Modified tapioca starch for iron nanoparticle dispersion in aqueous media: potential uses for environmental remediation

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Abstract

Synthesis of cost-effective surface-modified nanoscale zero-valent iron (NZVI) for use in environmental remediation is a challenge. Herein, we report the synthesis of modified tapioca starch-coated NZVI (CNZVI) particles and their application for effective aqueous nitrate remediation. We used 2-octen-1-ylsuccinic anhydride (OSA) to modify the native starch and, thus introduced carboxyl and ester groups for effective binding of the starch to the NZVI surface. Coating NZVI (3 g L^{-1}) with 35% OSA-modified tapioca starch (10 g L^{-1}) significantly improved colloidal stability of CNZVI in deionized (DI) water compared to bare (unmodified) NZVI ($p = 0.000$). Approximately 66% of CNZVI remained suspended till 2 h as compared to 4% of bare NZVI. Nitrate removal studies ($20, 40$, and $60 \text{ mg NO}_3^- \text{ N L}^{-1}$ and 1 g L^{-1} of nanoparticles) showed CNZVI removed nitrate effectively (54–71% removal). The nitrate removal by CNZVI followed second-order reactions with surface normalized reaction rate constants ranging from 0.003 to $0.007 \text{ L m}^{-2} \text{ h}^{-1}$. Shelf life of the coated nanoparticles was found to be 3 months. High biochemical oxygen demand was expressed during respirometric biodegradation studies indicating ease of biodegradation of the CNZVI particles. Coating NZVI particles with OSA-modified tapioca starch is expected to have widespread scientific and industrial application potentials for ex situ as well as in situ contaminant remediation. The authors opine that the use of tapioca starch as the raw material for coated nanoparticle synthesis will be a value addition for the crop, and thus, nanotechnology will contribute to agricultural economy.

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Graphic abstract

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1 Introduction

The use of nanoscale zero-valent iron (NZVI) for contaminant remediation and management has gained popularity over the years, and the recent efforts are targeted at improving treatment efficiency [38, 59, 67]. NZVI particles can treat contaminants effectively because of their high specific surface area-to-volume ratio, rapid kinetics, and high reactivity [5, 26, 55]. Researchers have used NZVI to treat different contaminants [38] including chlorinated compounds [10, 29], dichromate [66], pesticides [8, 11, 14], arsenic [9, 27], heavy metals [21, 30, 31, 34, 64], nitrate and ammonia [12, 56, 67], and phosphate [1, 49, 50, 62, 63]. Additionally, NZVI has been explored for possible use in algal (energy) production [2].

However, bare (unmodified) NZVI particles agglomerate easily in aqueous environment and that reduce the available reactive surface area of the particles [29, 55]. Agglomeration occurs because repulsive electrostatic forces are overpowered by attractive van der Waals and

magnetic forces [41]. The agglomerated particles are to be removed from the aqueous phase as they settle down in the treatment reactors or pore spaces in the aquifer. To improve the colloidal stability of NZVI particles, surface modification has been done [25, 27, 29, 42, 58]. Surface modification can provide both electrostatic and steric repulsion to prevent particle agglomeration [27, 29, 58]. To prepare physically more stable and chemically more reactive NZVI, different stabilizers like polymers have been used for coating. These polymers include poly(acrylic acid) (PAA) and poly(vinyl alcohol-co-vinyl acetate-co-itaconic acid) (PV3A) [23], poly(styrene sulfonate) (PSS) [40], amphiphilic polysiloxane graft copolymers (APGC) [29], guar gum [58], carboxymethyl cellulose (CMC) [36, 42, 53], and chitosan and polyaniline [68]. The polymer used needs to contain an anchoring group (e.g., hydroxyl, carboxyl, or ester) to bind to the surface of NZVI. These polymer-coated NZVIs not only have shown improved colloidal stability but also improved contaminants removal [18, 25, 29]. However,

high cost [57], limited biodegradability, and complex synthesis process have limited the use of these polymers.

Among different candidates, polysaccharides are potential biopolymers for coating NZVI particles which will be easy to prepare and apply [57]. Starch is one of the relatively cheap and green polysaccharides which is easily available across the globe. Starch is a mixture of polymers: linear amylose and branched amylopectin (SI, Fig. S1). The hydrophilic nature of starch can improve NZVI's colloidal stability [15]. Native (i.e., unmodified) starch-stabilized bimetallic iron nanoparticles significantly increased the degradation of trichloroethylene (TCE) in water [18]; an unnamed water-soluble analytical grade starch was used in that study, and starch chemistry was not elucidated.

