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Nitrate Uptake by Cellulose-Based Anion Exchange Polymers Derived from Wheat Straw

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Abstract: Nitrate contamination of ground water is a serious problem due to the intensive agricultural activities needed to feed the world's growing population. While effective, drinking water treatment using commercial ion exchange polymers is often too expensive to be employed. At the same time, lignocellulosic waste from crop production—an abundant source of the renewable polymer cellulose—is often burned to clear fields. This results in not only adverse health outcomes, but also wastes a valuable resource. In this study, wheat straw was pretreated to extract cellulose, then selectively oxidized with periodate, crosslinked with an alkyl diamine (1,7-diaminoheptane or 1,10-diaminodecane), and functionalized with a quaternary ammonium compound ((2-aminoethyl)trimethyl ammonium chloride) to generate a cellulose-based anion exchange polymer. This polymer lowered aqueous nitrate concentrations to health-based drinking water standards. Unlike commercial ion exchange polymers, its synthesis did not require the use of toxic epichlorohydrin or flammable solvents. The pretreatment conditions did not significantly affect nitrate uptake, but the crosslinker chain length did, with polymers crosslinked with 1,10-diaminodecane showing no nitrate uptake. Agricultural-waste-based anion exchange polymers could accelerate progress toward the sustainable development goals by providing low-cost materials for nitrate removal from water.

Keywords: nitrate; ion exchange; wheat straw; groundwater contamination; agricultural waste; lignocellulosic biomass

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1. Introduction

Nitrate has been called the world's most widespread ground water pollutant [1–3] due to the intensive and expanding agricultural production needed to feed the world's growing population [3,4]. The consumption of nitrate at levels above the U.S. [5] and World Health Organization (WHO) [6] drinking water standards (10–11 mg/L as N, or 0.7–0.8 mM) leads to methemoglobinemia in infants [7]. Nitrate consumption also increases the risk of certain cancers, thyroid disease, and neural tube defects via the in vivo formation of N-nitroso compounds that are carcinogens and teratogens, even at concentrations below U.S. and WHO drinking water standards [3].

In the United States, 5.6 million people are served by community water systems with nitrate concentrations greater than 5 mg/L as N (half the U.S. drinking water standard), a level that is associated with adverse health impacts [8]. Furthermore, evidence indicates that nitrate pollution of ground water disproportionally impacts low-income and minority individuals in the United States [8,9]. Small communities often lack resources for additional treatment [10,11] and may simply abandon nitrate-impacted wells [12]. For low-income families, ion-exchange-based water filters for point-of-use treatment for nitrate removal may consume a disproportionately large fraction of household income [13]. Lower-cost alternatives to commercial anion exchange polymers for efficient nitrate removal from drinking water supplies are therefore needed to address this significant domestic and worldwide water quality problem.

Commercial ion exchange polymers are not only expensive, but are also unsustainable as they employ a petroleum-based polystyrene or polyacrylic "backbone" and a divinylbenzene crosslinking agent [14]. Their manufacture also requires highly hazardous chemicals such as epichlorohydrin for crosslinking and functionalization [15]. According to the Globally Harmonized System (GHS) for the Classification and Labeling of Chemicals [16], epichlorohydrin is acutely toxic (toxicity classification 1—the most toxic) via oral ingestion, dermal contact, or inhalation [17]. At the same time, much of the embodied energy in agricultural waste—in the form of the renewable polymer cellulose—is wasted instead of being applied for useful purposes such as the preparation of anion exchange polymers. Furthermore, in much of the world, agricultural residues are burned in the fields, e.g., [18,19], contributing to acute air pollution episodes and chronic health effects caused by exposure to fine particulate matter [20].

A number of studies have utilized cellulose as a renewable "backbone" for biomass-waste-based anion exchange polymers, using wastes such as sugarcane bagasse [21,22], wheat straw [23–27], rice husks [21,22,28], sawdust, bark, and seed hulls from trees [22,29–31], peat [29], persimmon tea leaves [22], corn stalks [26,32], corn cobs [33], and coconut wastes [22,33]. In all these studies, however, cellulose functional groups were activated with epichlorohydrin [22] to facilitate bonding between cellulose and a cationic functional group responsible for nitrate uptake. These studies also used flammable solvents such as pyridine and dimethylformamide [22]. The use of such hazardous materials limits the safe preparation of these ion exchange polymers to well-controlled settings and highly trained individuals.

The objective of this work was to use cellulose obtained from wheat straw to develop anion exchange polymers for nitrate uptake, using less hazardous chemical procedures from the fields of fabric cationization, amphiphilic oil/water stabilizers, and others [34–46], without the need for epichlorohydrin, pyridine, or dimethylformamide. This approach has the potential to accelerate progress toward United Nations Sustainable Development Goal 6 ("Ensure availability and sustainable management of water and sanitation for all"), particularly Target 6.6 ("...restore water-related ecosystems, including...aquifers..."). [47]. The global production of wheat is third after corn and rice [48], and is estimated to be more than 529 million tons per year [49]. Thus, wheat straw is an abundant, and for the most part, currently wasted source of renewable cellulose that can be recycled for water treatment.

2. Materials and Methods

2.1. Overview

Overall, the process for the preparation of anion exchange polymers employed in this study (Figure 1) is the pretreatment of wheat straw with an acid or base for cellulose (Figure 1A) extraction, followed by periodate oxidation to form dialdehyde cellulose (Figure 1B), amination with a crosslinker (Figure 1C) and cationic functional group (Figure 1D) to form an imine (also called a Schiff base), followed by reduction with sodium borohydride to form a strong covalent bond between the crosslinker, cationic functional group, and the cellulose polymer (Figure 1E). None of the crosslinkers or the quaternary ammonium compound employed in this study had GHG oral, dermal, or inhalation toxicity classifications of 1, 2, or 3 (classifications that are considered fatal or toxic upon exposure [16]) [17]. Water was used as the solvent.

