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Cellulose nanocrystal zero-valent iron nanocomposites for groundwater remediation†

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Abstract

Zero-valent iron nanoparticles (nano-ZVIs) have been widely studied for *in situ* remediation of groundwater and other environmental matrices. Nano-ZVI particle mobility and reactivity are still the main impediments in achieving efficient *in situ* groundwater remediation. Compared to the nano-ZVI “coating” strategy, nano-ZVI stabilization on supporting material allows direct contact with the contaminant, reduces the electron path from the nano-ZVI to the target contaminant and increases nano-ZVI reactivity. Herein, we report the synthesis of nano-ZVI stabilized by cellulose nanocrystal (CNC) rigid nanomaterials (CNC-nano-ZVI; Fe/CNC = 1 w/w) with two different CNC functional surfaces (–OH and –COOH) using a classic sodium borohydride synthesis pathway. The final nanocomposites were thoroughly characterized and the reactivity of CNC-nano-ZVIs was assessed by their methyl orange (MO) dye degradation potential. The mobility of nanocomposites was determined in (sand/glass bead) porous media by utilizing a series of flowthrough transport column experiments. The synthesized CNC-nano-ZVI provided a stable colloidal suspension and demonstrated high mobility in porous media with an attachment efficiency (α) value of less than 0.23. In addition, reactivity toward MO increased up to 25% compared to bare ZVI. The use of CNC as a delivery vehicle shows promising potential to further improve the capability and applicability of nano-ZVI for *in situ* groundwater remediation and can spur advancements in CNC-based nanocomposites for their application in environmental remediation.

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1 Introduction

Among the nanomaterials used in environmental remediation, nanoscale zero-valent iron (nano-ZVI) has perhaps received the most attention and has been shown to effectively degrade a large spectrum of water contaminants, such as halogenated hydrocarbons, azo dyes, hexavalent chromium and various heavy metal ions.^{1–3} *In situ* use of nano-ZVI is achieved by direct injection of nano-ZVI slurries into the subsurface, with the aim of particle transport through the pores and channels of the subsurface sediments to increase the sphere of influence. However, it is well known that nano-ZVI particles generally aggregate due to surface charge and magnetic properties, resulting in low mobility and, consequently, a smaller sphere of influence in the subsurface environment.⁴ To obtain more stable suspensions, nano-ZVI is usually entrapped by a polyelectrolyte.^{5–8} Polyelectrolyte-stabilized nano-ZVIs show a limited attachment efficiency (α) towards porous media,^{5,9,10} which increases their dispersion and subsequent zone of influence in the subsurface. For example, commercial PAA-nano-ZVI shows an attachment efficiency of 0.2 and 1.20 to silica and carbonate sand, respectively, resulting in an estimated transport length (distance where 50% of the particles are retained) of 0.16 and 0.03 m, respectively.¹¹ Unfortunately, polyelectrolyte stabilization is also associated with a significant decrease in Fe(0) reactivity and contaminant degradation. Phenrat *et al.* showed that reactivity, as measured by trichloroethylene (TCE) degradation rate, decreased by 5 to 24 times when polyelectrolyte was added at the nano-ZVI surface in comparison with bare-nano-ZVI.¹² Reduced reactivity is thought to be due to blockage of surface reactive sites, slowing of electron transport and/or quenching by sorbed polyelectrolytes.

One solution to stabilize nano-ZVIs while maintaining their reactivity is to graft nano-ZVI particles on the surface of a supporting colloidal material such as silica, activated carbon, zeolites, or clays.^{13–17} Chen *et al.* synthesized a composite of bentonite and nano-ZVI (b-nano-ZVI) with a high efficiency to degrade methyl orange (MO) dye; b-nano-ZVI degraded 79% of MO at 100 mg L⁻¹ concentration.¹⁶ Carboiron, a promising composite of activated carbon and nano-ZVI, shows better colloidal stability and mobility than bare nano-ZVI.¹⁵ However, the authors had to add 1–3 wt% polyelectrolyte (carboxymethyl cellulose) to reduce the sedimentation rate and increase particle mobility.¹⁵