Starch is commonly used in food industry for dispersion (stabilization) of additives in foods such as salad dressings, custards, and puddings. Starch is made up of repeating glucose units bound together by glycosidic bonds $[(C_6H_{10}O_5)_n-(H_2O)]$, SI, Fig. S1a). Native starches can be modified through chemical, physical, and enzymatic routes [48] to make them effective in nanoparticle dispersion. Attaching hydrophobic groups to the repeating glucose units, we can create amphiphilic starch molecules that can function as effective emulsion stabilizers [5]. Further, introducing carboxyl and ester groups to the polymer may help in binding the starch to the surface of NZVI [19, 29, 44].

This work extensively explored the starch chemistry and used octenyl succinic anhydride (OSA) to modify starch for coating NZVI particles. OSA-modified starch is amphiphilic in nature and known to function as emulsion stabilizer [6]. An OSA-modified starch contains carboxyl and ester groups [7], and these two groups would bind strongly to the NZVI surface [19, 29, 44] and would be ideal for coating the NZVI particles. Importantly, NZVI particles have a protective oxide coating, and OSA with carboxyl and ester anchoring groups has affinities to bind with iron oxides. The hydrophilic blocks help NZVI particles disperse better and, thus, prevent them from agglomeration [29, 40, 42]. Additionally, starches have high molecular weights (a starch's molecular weight varies depending on its plant origin) which would improve colloidal stability by increasing steric repulsions [40]. We investigated the performance of coated NZVI (CNZVI) particles for their colloidal stability and ability to remediate aqueous nitrate in batch experiments.

2 Materials and method

2.1 Materials

Iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, Aldrich Chemical), sodium borohydride ($NaBH_4$, ACS grade, Alfa Aesar),

methanol (95 + %, BDH), sodium hydroxide (NaOH) (ACS grade, BDH), 2-octen-1-ylsuccinic anhydride (OSA) (Dixie Chemical Company), commercially available modified tapioca starch (Ingredion, Inc, USA), hydrochloric acid (HCl, EMD Millipore), deuterium oxide (D_2O , Sigma-Aldrich), sodium sulfate (Na_2SO_4 , Sigma-Aldrich), potassium hydroxide (KOH, Sigma-Aldrich), urea (Sigma-Aldrich), potassium nitrate (KNO_3 , Mallinckrodt Chemicals), ammonium sulfate ($(NH_4)_2SO_4$, J.T. Baker), BOD Nutrient Pillows (Hach, USA), lithium hydroxide pillows (LiOH, Hach, USA), and nitrogen gas (N_2 , Praxair) were used as received unless otherwise specified. Ingredion Incorporated (Illinois, USA) supplied native tapioca starches.

2.2 NZVI synthesis

NZVI was synthesized by borohydride reduction in ferrous iron in $FeSO_4 \cdot 7H_2O$ according to previously published method [10, 32]. After reduction, the black NZVI clusters were washed with ethanol to remove unreacted $NaBH_4$. The NZVI was dried overnight in a vacuum oven under nitrogen environment. The dried NZVI was ground using a ceramic mortar and pestle to produce NZVI particles. Powdered NZVI particles were stored in amber glass vials in nitrogen environment for later use.

2.3 Preparation of OSA-modified tapioca starch

Native tapioca starch was modified with octenyl succinic anhydride (OSA) to create an amphiphilic starch. OSA modification was performed as described in published reports [6, 17]. Briefly, starch (100 g) was dispersed in 225 mL DI (deionized water) water by constantly stirring in a 500-mL beaker, and the pH of the slurry (at $\sim 25^\circ C$) was adjusted to 8.5–9.0 by dropwise addition of 1 M NaOH. While maintaining the pH of the solution, OSA (3, 15, 35, and 50% w/w starch) was slowly added to the solution using a burette. Following the addition of OSA, the mixture was stirred for 6 h (pH 8.5). For high OSA concentrations ($\geq 15\%$), Na_2SO_4 was added (5% w Na_2SO_4 /w starch for 15% OSA, 13.6% for 35% OSA, and 20% for 50% OSA) to prevent the starch granules from swelling. Once the reaction was complete, the slurry was neutralized to pH 7 with 1 M HCL. The modified starch was washed three times with DI water by centrifuging at 2500 rpm for 15 min and once with acetone. Once washed, the modified starch was dried at $40^\circ C$ in nitrogen environment for 24 h and stored in glass bottles.