Evidence for the formation of dialdehyde cellulose upon periodate treatment (Figure 1B) comes from infrared spectroscopy [42], thermogravimetric analysis [35], and the loss of crystallinity (measured by X-ray diffraction) upon the opening of the cellulose glucopyranose ring [35]. Evidence for imine (C=N) (Figure 1C,D) and amine (C-N) (Figure 1E) functional groups upon amination and the reduction of dialdehyde cellulose comes from infrared spectroscopy [42,45], elemental analysis [45], and thermogravimetric analysis [35].

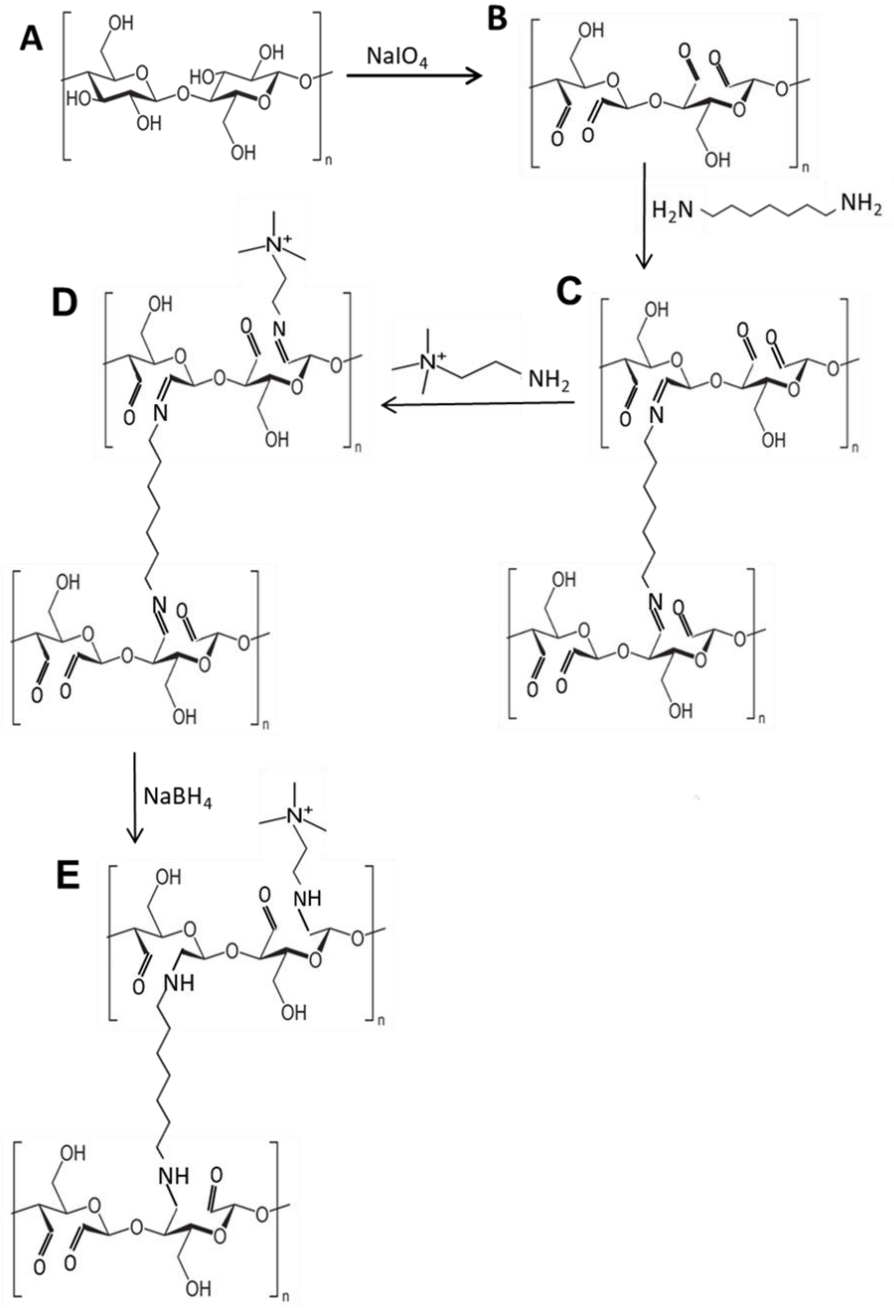

Figure 1. Polymer synthesis overview. (**A**): cellulose; (**B**): dialdehyde cellulose [50]; (**C**): crosslinked dialdehyde cellulose; (**D**): crosslinked and functionalized dialdehyde cellulose (adapted from Ref. [45]); (**E**): reduced crosslinked and functionalized dialdehyde cellulose [37]; image of cellulose (**A**) is from Wikimedia Commons. All amines are shown in their unprotonated form. While Figure 1 illustrates the crosslinking and functionalization of dialdehyde cellulose, the complete or stoichiometric saturation of cellulose dialdehyde functional groups with amine-based crosslinkers and cationic functional groups is not shown for simplicity.