Recently, there has been interest in applications of cellulose nanocrystals (CNCs), derived from natural cellulose fibers by controlled acid hydrolysis, owing to their properties of controlled size and morphology, surface chemistry, high specific surface area, nanometric dispersity, and good colloidal stability.^{18–21} In addition, CNC is a good candidate as a “green” support material for nano-ZVI used for *in situ* remediation of contaminated sites. The synthesis of nanomaterials in the presence of CNCs has been reported previously.^{22,23} CNCs with hydroxyl groups were used as a support for Pd(0) and Au(0) particle growth, with nanometals well dispersed on the CNC surface by C=O–metal binding and/or electrostatic interactions.^{23,24} CNC functionalized with carboxyl groups, to enable C=O–Ag binding, has also been used to stabilize nano-Ag(0).²⁵ CNC-Au was observed to degrade 84% of 4-nitrophenol (4-NP), whereas unsupported Au nanoparticles degraded only 35% after 14 min of reaction (Au 0.2 mol, 4-NP 0.12 mM). The authors attributed the increased reactivity to the better dispersion of CNC-supported nanocomposites.

In this study, we report the preparation, mobility, and contaminant reduction efficacy of CNC-supported nano-ZVI nanocomposites. Moreover, we report for the first time the mobility of carboxylated and unmodified CNC through porous media. The nanocomposites were thoroughly characterized using a combination of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform Infrared (FTIR) spectroscopy, and transmission electron microscopy (TEM) techniques. A series of batch and column experiments were conducted to quantify the reactivity of these nanocomposites with MO dye and their mobility in porous media. We applied the colloidal filtration theory to extrapolate the results obtained from column experiments and compare the potential for dispersion of the nanocomposites during *in situ* remediation.

2 Materials and methods

2.1 Surface functionalization of cellulose nanocrystals

Cellulose nanocrystal suspension (6.8 wt%) was obtained from The Process Development Center at University of Maine, Orono (see details, <http://umaine.edu/pdc/cellulose-nanocrystals/>). TEMPO-mediated oxidation of CNC was performed by following a procedure described previously.²⁶ Briefly, CNCs (1 g) were suspended in 90 mL of 0.05 M sodium phosphate buffer (Na₃PO₄) (pH 6.8) along with TEMPO (0.016 g, 0.1 mmol) and sodium chlorite (NaClO₂) (80%, 1.13 g, 10 mmol). A 0.1 M sodium hypochlorite solution (NaOCl 0.5 mL, 1.0 mmol in 0.05 M Na₃PO₄ buffer) was added in one step to the flask. The suspension was then stirred at 500 rpm at 120 °C for 24 h on a stirring plate. The TEMPO-oxidized cellulose was then thoroughly washed with water/ethanol by centrifugation/re-suspension for at least 8–10 times. The washed TEMPO-oxidized cellulose was then freeze-dried and re-suspended in deionized (DI) water (18.2 Ω s⁻¹). The carboxyl content of oxidized cellulose samples was determined by conductometric titration. Cellulose samples (50 mg) were suspended in 15 ml of 0.01 M hydrochloric acid (HCl) and, after 10 min of stirring, titrated against 0.01 M sodium hydroxide (NaOH). The conductivity measurements of the suspension against the NaOH volume utilized allowed us to calculate the amount of carboxyl groups and, therefore, the degree of oxidation. From here on, unmodified (as-received) cellulose nanocrystals are referred to as CNC-OH and TEMPO-oxidized cellulose nanocrystals are referred to as CNC-COOH.

The electrophoresis mobility of CNC-OH and CNC-COOH against a wide pH range was measured using a Nanosizer NanoZS instrument (Malvern Instruments).