2.4 OSA-modified tapioca starch-coated NZVI (CNZVI) preparation

To coat NZVI, various concentrations of native and OSA-modified starch (1, 5, and 10 g L^{-1}) were prepared in

deoxygenated deionized (DI) water. Native starch or OSA-modified starch suspensions were brought to boil, cooled to 50 °C, and stirred overnight (with the heating on) to produce a gelatinous solutions. Following starch preparation, NZVI particles (60 mg) were combined with 20 mL of starch solution (nitrogen purges) in clear glass vials. Each vial's head space was flushed with nitrogen gas, and the NZVI–starch mixture was sonicated for 30 min to prevent agglomeration of NZVI particles using previously published method [29]. Immediately following sonication, the reactors were placed in a custom-made end-over-end shaker (28 rpm) and rotated for 72 h (optimized as a part of preliminary work) for the starch to coat the NZVI particles. After 72 h, the coated NZVI (CNZVI) particles were centrifuged and washed with copious amount of deoxygenated DI water to remove excess starch. Fresh deoxygenated DI water (20 mL) was added to each vial, and the washed CNZVI particles were stored in the glass vials for future use.

2.5 Characterization of OSA-modified tapioca starch

FTIR spectrometer (FTIR, Nicolet 8700, Thermo Scientific) was used to confirm the substitution of carbonyl groups of OSA on the starch molecule in 15% and 50% OSA-modified tapioca starch and compared with FTIR data obtained for native starch. ~1.5 grams of sample was ground with potassium bromide (KBr) and pressed into a pellet disk. The samples were scanned over the wavelength of 400–4000 cm^{-1} . Background spectra were subtracted from the sample spectra.

Nuclear magnetic resonance (NMR) was used to confirm the presence of OSA methyl protons and to determine the degree of substitution (DS). The starch samples were purged with D_2O three times; samples were lyophilized between each purge. Next, the samples were dissolved in D_2O (0.6 mL) a final time at 80 °C for 1 h and placed in NMR tubes (8 inch, 5 mm, thick wall). ^1H spectra were obtained using a Bruker (Billerica, MA, USA) Ascend 400 MHz NMR. The analysis was conducted at 25 °C for 64 scans with a delay time of 1 s. DS was calculated according to the methods of Shih et al. [46]. The internal standard was the equatorial proton of the anhydroglucose unit (AGU) of starch (5.2–5.4 ppm). Extent of OSA substitution was determined by the integration of the methyl protons of the OSA (0.8–0.9 ppm). DS was calculated using the equation $\text{DS} = (A_{0.8-0.9}) / (3 * A_{5.2-5.4})$ where $A_{0.8-0.9}$ = methyl protons of OSA and $A_{5.2-5.4}$ = equatorial protons of the AGU of starch [46]. DS is the average number of hydroxyl groups substituted per glucose unit comprising a starch molecule [51]. The decreased number of hydroxyl groups indicates that more OSA molecules (containing esters and

carbonyls) have reacted with starch molecule to form ester derivatives during the modification [51].

2.6 Colloidal stability studies

Colloidal stability of bare NZVI and CNZVI was monitored using UV–Vis spectrophotometry. CNZVI particles stored in vials (see CNZVI preparation) were used. The content in a vial was sonicated for 15 min, and 2 mL suspension of CNZVI was pipetted into a glass cuvette (UV–Vis spectrophotometer, DR5000, Hach, USA) immediately; the sedimentation behavior (i.e., change of light intensity) was observed over 2 h at the wavelength of 508 nm [29]. A concentration of 3 g L^{-1} of bare NZVI (same iron concentration as in CNZVI) in deoxygenated DI water was evaluated as a control after 15 min of sonication.

2.7 Characterization of nanoparticles

NZVI particles were coated with 35% OSA-modified tapioca starch and were dried in a nitrogen environment for 24 h. Dried CNZVI samples were sprinkled onto carbon tabs attached to aluminum mounts. Images were obtained with scanning electron microscopy (SEM) (JEOL JSM-7600F, JEOL USA, Inc., Peabody, Massachusetts). Energy-dispersive spectroscopy (EDS) was done using an Ultra Dry silicon drift X-ray detector and NSS-212e NORAN System 7 X-ray Microanalysis System (Thermo Fisher Scientific, Madison, Wisconsin). Spent CNZVI particles were also characterized to compare with fresh CNZVI.

2.8 Nitrate removal studies

Nitrate (20, 40, and 60 $\text{mg NO}_3^- \text{N L}^{-1}$) removal batch experiments were conducted in commercial grade polyethylene terephthalate bottles (225 mL nitrate solution in deoxygenated DI water) used as sacrificial reactors. The nitrate stock solution (100 $\text{mg NO}_3^- \text{N L}^{-1}$) was prepared with 0.7218 g of KNO_3 (dried for 24 h at 105 °C) in 1 L of deoxygenated DI water. Deoxygenation was done by bubbling the DI water with pure N_2 gas for 2 h. The specific test solutions (20, 40, and 60 $\text{mg NO}_3^- \text{N L}^{-1}$) were prepared from the stock solution for removal experiments via dilutions with deoxygenated DI water. CNZVI (1 g L^{-1} of NZVI) particles were added into the $\text{NO}_3^- \text{N}$ solution, the reactors were sealed with a rubber stopper, and air was flushed out from the headspace with N_2 gas. Controls with only 35% OSA-modified tapioca starch (10 g L^{-1} , no CNZVI) in the $\text{NO}_3^- \text{N}$ solution and blanks (only $\text{NO}_3^- \text{N}$ solution with no starch and CNZVI) were used. The reactors were rotated in the end-over-end shaker at 28 rpm. Batches of sacrificial reactors were taken out at predetermined intervals (0, 30, 60, 120, 240, 360, and 720 min), and aliquots were