2.2. Sources of Materials and Reagents

Wheat straw was purchased from AA Plus Shop, El Monte, CA, USA. The chemicals were as follows (all from ThermoFisher Scientific, Waltham, MA, USA): sodium hydroxide (NaOH, ≥97%), sulfuric acid (H_2SO_4, Technical Grade), sodium metaperiodate ($NaIO_4$, Certified ACS), hydrochloric acid (HCl, ACS Grade), sodium carbonate (Na_2CO_3, Certified ACS), sodium bicarbonate ($NaHCO_3$, Certified ACS), phosphoric acid (H_3PO_4, Certified

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ACS), potassium permanganate ($KMnO_4$, Certified ACS), sodium borohydride ($NaBH_4$, 99%), and lithium nitrate ($LiNO_3$, 99%). The following chemicals were from TCI America (Portland, OR, USA): 1,7-diaminoheptane ($C_7H_{18}N_2$, ≥98%) and 1,10-diaminodecane, ($C_{10}H_{24}N_2$, ≥98%). Acetic acid (CH_3COOH, 99%), (2-aminoethyl)-trimethyl ammonium chloride hydrochloride ($C_5H_{16}Cl_2N_2$, 99%), and sodium oxalate ($Na_2C_2O_4$, Certified ACS) were from Sigma-Aldrich, St. Louis, MO, USA. The remaining chemicals and their sources were as follows: cupric sulfate ($CuSO_4 \cdot 5H_2O$, ACS Grade, Avantor, Radnor, PA, USA) and sodium molybdate dihydrate ($NaMoO_2 \cdot 2H_2O$, ≥99.5%, EMD Millipore, Burlington, MA, USA). The ResinTech SIR-100-HP anion exchange polymer was from ResinTech Inc., Camden, NJ, USA.

2.3. Acid or Base Pretreatment

Wheat straw was ground to pass a No. 14 sieve (1.4 mm), then chemically pretreated with acid or base under either "mild" or "high" temperature and pressure conditions, which are described below and summarized in Table 1. For the mild temperature and pressure acid pretreatment, 10 g of wheat straw was added to 120 mL of 0.4% *w*/*w* sulfuric acid, then heated for four hours at 60 °C under ambient pressure [51,52]. For the mild temperature and pressure base pretreatment, 10 g of wheat straw was added to 150 mL of 0.72% *w*/*w* NaOH, then heated for 1.5 h at 110 °C under ambient pressure [53,54]. After mild acid or base pretreatment, the wheat straw was dried at 60 °C [55], then rinsed with deionized (DI) water until the pH reached a constant value. For the high temperature and pressure acid or base pretreatment, 1.25 g of wheat straw was added to 25 mL of 1% *w*/*w* sulfuric acid or sodium hydroxide in a sealed serum bottle no more than one third full, then heated in a pressure cooker (Instant Pot 6 Qt. Max, Instant Brands, Kanata, ON, Canada) at 15 psig and 120 °C for 1.5 h [56]. After pretreatment, the wheat straw was rinsed until the rinsate pH was constant, then oven-dried for at least 12 h at 60 °C [55].

Table 1. Mild and high temperature and pressure acid and base pretreatment conditions. The conditions labeled with IDs 1–3 are referenced in subsequent figures and Table 2.

	Mild Acid (ID 1)	Mild Base (ID 2)	High Acid	High Base (ID 3)
Concentration of acid or base	0.4% H_2SO_4	0.72% NaOH	1% H_2SO_4	1% NaOH
Duration and temperature	4 h at 60 °C	1.5 h at 110 °C	1.5 h at 120 °C	1.5 h at 120 °C
Pressure	Atmospheric	Atmospheric	15 psig	15 psig
Ratio of acid or base to wheat straw	12 mL per g wheat straw	15 mL per g wheat straw	20 mL per g wheat straw	20 mL per g wheat straw

2.4. Periodate Oxidation

Periodate was used to oxidize the C2 and C3 hydroxyl groups in cellulose to aldehydes, e.g., [34] (Figure 1B). One gram of pretreated wheat straw was soaked in 100 mL of either 0.031 M or 0.12 M sodium periodate, which are concentrations of periodate equal to one half (0.031 M) and two times (0.12 M) the estimated stoichiometric amount required to oxidize the C2 and C3 hydroxyl groups, assuming that the acid or base-pretreated wheat straw was mainly cellulose with a molecular weight of 162.14 g/mol. The treatment duration was one [57] or ten [36,58] days on a reciprocating Cole Parmer Ping-Pong Shaker (51504-00, Vernon Hills, IL, USA) at 75 rpm. The periodate solution was pre-adjusted to pH 4.25 with HCl [57], and the treatment was performed in foil-wrapped polyethylene bottles to prevent periodate photodegradation [36,57,58]. After oxidation, the wheat straw was centrifuged, washed with DI water, and air-dried. UV absorbance spectroscopy (280 nm, Shimadzu UV-1601 Spectrophotometer (Shimadzu Corporation, Missouri City, TX, USA) [36] confirmed that excess periodate remained in the supernatant after ten days of treatment with 0.12 M periodate.

Table 2. Cu# and estimated concentration of aldehyde functional groups for chemically pretreated and periodate oxidized wheat straw. Uncertainties are standard deviations of the means of triplicate samples. Polymer IDs (first column) and acid and base pretreatment conditions (second and third columns) are given in Table 1.