2.2 Preparation of CNC-supported Fe(0)

All experiments were conducted in a nitrogen glove box with N₂ flushed DI water. Oxygen was removed from water by first autoclaving, followed by N₂ sparging while cooling for a minimum of 30 min. In a typical experiment, 80 mL of CNC-COOH at 0.125 wt% was mixed for 30 min with 10 ml of FeSO₄·7H₂O solution (1.8 mM). Iron reduction was achieved by using borohydride at a BH₄⁻/Fe²⁺ molar ratio of 2, by adding 10 ml of NaBH₄ at a flow rate of 2 ml min⁻¹. The final mixture had a CNC-COOH/Fe mass ratio of 1, with a total concentration of 1 g L⁻¹. After 30 min of agitation, the CNC-COOH-nano-ZVI composites were isolated by magnetic separation, the supernatant containing Na⁺ and SO₄²⁻

ions were decanted, and the particles were re-suspended in 1 mM NaHCO₃ de-oxygenated solution using an ultrasonic bath (Branson 1510) for 15 min. Composites from unmodified cellulose nanocrystals (CNC-OH) were also prepared similarly. From here on, composites made from unmodified nanocrystals are referred to as CNC-OH-nano-ZVI, and composites made from TEMPO-oxidized cellulose nanocrystals are referred to as CNC-COOH-nano-ZVI.

2.3 Characterization of nanocomposites

Transmission electron microscopy (TEM, FEI Tecnai G² Twin, Japan) was used to observe the morphology and structure of the synthesized CNC-COOH-supported nano-ZVI nanocomposite. The particle sizes of the CNC(–OH);(–COOH)-nano-ZVI NPs were then determined using ImageJ software by averaging the sizes of at least 100 particles from different TEM images. X-ray diffractograms were collected using a Panalytical X'Pert PRO MRD HR X-Ray Diffraction System (Philips Co., Netherlands) equipped with a Cu-K α radiation source ($\lambda = 1.5406 \text{ \AA}$) at an accelerating voltage of 45 kV and a current of 40 mA. Diffractograms were recorded from $10^\circ \theta$ to $60^\circ \theta$ with a step size of 0.05 and a step time of 2 s. The crystallinity index (CrI) of cellulose was calculated from the intensity of the 200 peak (I_{200} , $2\theta = 22.6^\circ$) and the minimum intensity between the 200 and the 110 (I_{am} , $2\theta = 18.7^\circ$) peaks by using the empirical equation

$$\text{CrI} = \frac{I_{200} - I_{am}}{I_{200}} \quad (1)$$

FTIR measurements were taken using a Thermo Electron Nicolet 8700 (USA) spectrophotometer. Powdered samples of pristine CNC(–COOH) and CNC(–COOH)-supported nano-ZVI nanocomposite were mixed with an inert medium (boron nitride) to make solid pellets for FTIR measurements. The spectra were recorded from 4000 to 400 cm^{–1} at a resolution of 4 cm^{–1} from an accumulation of 64 scans. X-ray photoelectron spectroscopy (XPS) analysis was performed using the Kratos Analytical Axis Ultra spectrometer using Al K α (1486.6 eV) radiation at 10 kV and 15 mA. The peak fitting procedure was performed using the “CasaXPS” software. The binding energies (BEs) over the samples were calibrated using the C1s peak at 285.0 eV. XPS spectra were recorded at $\theta = 90^\circ$ of the X-ray sources.

2.4 Nanocomposite mobility in porous media

Nanocomposite mobility in porous media was determined by conducting flow-through column experiments. A borosilicate glass column ($\Phi = 2 \text{ cm}$; $L = 20 \text{ cm}$, Omnifit, Germany) was filled with glass beads ($\Phi = 320 \text{ }\mu\text{m}$, spheric) and fed from bottom to top using a syringe pump (Ismatec, Germany). Commonly used field site injection velocities (Phenrat *et al.*, 2009⁴⁶) of $3.2 \times 10^{-4} \text{ m s}^{-1}$ were used to inject either nano-ZVI suspension or tracer (NaCl). For each experimental run, a fresh column was dry packed with a porous medium and flushed with at least an equivalent of 10 pore volumes of DI water and 10 pore volumes of background solution (de-oxygenated water at 1 mmol of NaHCO₃) before injecting nano-ZVI particles in order to remove background turbidity. An inert tracer solution (0.01 M