withdrawn. NZVI particles were filtered from the aliquots using 0.2- μm syringe filters [29, 55], and the samples were tested for NO_3^- -N using a double-junction nitrate electrode (VWR, USA) as per Standard Method 4500 [3]. The nitrate removal data were fitted into zero-, first-, and second-order reaction models to understand the reaction kinetics.

Since ammonium and nitrite were expected to be generated when iron reduces nitrate [22], samples were also analyzed for all nitrogen species. Nitrogen mass balances were done for samples used in the 20 mg NO_3^- -N L^{-1} removal studies. These samples were collected at 0, 1, 2, 6, and 12 h and tested for nitrite (NO_2^- -N), ammonium (NH_4^+ -N), and nitrate (NO_3^- -N) using an Auto Analyzer 3 (AA3, High Resolution Digital Colorimeter, Seal Analytical, USA) and Auto Analyzer Method G-139-95, Rev. 5. The nitrates in the sample were converted to nitrite when passed through the cadmium reduction column and analyzed as nitrite, whereas the nitrite samples were analyzed directly as nitrite. The difference between the combined nitrogen (nitrate plus nitrite) and the nitrite concentration in the sample was the nitrate concentration. Ammonium samples were analyzed as NH_4^+ -N using the Berthelot reaction [45] and Auto Analyzer Method 145-95, Rev. 4.

2.9 Shelf-life study

Many batches of CNZVI (1 g NZVI/L) were prepared and stored in a laboratory cabinet at room temperature ($22 \pm 2^\circ\text{C}$). NO_3^- -N removal studies were conducted at pre-determined time interval over a 4-month period.

2.10 Starch biodegradation

The biodegradation behavior of OSA-modified starch and CNZVI particles was studied using respirometric experiments following the OECD 301 C Modified MITI test (I) [39]. Biochemical oxygen demand (BOD) was monitored using an automated closed-system respirometer (BODTrak Apparatus, Hach, USA). BODTrak measures the quantity of oxygen consumed in the system by monitoring changes in headspace pressure (Hach. BODTrak II User Manual, 2013). Headspace pressure decreases as the bacteria use the oxygen present while they consume the organic matters in the sample [16]. BOD data were collected continuously using a data logger and stored in a computer connected to the instrument during the 28-day test period. Mixed liquor suspended solids (MLSS) were collected from the City of Moorhead Wastewater Treatment Plant (Moorhead, MN) and used immediately as seeds (i.e., the microorganisms to start the degradation study).

2.11 Quality control and statistical analysis

All experiments were conducted in triplicates, and the average values are reported along with the standard deviations. One-way ANOVA was done to compare the sedimentation data to determine statistically significant differences in datasets. Tukey's pairwise comparison was used after the one-way ANOVA to identify which groups among the samples were significantly different.

3 Results and discussion

3.1 Synthesis of octenyl succinic anhydride (OSA)-modified tapioca starch

OSA-modified tapioca starch was successfully produced. A number of characterization techniques were used to ensure that modification was done to the extent expected.

FTIR analyses: FTIR was used as an initial screening tool to confirm the esterification reaction between starch hydroxyl groups and OSA. FTIR spectra of native and OSA-modified tapioca starch (Fig. 1a) show different types of C–O bond stretching between 800 and 1200 cm^{-1} . The band near 860 cm^{-1} represents the C–H and CH_2 deformation [35, 47]; the band near to 1081 and 1160 cm^{-1} is attributed to the anhydroglucose ring C–O stretch; the peak close to 1015 cm^{-1} is assigned to the C–O of the C–O–C in the polysaccharide [35, 47, 61]. Band at 2931 cm^{-1} represents the C–H stretching vibration, and the one at 1650 cm^{-1} is for bound water present in the starch [35, 47]. OSA modification is confirmed by the presence of adsorption bands around 1720 and 1570 cm^{-1} . The band around 1720 cm^{-1} corresponds to C=O stretching vibration caused by the formation of an ester group and that at 1570 cm^{-1} represents the asymmetric stretching vibration of carboxyl groups [7, 47, 51, 54]. These results confirm the substitution of hydroxyl groups in starch by carbonyl and carboxyl groups of OSA.