Polymer ID	Pretreatment	Temperature & Pressure	Periodate Concentration (M)	Oxidation Time (Days)	Cu# (g Cu/100 g Solid) (before Periodate Oxidation)	Cu# (g Cu/100 g Solid) (after Periodate Oxidation)	Aldehyde Concentration (μmol/g) (after Periodate Oxidation)
	acid	mild	0.031	1	0.706 ± 0.061	5.30 ± 0.49	87.1 ± 8.2
1	acid	mild	0.031	10	0.706 ± 0.061	5.30 ± 0.18	87.1 ± 3.0
	acid	high	0.12	1	1.48 ± 0.49	5.29 ± 0.18	87.0 ± 3.1
	acid	high	0.12	10	1.48 ± 0.49	4.56 ± 0.37	74.8 ± 6.1
	base	mild	0.031	1	0.211 ± 0.000	4.65 ± 0.96	76.4 ± 16.1
2	base	mild	0.031	10	0.211 ± 0.000	5.58 ± 0.06	91.8 ± 1.0
	base	mild	0.12	1	0.211 ± 0.000	5.51 ± 0.10	90.6 ± 1.7
	base	high	0.12	1	0.317 ± 0.001	5.40 ± 0.32	88.8 ± 5.0
3	base	high	0.12	10	0.317 ± 0.001	6.30 ± 0.18	103.1 ± 2.9

2.5. Determination of the Copper Number

The procedure followed the ASTM method D919-97 [59] and Dash [37], with the following details. A mass of 0.3 g of air-dried periodate-treated wheat straw was mixed with 1 mL of 0.40 N cupric sulfate and 19 mL of a solution containing 4.80 M sodium carbonate and 1.04 M sodium bicarbonate, then heated for three hours at 100 °C [37]. Samples were then filtered (Whatman Grade 1, 110 mm) and washed, first with 50 mL of boiling DI water, and then with 20 mL of 5% sodium carbonate [37]. The filter paper and the solids therein were transferred to a 100 mL beaker and mixed with 5 mL of 5% phosphomolybdic acid, prepared by mixing 50 g of sodium molybdate with 37.5 mL of concentrated phosphoric acid, then adding the mixture to another that contained 875 mL of DI water and 137.5 mL of concentrated sulfuric acid [37]. Phosphomolybdic acid turns blue upon reaction with Cu(I) [60], and Cu(II) is reduced to Cu(I) by oxidizable functional groups [59] such as carbonyls [61]. The beaker contents were then filtered (Whatman Grade 1110 mm) and rinsed with DI water until the rinsate was colorless, indicating the complete transfer of Cu(I) to the rinsate. The rinsate was then titrated with 0.05 N (0.01 M) potassium permanganate until a faint pink endpoint was reached, indicating that all Cu(I) in the sample was oxidized by potassium permanganate. Based on the titration results, the copper number (Cu#) in units of g Cu per 100 g sample was calculated [59]:

$$\text{Cu\#} = (6.36 \times (\text{V} - \text{B}) \times \text{N})/\text{W} \quad (1)$$

where V is the volume of potassium permanganate (mL) needed to titrate the rinsate, B is the volume of potassium permanganate (mL) needed to titrate the blank rinsate, N is the normality of potassium permanganate (0.05 N), and W is the mass of wheat straw (g).

The blank value (B) in Equation (1) was determined via the treatment and titration of a fresh, unused filter, and accounts for the oxidation of the cellulose in the paper filter. The Cu# was used to estimate the concentration of aldehyde groups in the sample using an empirical relationship [61]:

$$\text{Aldehyde content } (\mu\text{mol/g}) = (\text{Cu\#} - 0.07)/0.06 \quad (2)$$

2.6. Crosslinking and Functionalization

The concentration of aldehyde functional groups (Equation (2)) was used to estimate the required concentrations of compounds for the crosslinking and functionalization of the pretreated and periodate-oxidized wheat straw using either 1,7-diaminoheptane (1,7-DAH) or 1,10-diaminodecane (1,10-DAD) as the crosslinker, and (2-aminoethyl)trimethyl ammonium chloride (ATAC) as the quaternary ammonium functional group. These compounds are illustrated in Figure 2. The primary amine functional group (i.e., R-NH_2) in each compound (Figure 2) forms a bond with dialdehyde cellulose (Figure 1C,D). These aliphatic amines have pK_as well above the pH (4.8–5.0) of nitrate adsorption experiments [62], indicating that they were in the protonated form, and therefore that each amine or quaternary ammonium functional group could potentially adsorb nitrate. Both 1,7-diaminoheptane and 1,10-diaminodecane are comparable in size (1.00 nm and 1.40 nm) to the divinylbenzene isomers (0.71–0.92 nm) that are commonly used as crosslinkers in commercial anion exchange polymers. (All dimensions were estimated with Jmol [63]).

For crosslinking and functionalization, 0.2 g of pretreated and periodate-oxidized wheat straw was added to 100 mL of an aqueous solution containing both crosslinker and functional group in a serum bottle [37]. The concentrations of the crosslinker and functional group were each equal to approximately half the aldehyde concentration estimated using Equation (2). These values were equal to 7.53×10^{-5} M, 8.65×10^{-5} M, and 9.77×10^{-5} M for the mild-acid-, mild-base-, and high-base-pretreated wheat straw, respectively (IDs 1, 2, and 3 in Table 1). The solution pH was pre-adjusted to 4.5 with acetic acid [37], then serum bottles were sealed with Teflon-lined rubber septa and aluminum crip seals and heated in an incubator (Benchmark Scientific H2200-HC, ±0.5 °C, Sayreville, NJ, USA)

at 45 °C for 6 h [37]. After cooling, the bottles were opened, and sodium borohydride was added at a concentration three times the crosslinker concentration (as was equimolar to the total concentration of the primary amine functional groups that required reduction (Figure 1E). The bottles were then resealed and mixed on a reciprocating shaker at room temperature for 3 h [37] at 75 excursions per minute, followed by filtration (Whatman Grade 1, 110 mm), and washing three times with five gallons of DI water in dialysis tubing (pore diameter of 4.8 nm, S25645H, ThermoFisher Scientific, Waltham, MA, USA). Each wash duration was 24 h. The solids were then air-dried. The pretreated, oxidized, crosslinked, and functionalized wheat straw is hereafter referred to as the polymer.