NaCl) was injected into the column to achieve a breakthrough curve using conductivity measurements of the effluent at the outlet using a handheld conductivity meter (ICS-1000, Dionex, Austria). The porosity of the medium was measured to be 0.38 (weight difference of dry and water saturated column). Nanocomposite suspensions containing 1 g L^{-1} total Fe (58 ml) were introduced without any agitation, where the maximum time taken by the syringe was 40 minutes. This injected concentration of nano-ZVI was selected on the basis of concentrations used in field applications as reported in the literature.^{1,3} The column effluent was collected at the outlet with a minimum of 5 samples per pore volume (3 ml). Collected samples were analyzed for total Fe concentrations by ICP-MS (Agilent Technologies 7900 ICP-MS, helium mode, 3% HNO_3 background) or for carbon concentration as total organic carbon (TOC) using a TOC-L analyzer (Shimadzu) with an ASI-L autosampler. The breakthrough curves for each column experiment were plotted as normalized total Fe or C concentration (C/C_0) against the number of pore volumes. The data presented are the mean average results from duplicate experiments.

2.5 Reactivity measured by methyl orange (MO) degradation

A stock solution of MO dye was prepared by adding 440 mg of MO dye in 0.5 L DI water. Batch experiments were carried out under a nitrogen environment. A MO stock solution with a known concentration (880 ppm) was purged with N_2 for 30 min before use. After adding the desired amount of nano-ZVI particles (or CNC), the solution was shaken vigorously at 200 rpm (TSHZ-A, Shanghai, China). Samples were withdrawn at pre-determined time intervals and filtered through a $0.22 \mu\text{m}$ (cellulose nitrate) membrane filters. The UV-vis spectra of MO were recorded from 200 to 700 nm using a UV-vis spectrophotometer (TU1900-PC, Beijing, China) equipped with a quartz cell of 1.0 cm path length. The concentrations of MO samples were quantified by measuring the absorption intensity at 463 nm. If needed, sample solutions were diluted using DI water before measurement. The decolorization efficiency of MO was determined as:

$$\text{Decolorization efficiency} = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \quad (2)$$

where C_0 is the initial concentration of MO, and C_t is the concentration of MO at the reaction time t (min). Using our experimental data, the residual MO concentration can be expressed by the empirical equation²⁷

$$C_t = C_{\text{ultimate}} + (C_0 - C_{\text{ultimate}}) \times \exp(-kt) \quad (3)$$

where C_0 is the initial MO concentration, C_t is the residual MO concentration at a given reaction time t , C_{ultimate} is the ultimate residual MO concentration, and k denotes the empirical rate constant (min^{-1}). The constants C_{ultimate} and k were obtained by nonlinear regression (first order exponential decay) analysis from the experimental data. The correlation coefficients (r^2) indicated that the decolorization process in our experiments fits well with the first order exponential decay kinetics.

3 Results and discussion

3.1 Characterization of CNC

TEM images of CNC deposited from a dilute suspension are shown in Fig. 1A. Nanocrystals appear as slender rods of 10–20 nm diameter and 100–200 nm length. FTIR spectroscopy was used as a useful tool to obtain rapid information about the structure of cellulose.

Fig. 2 shows the FT-IR transmission spectra of the initial sulfuric acid hydrolyzed CNC-OH and oxidized CNC-COOH. The representative peaks located at around 3200–3500 cm^{-1} (O–H stretching), 2850–3000 cm^{-1} (C–H stretching), and 1059–1162 cm^{-1} (C–O and C–O–C stretching bond in cellulose) can be identified easily. CNC-OH and CNC-COOH present a singular peak at 1652 and 1616 cm^{-1} corresponding to the –OH group of adsorbed water and the C=O–Na group of the carboxyl group, respectively.²⁸