$^1\text{H-NMR}$ analyses: $^1\text{H-NMR}$ was used to quantify the chemical modification of the OSA starches and to determine the degree of substitution (DS) [5, 54]. Since OSA starches are amphiphilic, they tend to form aggregates in aqueous media [54] and that inhibits water solubility. Poor solubility can significantly reduce NMR signals, which can result in an error in estimated DS [54]. To overcome solubility issues, the samples were prepared and scanned in D_2O [46, 54] which partially dissolves starch samples. $^1\text{H-NMR}$ spectra were analyzed for native tapioca starch, commercially available modified (OSA) tapioca starch, and 3, 15, 35, and 50% OSA-modified starches (Fig. 1b). The peaks at 4.10–3.18, 4.64, 4.96, and 5.38 ppm represent the hydrogen of glucose units at different positions [5,

Fig. 1 **a** FTIR spectra of native and OSA-modified tapioca starch; **b** ¹H NMR spectra of OSA-modified tapioca starch samples. (i) Native; (ii) commercially available modified tapioca starch; (iii) 3% OSA; (iv) 15% OSA; (v) 35% OSA; (vi) 50% OSA. Inserts: spectra expansion of 0.5–2.7 ppm; **c** ¹H NMR of 50% OSA-modified tapioca starch

Table 1 Degree of substitution (DS) in OSA-modified tapioca starch

Tapioca starch	Degree of substitution	Reported DS values
Commercially available modified (OSA) tapioca starch	0.019	NA ^a
3% OSA	0.018	0.016–0.017 [46, 51, 52]
15% OSA	0.110	0.045–0.051 [5, 51]
35% OSA	0.126	NA ^a
50% OSA	0.093	0.088 [5]

^aNA not available

6, 46, 47]. OSA modification is confirmed by the addition of signals between 0.8 and 2.7 ppm [5] and changes in signals around 5.50 ppm [6, 54]. The peaks between 0.8 and 2.7 ppm (Fig. 1b, c) match with the results reported by others for OSA substitution [5, 6, 46, 54]. The peak assignments and molecular structure of OSA-modified starch are shown separately (Fig. 1c). The peak (Fig. 1b, c) observed at 0.8 ppm are from the methyl protons of the octenyl succinate (OS) group. The intensity of this peak varied with the amount of modification reflecting different DS of each modification. OSA modification also introduced a low-intensity peak at 0.9 ppm. This peak indicates the shift of terminal methyl protons in some substituted octenyl succinate group [6]. The octenyl succinate groups are hydrophobic, and this hydrophobicity might cause aggregation in aqueous media and shifting of methylene proton [6]. The peaks located around 1.2–2.7 ppm in OSA-modified starches were from the protons of the methylene groups of OSA [13]. These peaks were integrated using Bruker Topspin v3.2 software, and the DS for each starch was determined (Table 1) as described in the Materials and Method section.

The DS for 15% OSA starch in this research is twice the reported values (Table 1), which could be attributed to differences in the addition rate of OSA, solution pH, and reaction time. Bai et al. [5] reported that the solution's pH dropped rapidly and was difficult to maintain at OSA concentrations $\geq 15\%$. As DS decreases when the solution pH drops below 8.5 [51], it is possible that the reduced amount of OS substituted in Bai et al.'s study was because of the rapid pH drop during OSA addition. Song et al. [51] used a reaction time of 4 h, while the current study allowed the reaction to continue for 6 h and the authors think that the extended contact time between OSA and starch molecules helped in achieving higher DS.

Higher DS values on starches modified with increased OSA concentrations match literature reports [6]. Others reported DS = 0.11 for 25% [7] and 0.088 for 50% [5] OSA starch, and the current study mirrors those results (Table 1). The DS likely decreased at 50% OSA because

the solution's pH was difficult to maintain, and the starch granules swelled despite the addition of Na_2SO_4 . Swelling starch granules made the solution difficult to stir and that might have limited the number of starch molecules contacting OSA. The results presented here and by Bai et al. [5] suggest that there is a critical OSA concentration for optimizing the DS. The authors have decided to designate that OSA-modified starch which showed best dispersibility of CNZVI to be the optimal for this research.