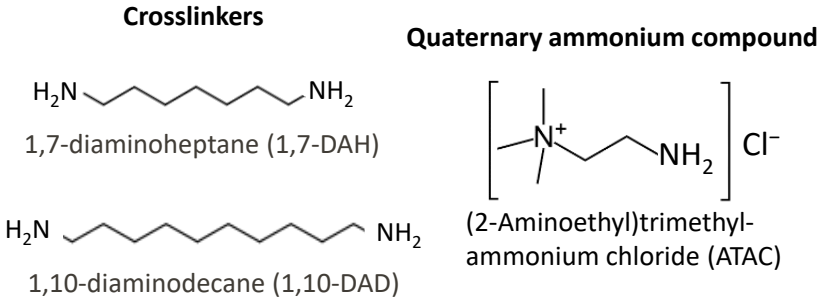

Figure 2. Chemical structure of crosslinkers 1,7-diaminoheptane (1,7-DAH), 1,10-diaminodecane (1,10-DAH) and (2-aminoethyl)trimethylammonium chloride (ATAC).

2.7. Scanning Electron Microscopy

Images were collected using a ThermoFisher (Waltham, MA, USA) Quattro S-field environmental scanning microscope under low-vacuum conditions.

2.8. Nitrate Adsorption

Equation (2) was measured in adsorption experiments with a solid-to-liquid ratio of 4 mg of polymer to 5 mL of high-nitrate solution prepared in DI water in 50 mL polyethylene screw-cap centrifuge tubes. The solution pH ranged from 4.8 to 5.0. Samples were mixed on a reciprocating shaker for 24 h at room temperature, centrifuged for 15 min at a relative centrifugal force of 3661 × *G*, then filtered with a Simsii (Issaquah, WA, USA) 0.22 µm syringe filter. Nitrate in solution was measured using an ion-selective electrode (9707BNWP, ThermoFisher Scientific, Waltham, MA, USA). Prior to analysis, the samples were amended with ammonium sulfate as an ionic strength adjustor (ISA) at a final concentration of 0.0038 M.

"Biomass blanks" containing only pretreated, oxidized wheat straw in DI water led to nitrate ion-selective electrode potentials corresponding to a nitrate concentration of approximately 10^{-6} M. To correct for this, biomass blanks were prepared and analyzed in parallel with the samples. The measured concentrations of the biomass blanks were subtracted from the measured concentrations in the samples spiked with nitrate. Each standard, biomass blank, and sample was prepared in duplicate.

3. Results

3.1. Polymer Characterization

The periodate treatment significantly increased the Cu# in wheat straw samples pretreated under a range of conditions compared to the untreated wheat straw (Table 2). The pretreatment and periodate oxidation of wheat straw under different conditions led to similar Cu#s and concentrations of aldehyde functional groups estimated with Equation (2) (Table 2). There was no pretreatment or periodate oxidation condition (acid or base, mild or high temperature and pressure, periodate concentration, or periodate exposure time) that yielded a Cu# significantly different from others in the same category (Figure A1), although the base-pretreated wheat straw more often had the highest mean Cu# values than the acid-pretreated wheat straw (Figure A2).

SEM images of unamended wheat straw, as well as the polymers prepared from wheat straw under different conditions, show the effects of pretreatment on polymer morphology (Figure 3). The compact biomass structure of the unamended wheat straw (Figure 3a) was disrupted by treatment under mild base conditions (Figure 3b) due to the alkaline dissolution of lignin and hemicellulose that provides stiffness in the plant structure [64]. In another study, wheat straw treated under mild base conditions similar to those used here showed only partial removal of lignin and hemicellulose [65]. Wheat straw treated under high temperature and pressure conditions, on the other hand, showed complete separation of cellulose fibers (Figure 3c), due to water release from the biomass matrix upon pressure reduction [19]. Figure 3a,b, and to a lesser extent Figure 3c, also illustrate discrete white granules identified as silica via energy-dispersive X-ray spectroscopy, similar to observations made by others, e.g., [66,67]. The heavier mass of silicon compared to major biomass constituents (carbon, oxygen, nitrogen, and hydrogen) appears brighter on the backscattered electron images.

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major biomass constituents (carbon, oxygen, nitrogen, and hydrogen) appears brighter on the backscattered electron images.