Our FT-IR results confirm that the introduction of carboxyl groups was achieved by the TEMPO mediated oxidation of primary alcohol groups at the CNC surface. The degree of oxidation (DO_x) or total amount of carboxyl groups is determined by conductometric titrations. Typical titration curves are shown in Fig. S1 in the ESI.† According to the literature, the maximum degree of oxidation of nanocellulose is roughly close to 0.10.²⁰

Based on the data from titration curves, the values of DO_x are 0.0036 and 0.090 for CNC-OH and CNC-COOH, respectively. CNC oxidation appears to be nearly complete in our experiment. The XRD diffractogram of CNC-COOH shows the main characteristic peaks of CNC materials at 34.5°, 22.3°, 19.8°, 16.7°, 15° and 12.1° (2 theta) associated with the crystal plane (004) of cellulose 1 (C1), (200) of C1 and cellulose 2 of C2, (100) of C1, (1–10) of C1 and (1–10) of C2 (Fig. S2, ESI†). The CrI calculated from eqn (1) increased from 65% to 84% following TEMPO oxidation, as amorphous cellulose could have been dissolved.²⁸ These results confirm the incorporation of carboxyl groups at the CNC surface, which were subsequently employed to act as anchors for nano-ZVI particles.²⁹

3.2 CNC-nano-ZVI nanocomposite characterization

After treatment with a NaBH_4 solution, the colorless Fe^{2+} solution turned black upon reduction, indicating the formation of nano-ZVI. FT-IR analysis of CNC-OH and CNC-COOH mixed with iron salt (FeSO_4) and after iron reduction was performed to analyze the nature of the chemical binding of crystal nanocellulose with iron.

The chemical binding with CNC-OH and Fe^{2+} is expected to be through the –OH group by electrostatic interactions as described previously.^{9,30} In contact with iron salt and after iron reduction, the FT-IR spectrum does not show any new peak or shift in the CNC–OH group peak around 3400 cm^{-1} , limiting the occurrence of iron binding at the CNC surface. The interaction of CNC-OH and nano-ZVI appears to be limited to electrostatic interactions (pH = 6.8).

Carboxylate groups of the CNC-COOH are initially bound to Na^+ ions (residual salt from CNC TEMPO oxidation procedure).²⁹ During this reaction, an ion exchange likely occurs, with Fe^{2+} displacing Na^+ of the COOH groups, as carboxylates have a strong affinity

towards transition metal cations.^{31,32} In contact with iron salt, the carboxylate anion peak of CNC-COOH shifts from 1616 (COO–Na) to 1625 cm⁻¹ (COO–Fe), suggesting that iron ions are adsorbed on CNC-COOH *via* the –COO– group. After borate reduction the carboxylate anion peak of CNC-COOH/nano-ZVI shifts from 1625 to 1618 cm⁻¹; in addition, a new peak appears at 1716 cm⁻¹. This suggests that the number of COO–Fe is highly reduced and undetectable after iron nucleation. The carboxyl group (COO–) appears not only as COO–Na⁺ (peak at 1618 cm⁻¹) but also as an ion free COO–(H) group (peak at 1716 cm⁻¹). Chemisorption of Fe²⁺ through COO⁻ functional groups of CNC-COOH is evident, and nano-ZVI chemical binding is likely possible. The binding type between carboxylate groups is assumed to be a monodentate type, as described previously.^{9,33}

Both CNC-nano-ZVIs exhibit the characteristic IR peaks including a broad band at 3373 cm⁻¹ attributed to O–H stretching vibration, the band at 2904 cm⁻¹ assigned to aliphatic C–H stretching vibration and the C–O–C motions of the β -glycosidic linkages (1108 cm⁻¹ and 1058 cm⁻¹) cm⁻¹, indicating that CNC is not degraded during nano-ZVI reduction.³⁴