3.2 Colloidal stability studies

NZVI particles (3 g L^{-1}) were coated with three different concentrations (1, 5, and 10 g L^{-1}) of OSA-modified tapioca starch, and their sedimentation behavior was monitored using UV–Vis spectrophotometry. Bare NZVI was used as the control in the sedimentation studies. The sedimentation data indicate that OSA-modified tapioca significantly improved sediment behavior of CNZVI compared to the control (Fig. 2; detailed data with standard deviations are shown in SI, Fig. S2). However, over the 2-h sedimentation study, some of the NZVI particles apparently got oxidized and changed the color of the solution to light red. This color has increased the value of absorbance and might have shown a higher dispersion value for CNZVI (Fig. 2). The NZVI coated with 10 g L^{-1} 35% OSA-modified tapioca starch formed the most stable suspension as compared to the lower concentrations of OSA-modified tapioca starch (Fig. 2). Approximately 66% of CNZVI remained suspended till 2 h as compared to only 4% of bare NZVI (Fig. 2d). The remaining studies presented in this work used CNZVI obtained with 35% OSA-modified tapioca starch (concentration = 10 g L^{-1}). The 35% OSA-modified tapioca starch had the highest DS as well (Table 1).

3.3 Characterization CNZVI particles

SEM images of CNZVI (Fig. 3a, b) show discrete particles surrounded by a starch coating (the layer around the particles). CNZVI particle size ranges from 47.5 to 325 nm (Fig. 3d) with an average particle size of 118.6 nm ($n = 200$) while bare NZVI particles had a particle size of 10–90 nm (average $\sim 35 \text{ nm}$). Some of the coated particles have formed chains (Fig. 3a, b), but individual particles are visible in the chains. The individual particles in each chain are well coated with the OSA-modified starch. Others [65] also observed chain formation with potato starch-coated NZVI particles. A magnified image (Fig. 3b) shows mostly small chains with occasional large clusters. The CNZVI/starch matrix also appears to be relatively porous (Fig. 3b).

SEM/EDS spectra (Fig. 3a–c) of freshly prepared CNZVI show the presence of sodium (0.9%), carbon (7.7%), and oxygen (25.1%) in addition to iron (65.9%). CNZVI particles

Fig. 2 Sedimentation behavior of NZVI coated with OSA-modified tapioca starch concentration of **a** 1 g L⁻¹; **b** 5 g L⁻¹; **c** 10 g L⁻¹. NZVI concentration = 3 g L⁻¹ (Fig. 2d is a select presentation from this plot at time points 60 and 90 min); **d** comparison of aqueous dispersion of bare NZVI and CNZVI (10 mg L⁻¹ 35% OSA-modified tapioca starch was used for CNZVI)—the vertical error bars repre-

sent $\pm$ standard deviations (... * ... bare NZVI; —○— native tapioca starch-coated NZVI; —△— 3% OSA tapioca starch-coated NZVI; —□— 15% OSA tapioca starch-coated NZVI; —X— 35% OSA tapioca starch-coated NZVI; —◇— 50% OSA tapioca starch-coated NZVI) (A =measured light absorbance, A_0 =initial light absorbance)

show higher oxygen content than bare NZVI particles (16% oxygen and 84% iron) that can be attributed to the ester and carbonyl groups from the OSA-modified starch. Sodium is likely present because of side reactions that occurred during starch modification from NaOH used for pH control [5, 51, 54] as well from NaBH₄ used in NZVI synthesis. The percentage of sodium is very low indicating that the side reactions probably were not dominant.

3.4 Kinetics of nitrate removal studies

Kinetic studies were conducted to investigate how the nitrate is removed by CNZVI particles. During the 12-h study, CNZVI reduced NO₃⁻-N concentrations from 20 to 5.81 mg L⁻¹ (71% removal), 40 to 11.68 mg L⁻¹ (69%), and 60 to 28.4 mg L⁻¹ (54%) in 12 h while there was no removal in the control (only OSA-modified starch in nitrate solution) and the blank (only nitrate solution with no CNZVI or starch) (Fig. 4). The maximum nitrate removal capacity

by CNZVI has been compared with other nanomaterials reported in the literature (Table 2), and it can be seen that CNZVI could achieve the way higher efficiency in nitrate removal compared to other modified NZVI but lower than the two hybrid nanomaterials (viz., Pd-Cu-NZVI and graphene oxide-NZVI).

CNZVI was found to reduce nitrate following second-order kinetics [$dC/dt = -k_{SA} \cdot \rho_A \cdot C$, where k_{SA} = surface normalized reaction rate constant (L m⁻² h⁻¹), ρ_A = iron surface area concentration in the solution (m² L⁻¹), t = time (h), and C = nitrate concentration (mg NO₃⁻-N L⁻¹)]. Surface normalized reaction rate constants for nitrate removal ranged from 0.003 to 0.007 L m⁻² h⁻¹ for CNZVI (SI, Table S1). It is important to point out that a second-order reaction, instead of a commonly reported first-order/pseudo first-order reaction, was observed in our experiment. Johnson et al. [24] postulated that if contaminant removal by iron metal follows a second-order reaction kinetics, then change in specific reactivity of the metal surface