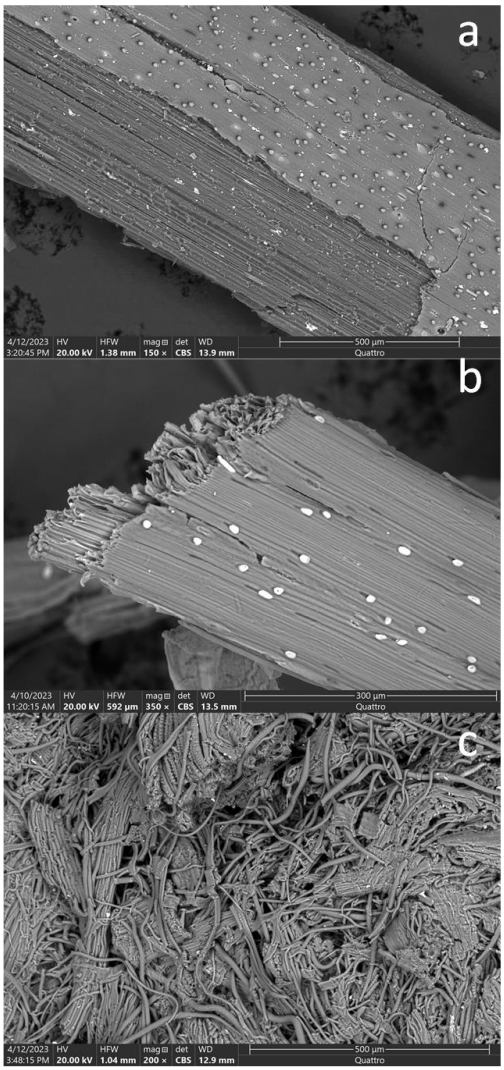

Figure 3. Backscattered electron SEM images of (**a**) untreated wheat straw, (**b**) mild-base-pretreated polymer (1,7-DAH/ATAC) (ID 2 in Table 2), and (**c**) high temperature/pressure base-pretreated polymer (1,7-DAH/ATAC) (ID 3 in Table 2).

Figure 3. Backscattered electron SEM images of (**a**) untreated wheat straw, (**b**) mild-base-pretreated polymer (1,7-DAH/ATAC) (ID 2 in Table 2), and (**c**) high temperature/pressure base-pretreated polymer (1,7-DAH/ATAC) (ID 3 in Table 2).

3.2. Nitrate Adsorption

Wheat straw treated under mild acid and base conditions (IDs 1 and 2, Table 1) was crosslinked with 1,7-DAH and functionalized with ATAC (1,7-DAH/ATAC), then exposed to dissolved nitrate. Sorption of nitrate occurred only in crosslinked and functionalized

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polymers, and not in pretreated, periodate-oxidized wheat straw that was not crosslinked and functionalized with 1,7-DAH/ATAC (Figure 4). This indicates that the amine and/or quaternary ammonium functional groups in the crosslinked and functionalized polymer were responsible for nitrate uptake. The extent of nitrate uptake by the acid- and base-pretreated wheat straw polymers was very similar (Figure 4), suggesting limitation or control by the concentrations of ATAC and/or 1,7-DAH, which were very similar for acid- and base-pretreated wheat straw (mild acid: 7.53×10^{-5} M (ID 1 in Table 1); mild base: 8.65×10^{-5} M (ID 2 in Table 1)).

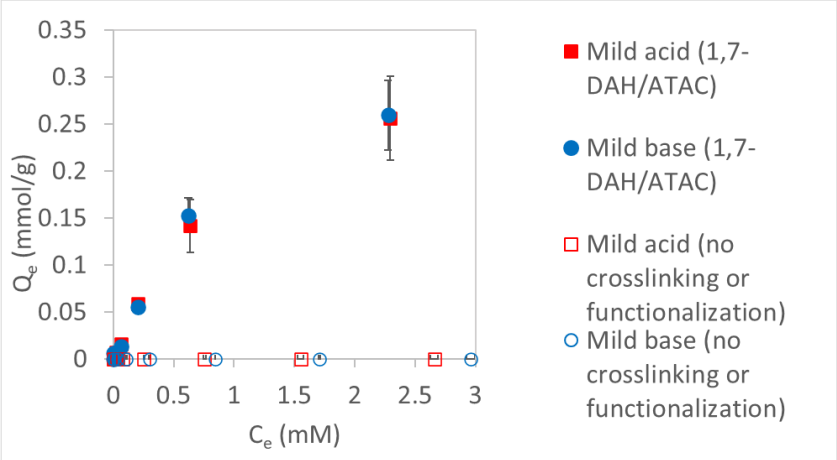

Figure 4. Nitrate uptake by mild-acid- and mild-base-pretreated and periodate-oxidized wheat straw that was crosslinked and functionalized with 1,7-DAH and ATAC (filled symbols) compared to wheat straw that was only pretreated with mild acid or base and oxidized with periodate (open symbols). Error bars are one standard deviation of the mean of duplicate samples. Some error bars are not visible as they are smaller than the data symbols.

Nitrate uptake by the acid- and base-pretreated polymers (1,7-DAH/ATAC) was compared to the commercial nitrate anion exchange polymer ResinTech SIR-100-HP (Figure 5), which is a macroporous divinylbenzene crosslinked polystyrene polymer functionalized with triethylamine functional groups that is marketed for nitrate uptake (ResinTech 2023). Like the polymers synthesized in this study, it is a strong base quaternary ammonium polymer.

At an equilibrium dissolved nitrate concentration equal to the U.S. EPA MCL (0.7 mM), ResinTech SIR-100-HP adsorbed approximately seven times more nitrate than the mild-acid- or base-pretreated wheat straw polymers (1,7-DAH/ATAC) (Figures 4 and 5). In addition, the maximum nitrate uptake capacity of the wheat straw polymer crosslinked and functionalized with 1,7-DAH and ATAC approached 0.30 mmol/g (Figure 4), while the nitrate uptake capacity of ResinTech SIR-100-HP was 1.5–1.6 mmol/g. (This value for ResinTech SIR-100-HP was calculated using the polymer nitrate uptake capacity (in meq/mL) and polymer density (in g/L) from the manufacturer [68], and is consistent with Figure 5).

