limit by only 10% could be treated by an electrochemically-mediated GAC system set to a 1 minute HRT, consuming the minimum necessary energy. In addition, this technique is extremely environmentally friendly. While the energy consumption in the prototype stage is comparable to that of brackish water RO treatment, the system could be optimized to reduce water splitting and improve energy efficiency. More importantly, there is no production of brines, disinfection byproduct precursors, or used filter cartridges.

Further research on the electrochemical transformation of nitrate on this system, specifically on its interaction with chloride, is needed to fully characterize the nitrate transformation mechanism and the adsorption behavior of the GAC. Additionally, optimization and expansion of the system would be necessary to determine if it is economically viable as a water treatment method. Given a more energy-efficient design, electrochemically-mediated nitrate removal could provide an extremely affordable and accessible method for treating nitrate, particularly in rural areas with limited funds and infrastructure.

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