Fig. 3 **a** Scanning electron micrograph of CNZVI; **b** scanning electron micrograph of CNZVI (magnified); **c** EDS spectra of freshly prepared CNZVI; **d** CNZVI particle size distribution

significantly affects the reaction kinetics [24]. They presented the following surface area normalized equation (Eq. 1) to incorporate the effect of reactive surface sites in a contaminant removal/degradation reaction.

$$dC/dt = -k_2 * \Gamma * \rho_A * C \quad (1)$$

where k_2 is the second-order rate constant for removal/degradation at a particular reactive surface area ($\text{Lh}^{-1}\text{mol}^{-1}$) and Γ is the surface concentration of reactive sites (mol m^{-2}). Through this equation, they proposed that the contaminant removal/degradation occurs favorably in distinct sites such as kinks, impurities, pits, steps, other crystal faces, or surface defects. However, data are not typically available to quantify Γ , but according to Johnson et al. [24] it is prudent to use k_{SA} (surface normalized reaction rate constant) to incorporate k_2 and Γ ($k_{SA} = k_2 * \Gamma$) in order to elucidate the factors that affect the reaction rate. In this study, iron in CNZVI particles was oxidized during nitrate removal and due to water-mediated corrosion. Here, nitrate was reduced and we detected ammonium

(NH_4^+) and nitrite (NO_2^-) as the two dominant degradation products (Fig. 5). The iron oxides did not participate in nitrate reduction, but only Fe^0 did. The particle size of zero-valent iron (core of the CNZVI) and consequently reactive iron surface area concentration (ρ_A) decreased over time. The decrease in both NO_3^- and surface area concentrations affected overall nitrate reduction, and it followed a second-order kinetics.

The mass balance for nitrate reduction by CNZVI (Fig. 5) shows low ammonium production with very low nitrite generation. The samples contained 60% ammonium when nitrate was reduced by CNZVI for 12 h. The mass balance of nitrogen species in the reactor changed throughout the experiment. This balance line declined during the first hour and then increased between hours 1 and 2 (Fig. 5). The initial decline is related to the increase in pH to 9.46 and partial stripping of ammonium at this pH. Hwang et al. [22] reported the similar nitrogen mass balance scenario while reducing nitrate with NZVI. The value of pH increased from 7.52 to 9.92 in the first hour possibly due

Fig. 4 Nitrate reduction by CNZVI with initial NO_3^- -N concentration of **a** 20 mg L^{-1} ; **b** 40 mg L^{-1} ; **c** 60 mg L^{-1} . NZVI concentration = 1 g NZVI/L, 35% OSA starch concentration = 10 g L^{-1} . The data points are connected with straight lines for ease of reading only, and they do not represent trendlines. The vertical error bars indicate $\pm$ standard deviations (— Δ — CNZVI; $\cdots$ — $\circ$ — OSA starch; — $\diamond$ — blank)

Table 2 Comparison of nitrate removal by different modified NZVI

Nanomaterial Type	Modification	Initial concentration (mg NO_3^- -N L^{-1})	Nanomaterial dose (g L^{-1})	Contact time (h)	Removal efficiency (%)	Source
NZVI	Integrated with <i>A. eutrophus</i> cells	80	0.5	NA	25	[4]
NZVI	Capped with polyphenol	20	1	2	41	[60]
NZVI	Entrapped in calcium alginate beads	20	2	2	50	[8, 11]
NZVI	OSA starch	20	1	12	71	Current study
NZVI	Pd-Cu deposited on NZVI	23 ^a	0.25	1	78	[33]
NZVI	Coated with graphene oxide (GO)	11 ^a	1	8	90	[37]

NA not available

^aReported as $\text{mg NO}_3^- \text{L}^{-1}$. Here, it is converted to mg NO_3^- -N L^{-1} , and the values have been rounded off

to proton consumption during the nitrate reduction [22], and the pH remained at ~ 10.00 for the rest of the experiment (Fig. 5).

3.5 Spent CNZVI characterization

The surface morphology of spent CNZVI and fresh CNZVI was examined in this study (SI, Fig. S3). Spent CNZVI particles appear to be irregularly shaped and have rougher surfaces (compared to fresh CNZVI). The average particle size of spent CNZVI (75.89 nm, $n = 200$, SI, Fig. S3a) is lower than fresh CNZVI (118.6 nm), indicating the starch layer

might have degraded or sloughed off. Since the particles were still larger than bare NZVI (average diameter of bare NZVI ~ 35 nm), it can be assumed a starch layer was still present on the particles, which prevented the particles from aggregating. SEM images of spent CNZVI particles have flake like structures, which could be free/detached starch or iron oxide plates. Ryu et al. [43] also reported the formation of iron oxide plates when nitrate reacted with NZVI. EDS analyses of spent CNZVI indicated oxidation of iron (during nitrate reduction) as indicated by the 7% increase in oxygen [25.06% oxygen and 65.89% iron in