The nitrate adsorption capacity of the wheat straw polymer prepared in this study could theoretically be increased by increasing the density of cationic functional groups. This was attempted by employing a higher temperature and pressure in wheat straw pretreatment in order to increase the available biomass surface area for periodate oxidation, dialdehyde cellulose formation (Figure 1B), and subsequent amination for crosslinking and functionalization (Figure 1C–E). While the Cu# and estimated aldehyde concentration in this wheat straw were higher than in the wheat straw pretreated under mild acid or base conditions (Table 2, ID 3), and it was mixed with proportionally greater concentrations of 1,7-DAH and ATAC, the resulting polymer did not adsorb nitrate at all. This can be attributed to the high temperature and pressure conditions during pretreatment (Table 1),

possibly removing one or more reactive species capable of forming Schiff bases upon crosslinking and functionalization (Figure 1C,D), and/or changing the physical polymer structure in a way that hindered crosslinking and functionalization. Consistent with this theory, the pretreatment of poplar wood with base (KOH) was shown to result in a greater loss of acetyl functionality as the concentration of base increased [69]. In another study, the pretreatment of wheat straw with increasing concentrations of NaOH resulted in a greater loss of hemicellulose [64], which is associated with acetyl functional groups [70] that are involved in crosslinking and functionalization.

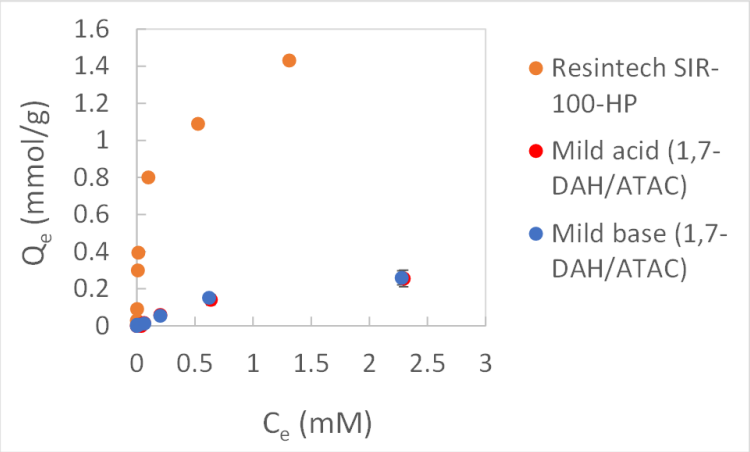

Figure 5. Nitrate uptake by mild-acid- or mild-base-pretreated and periodate-oxidized wheat straw that was crosslinked and functionalized with 1,7-DAH and ATAC compared to ResinTech SIR-100-HP. Error bars are one standard deviation of the mean of duplicate samples. Some error bars are not visible as they are smaller than the data symbols.

The nitrate adsorption capacity of the wheat straw polymer prepared in this study could theoretically be increased by increasing the density of cationic functional groups. This was attempted by employing a higher temperature and pressure in wheat straw pretreatment in order to increase the available biomass surface area for periodate oxidation, dialdehyde cellulose formation (Figure 1B), and subsequent amination for crosslinking and functionalization (Figure 1C–E). While the Cu# and estimated aldehyde concentration in this wheat straw were higher than in the wheat straw pretreated under mild acid or base conditions (Table 2, ID 3), and it was mixed with proportionally greater concentrations of 1,7-DAH and ATAC, the resulting polymer did not adsorb nitrate at all. This can be attributed to the high temperature and pressure conditions during pretreatment (Table 1), possibly removing one or more reactive species capable of forming Schiff bases upon crosslinking and functionalization (Figure 1C,D), and/or changing the physical polymer structure in a way that hindered crosslinking and functionalization. Consistent with this theory, the pretreatment of poplar wood with base (KOH) was shown to result in a greater loss of acetyl functionality as the concentration of base increased [69]. In another study, the pretreatment of wheat straw with increasing concentrations of NaOH resulted in a greater loss of hemicellulose [64], which is associated with acetyl functional groups [70] that are involved in crosslinking and functionalization.

The mild-base-pretreated wheat straw (Table 1, ID 1) was also crosslinked with a ten-carbon linear diamine (1,10-DAD, Figure 2) and functionalized with the same quaternary ammonium compound ATAC (Figure 2). However, this polymer was also not effective in nitrate uptake from water. The longer chain length and greater hydrophobicity of 1,10-DAD compared to not only 1,7-DAH, but also the much smaller quaternary ammonium compound ATAC (Figure 2), may have physically shielded the hydrophilic amine and ammonium functional groups from nitrate access. In polymer-based anion exchange membranes, continuous, hydrophilic, ion-conducting pathways were required [71]. Future experiments will optimize the type and concentration of the crosslinker and functional group to promote nitrate access to the polymer surface.

4. Conclusions

Anion exchange polymers prepared from wheat straw without the use of epichlorohydrin or flammable solvents were able to achieve nitrate concentrations well below the U.S. and WHO health-based drinking water standards (0.7 mM for U.S. EPA and 0.8 mM for WHO), and therefore have the potential to accelerate progress toward the sustainable development goals related to water supply, health, and waste recycling and reuse. The use of wheat straw for water treatment applications would prevent it from being cleared from agricultural fields via burning and does not require the diversion of arable land to produce a non-food crop, which is also consistent with the sustainable development goals. Wheat straw pretreatment using mild acid and mild base were equally effective, and such lignocellulosic pretreatment technologies are currently commercially viable [72]. Future studies should address questions related to effectiveness and scale-up, such as rate-controlling processes, potential interference from ionic species in groundwater, improved nitrate removal efficiency, and cost.