As shown by the TEM images (Fig. 1E), the morphology of CNC was well preserved during the synthesis. The CNC-OH/nano-ZVI, CNC-COOH/nano-ZVI and bare nano-ZVI showed a broad size distribution with similar mean sizes of 117 $\pm$ 36, 112 $\pm$ 26 and 107 $\pm$ 37 nm, respectively. Bare-nano-ZVI particles were aggregated in a typical chain-like cluster morphology (Fig. 1B). In nanocomposite samples, the nano-ZVIs are spherical particles showing surface imperfections; they were always observed as surrounded by cellulose. The affinity between nano-ZVI and both cellulose types was also evident; the nano-ZVI surface is mostly surrounded by nanocellulose (Fig. 1D). In Fig. 1E, the CNCs are present in high density around the nano-ZVI, creating a CNC protective “shell” around it. CNCs are rigid structures and would therefore not wrap around the spherical nano-ZVI particles like the traditionally used polymeric stabilizers do.³⁵ In contrast, multiple CNCs surrounding the nano-ZVI could potentially form a porous “mesh” around the nano-ZVI. In contrast to nano-ZVI polyelectrolyte stabilization, the structure of the CNC-nano-ZVI nanocomposite could lead to a difference in the number of available reactive sites at the nano-ZVI surface.

Fe 2p XPS data were used to identify Fe(0) and iron oxide on the surface of the nanocomposite of nano-ZVI (Fig. 3). An Fe 2p spectrum of the samples shows a shape similar to the binding energies of Fe 2p_{1/2} 725 eV and Fe 2p_{3/2} 711 eV, which are assigned to oxidized iron, indicating that the surface of nano-ZVI is covered with an oxide film.³⁶ The photoelectron peaks at 711 eV indicate the potential presence of iron oxides and oxyhydroxides, such as Fe₂O₃, Fe₃O₄, Fe(OH)₃, and FeOOH, while the peak at 725 eV further proves the presence of ferric (Fe^{III}) iron oxide. These observations are consistent with previous studies, where Fe-oxides were detected at the nano-ZVI surface even in strict anaerobic environments.³⁷ The presence of Fe(0) is unclear here (peak at 707 eV);³⁸ as XPS analysis is a sensitive surface analysis only up to 10 nm depth, the presence of CNC and iron oxide at the nano-ZVI surface limits the Fe(0) detection with XPS.

The XRD diffractogram of the nano-ZVI composite showed the main peak of cellulose and nano-ZVI ($2\theta = 44.5$; $\lambda = 1.5406$ Å). No extra peaks for Fe were detected in this pattern,

indicating limited nano-ZVI oxidation. The results from XRD and XPS analysis are in accordance with the typical core-shell structure of nano-ZVI shown in Fig. 1C.

3.3 Transport properties of crystal nanocellulose

In a dilute system, the colloidal stability of charged particles is often controlled by the electrostatic interactions. The size and zeta potential of 0.1 g L⁻¹ CNC-OH and CNC-COOH suspensions in 1 mM NaHCO₃ solution were measured from pH 10 to 2 (Fig. S3, ESI†). At neutral pH, CNC and CNC-COOH were highly negatively charged at -46.3 and -49.3 mV, respectively. The CNC-OH was produced by hydrolysis using sulfuric acid; residual sulfonic acid groups (pK_a -2.6) are present at the surface of CNC-OH (confirmed by XPS of CNC-OH and CNC-COOH, data not shown) that provide a negatively charged stable suspension. Zeta potential values of CNC-COOH appeared slightly lower than those of CNC-OH over this pH range due to the presence of COOH groups, which increases the charge density.

The surface charge of CNC-OH and CNC-COOH was only slightly influenced by the pH from pH 2 to 10 (Fig. S3, ESI†).³⁹ From pH 4 to 10, zeta potential values remained close to -40 mV, suggesting a high surface (-) charge. The mean hydrodynamic diameter of CNC-OH and CNC-COOH was about 130 nm; this is consistent with the length of CNC observed by TEM.

CNC-COOH aggregation in the presence of salt has been previously studied; the main mechanism of surface charge reduction is through specific interactions of counter ions with the deprotonated carboxyl groups. Fall *et al.*³⁹ suggested that the aggregation of CNC-COOH occurs at pH 3 and/or with salt concentrations up to 100 mmol L⁻¹.³⁹ However, aggregation of CNC can occur at relatively lower salt concentration, at 1.5 mmol and 10 mmol for divalent (Ca²⁺) and monovalent (Na⁺) ions, respectively.⁴⁰ All column experiments were conducted in the presence of 1 mM NaHCO₃ salt, below the critical salt concentration for both CNC types.