Fig. 5 Nitrogen mass balance when nitrate solution ($C_0=20 \text{ mg L}^{-1}$) was treated with CNZVI. CNZVI concentration= 1 g NZVI/L (— $\square$ — ammonium; ... $\diamond$... nitrite; — $\triangle$ — nitrate; — $\circ$ — total nitrogen species (aqueous phase); the solid line is for pH in the secondary axis)

Fig. 6 Shelf-life evaluation of OSA-modified starch-coated NZVI was done over a 4-month period. There was no change in the ability of the coated NZVI to degrade nitrate over a period of 4 months. C_0 =initial nitrate concentration (60 mg L^{-1} as NO_3^- -N) and C is nitrate (mg L^{-1} as NO_3^- -N) remaining at the end of the time interval

Fig. 7 Organics degradation (BOD expression) during biodegradation studies (— CNZVI, — OSA starch, and — seed)

fresh CNZVI (Fig. 3c), and 31.93% oxygen and 35.56% iron in spent CNZVI (SI, Fig. S3b)].

3.6 Shelf-life study

The CNZVI particles need to have long shelf life to be commercially viable (storage and transportability requirements). The results showed that there is no significant difference in NO_3^- -N removal by CNZVI up to 120 days after production ($p=0.079$ – 0.999) with exceptions on Day 30 ($p=0.043$) and Day 50 ($p=0.013$). The CNZVI particles maintained their shelf life till 120 days ($\sim 63\%$ nitrate removal, Fig. 6). There is no logical explanation for the exceptions for Day 30 and Day 50 data, but Data from Day 30 (67% removal) and Day 50 (66%) also indicate that removal efficiency did not decrease below the 0-day value (56%, Fig. 6). The 3-month shelf life is significant because that make it feasible transport the CNZVI particles to remote remediation sites from the production units and increases their storability in the production unit and on-site.

3.7 Starch biodegradation

Respirometric experiments were conducted for 28 days to monitor BOD expression (Fig. 7). There was a significant increase ($p=0.000$) in BOD with the addition of either OSA starch or CNZVI particles (Fig. 7). The increase in BOD production suggests that OSA starch is easily biodegradable. It was observed that the CNZVI particles produced significantly more ($p=0.000$) BOD than just OSA starch, suggesting that the iron in CNZVI possibly promotes microbial activity. There was a significant difference ($p=0.000$) between the biodegradability of just OSA starch and CNZVI ($\sim 67\%$ for OSA starch and 97% for CNZVI, SI, Fig. S4). Increased microbial populations in the presence of modified NZVI have been reported by others [20, 28]. As per OECD standard, a polymer is considered biodegradable if the percent biodegradation is greater than 60% within the first 10 days [39], and both OSA starch and CNZVI met this requirement (SI, Fig. S4).

4 Conclusion

This study reports the first use of OSA-modified tapioca starch as a surface modifier for NZVI and the use of coated NZVI (CNZVI) for aqueous contaminant (nitrate) removal. Modified tapioca starch can be used as an effective surface modifier for NZVI particles. Coating NZVI particles with 10 g L^{-1} 35% OSA-modified tapioca starch had significantly improved the colloidal stability of the nanoparticles; $\sim 66\%$ of CNZVI remained suspended till

2 h as compared to only 4% of bare NZVI. The CNZVI also showed good nitrate reduction efficiency (54–71%). The coated nanoparticles were found to have shelf life of at least 3 months that makes their long-distance transport and long-term storage post-production feasible. Biodegradation studies indicated that CNZVI stimulates microbial growth which results in improved biodegradation of OSA starch and that makes the current CNZVI a good candidate for in situ application. Additionally, the use of tapioca starch is expected to add value to the crop.

5 Supplementary material

Second-order rate constants for nitrate reduction by CNZVI (Table S1); chemical structure of (a) starch (amylose); (b) octenyl succinic anhydride (OSA); and (c) OSA-modified starch (Fig. S1); Sedimentation behavior of NZVI coated with OSA-modified tapioca starch concentration of (a) 1 g L⁻¹; (b) 5 g L⁻¹; (c) 10 g L⁻¹. NZVI concentration = 3 g L⁻¹ (Fig. S2); spent CNZVI Characterization. (a) Particle size distribution; (b) EDS spectra of spent CNZVI; (c) scanning electron micrograph of fresh CNZVI; (d) scanning electron micrograph of spent CNZVI (Fig. S3); and percent biodegradation of starch on CNZVI and OSA-modified starch (Fig. S4).

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Human and animal rights statement This article does not contain any studies with human participants or animals.

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