Author Contributions: Author Contributions: Conceptualization, E.C.B.; methodology, E.C.B. and D.A.S.; validation, S.E.J.; formal analysis, S.E.J. and E.C.B.; investigation, S.E.J. and Y.D.; data curation, S.E.J.; writing—original draft preparation, S.E.J.; writing—review and editing, E.C.B., Y.D. and D.A.S.; visualization, S.E.J.; supervision, E.C.B.; project administration, E.C.B.; funding acquisition, E.C.B. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available in the article.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Figures A1 and A2 are shown below.

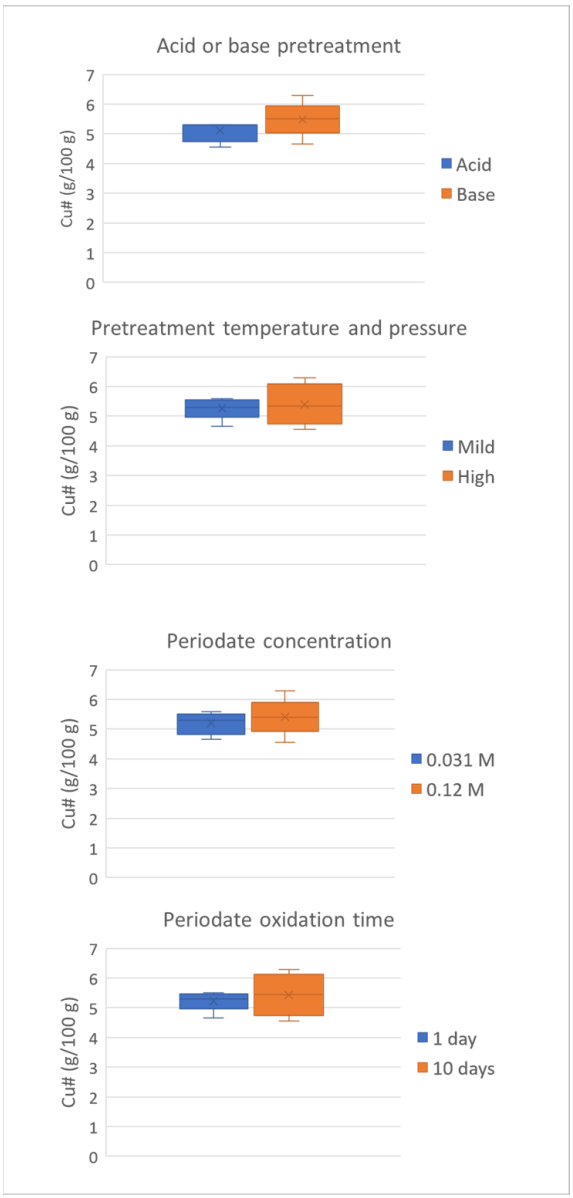

Figure A1. Box and whisker plots of Cu# values for different wheat straw pretreatment and periodate oxidation conditions. (All Cu# values are shown in Table 2.). The whiskers on each box show the 10th and 90th percentiles, and the box includes values between the 25th and 75th percentiles. The center line in the box is the dataset median and the "X" is the mean.

Figure A1. Box and whisker plots of Cu# values for different wheat straw pretreatment and periodate oxidation conditions. (All Cu# values are shown in Table 2.). The whiskers on each box

show the maximum and minimum values, and the box encloses values between the 25th and 75th percentiles. The center line in the box is the dataset median and the "X" is the mean.

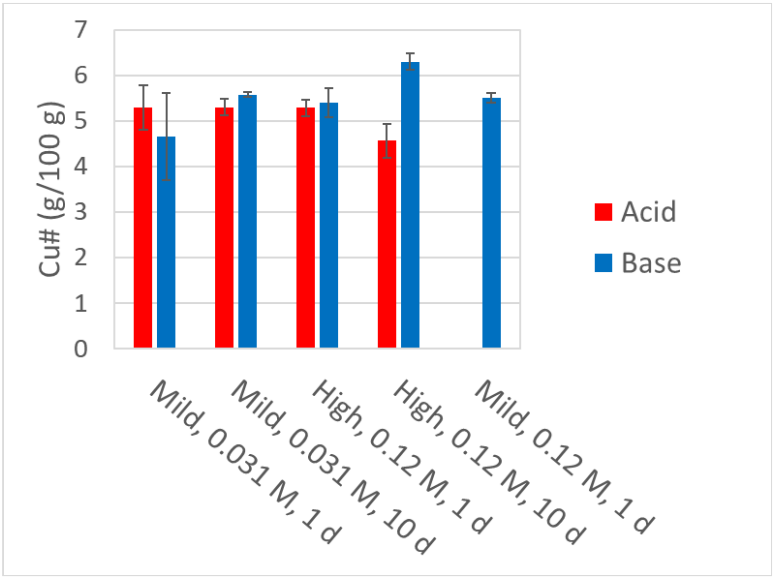

Figure A2. Effect of pretreatment conditions on Cu#. Error bars are one standard deviation of the mean of duplicate samples. X-axis legends refer to mild or high temperature and pressure conditions (Table 1) for acid (red) or base (blue) pretreatment, periodate concentration, and periodate exposure time.

Figure A2. Effect of pretreatment conditions on Cu#. Error bars are one standard deviation of the mean of duplicate samples. X-axis legends refer to mild or high temperature and pressure conditions (Table 1) for acid (red) or base (blue) pretreatment, periodate concentration, and periodate exposure time.

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