Transport experiments using 1 g L⁻¹ CNC-OH and CNC-COOH were conducted using glass beads as a porous medium having a streaming potential of -39 mV at pH 6.8. Breakthrough curves for both types of CNC follow perfectly the tracer breakthrough curve, without any elution delay (Fig. 4), indicating that there were no preferential flow paths in the column and nanocrystals have moved thoroughly along the porosity of the porous medium. The average C/C_0 of the plateau was 0.98 and 0.99 for CNC-OH and CNC-COOH, respectively, suggesting near complete mobility of the nanocrystal in the porous medium. To the best of our knowledge, this is the first report investigating the mobility of CNC in porous media. In our experiments, the nanocomposites showed low affinity for the glass bead surfaces, with α values calculated to be 0.015 and 0.007 for CNC-OH and CNCCOOH, respectively. The transport experiment of CNC-OH and CNC-COOH is the first validation for their potential use as a solid support/stabilizer for nano-ZVI in order to achieve better mobility of the nano-ZVI during field applications.

3.4 Transport property of nano-ZVI nanocomposite

After the synthesis, CNC-(COOH)/nano-ZVI nanocomposites were isolated *via* magnetic separation. The nanocomposite has a gel like structure. The gel structure of CNC materials is well known and commonly observed when the CNC concentration is increased up to a few wt%.²¹ It appears that the gel structure of CNC-(COOH)-nano-ZVI nanocomposite aids in re-suspension in water. In order to study the influence of the mass ratio of CNC and Fe on CNC/nano-ZVI colloidal stability, different syntheses were conducted at varying CNC-OH/Fe ratios (wt%) of 0.2, 0.33, 1 and 3. The zeta potential values of CNC/Fe obtained from each synthesis are shown in Fig. 5. Results are compared with the zeta potential values of bare nano-ZVI and CNC alone. The CNC-nano-ZVI composites present zeta potential values in between those of bare nano-ZVI (−8.9 mV) and CNC (−46.3 mV). The zeta potential of the nanocomposites decreased strongly at a CNC/Fe wt% ratio of below 1. Our results show that the CNC/Fe wt% ratio is directly related to the zeta potential of the nanocomposite; logically by increasing the amount of CNC, the influence of the nano-ZVI surface on the zeta potential decreases. The CNC/Fe wt% of 1 seems to be optimal in order to have lower zeta potential values; additionally, it limits the amount of CNC added. In our study, we performed our synthesis using a CNC/Fe mass ratio of 1. It should also be noted here that according to the nano-ZVI and CNC densities, the CNC volume is about 4.8 times higher than that of the nano-ZVI.

CNC=OH/nano-ZVI and CNC-COOH/nano-ZVI with a CNC/Fe mass ratio of 1 showed a final zeta potential of −38 mV and −48 mV and a mean hydrodynamic diameter of 750 and 550 nm, respectively. The CNC-COOH/nano-ZVI showed a significantly higher zeta potential and a smaller size in comparison to CNC-OH/nano-ZVI.

Fig. 6 represents the breakthrough curves obtained from the glass bead column experiments using 1 g L^{−1} Fe nanoparticle/nanocomposite suspensions. NaCl was used as an inert conservative tracer for these columns prior to nano-ZVI/nanocomposite injection. C/C_0 for CNC-OH/nano-ZVI and CNC-COOH/nano-ZVI shows a stabilized plateau after 1.5 PV, with a mean C/C_0 of 0.74 and 0.90 (calculated in between PV 2 and 3), respectively. Elution of bare nano-ZVI is significantly lower with a maximum C/C_0 at 0.06. This observation is consistent with previous studies showing the low mobility of bare nano-ZVI in porous media.^{7,41} Thus, this data indicates that CNC-OH and CNC-COOH can be used as a support/stabilizer to significantly improve the nano-ZVI mobility. The total iron mass recovery was 4%, 83% and 87% for bare nano-ZVI, CNC-nano-ZVI and CNC-COOH-nano-ZVI, respectively.

CNC-COOH-nano-ZVI exhibited a slight “ripening” type deposition behavior whereby deposited particles act as additional collectors for the deposition of approaching particles, resulting in a temporal decrease of C/C_0 (slope of linear line of −0.033) during the plateau phase. Based on the symmetrical shape and the lack of tailing of the breakthrough curve of the conservative tracer, it can be concluded that the extended tailing of CNC-nano-ZVI and CNC-COOH-nano-ZVI concentrations during elution was not due to the potential presence of advective pore space³⁵ but rather was a result of re-entrainment of nano-ZVI.

The colloid filtration theory (CFT) was used to describe the deposition of particles in the porous media. Attachment efficiencies (α) were calculated from the normalized concentrations (C/C_0) at the plateau phase of the breakthrough curves,⁴² using the following equation:

$$\alpha = \frac{2d_c}{3(1-f)\eta_0} \ln\left(\frac{C}{C_0}\right) \quad (4)$$

where d_c is the diameter of the collector, f is the porosity and η_0 is the predicted single-collector contact efficiency determined from ref. 43 using the following equation.

$$\eta_0 = 2.4A_s^{1/3}N_R^{-0.081}N_{Pe}^{-0.715}N_{vdW}^{0.052} + 0.55A_sN_R^{1.675}N_A^{0.125} + 0.22N_R^{-0.24}N_G^{1.11}N_{vdW}^{0.053} \quad (5)$$

All parameters used in the calculation are described in the ESI.† These calculations used values of particle diameter obtained from DLS measurements. The calculated α values were 2.15, 0.23 and 0.12 for bare-nano-ZVI, CNC-nano-ZVI and CNC-COOH-nano-ZVI, respectively. Accurate measurements of particle size for the bare-nano-ZVI by DLS were not possible due to rapid aggregation of these particles and thus the TEM observed size of bare-nano-ZVI was used for the calculation of α . However, it is likely that aggregation in this case also occurred in the feed stream to the column. For these reasons, α values for bare-nano-ZVI are not likely to be greater than unity. The difference in attachment efficiency between CNC-nano-ZVI and CNC-COOH-nano-ZVI can be explained by the nanocomposite colloidal properties. The hydrodynamic diameter and the zeta potential of CNC-COOH-nano-ZVI are significantly lower. In addition, the CNC-COOH-nano-ZVI nanocomposite may have been more stable due to chemical binding between nano-ZVI and the carboxyl group of CNC-COOH.

Mobility assessment of surface supported nano-ZVI is not well reported in the literature. For example, supported nano-ZVIs on clay (zeolite, kaolinite, montmorillonite) have been highly reported in the literature; no transport study has been reported for these composites. Busch *et al.*⁴⁴ reported a mobility experiment of nano-ZVI supported on activated carbon (AC) and showed poor mobility of nano-ZVI-AC, but observed an increase in mobility when carboxymethyl cellulose (CMC) polyelectrolyte was added to the nano-ZVI-AC composite. The same strategy was also used successfully on nano-ZVI-AC composite (carbo-iron). The composite (nano-ZVI + activated carbon + CMC) shows a C/C_0 of 0.8 through silica sand (22×2 cm column, Darcy velocity: 1 ml min^{-1} , $C = 219 \text{ mg l}^{-1}$, $\text{CMC} = 0.2 \text{ wt\%}$).¹⁵ Nano-ZVI on mesoporous silica has also been investigated previously; the composite showed limited mobility with $C/C_0 = 0.15$ through a SiO_2 sand column (20×2.5 cm column, sand mesh 30 to 50, Darcy velocity: 12 ml min^{-1}).⁴⁵ In these studies, the authors did not report the attachment efficiency (α) which could allow us to directly compare with our results. However, we can compare our results with polyelectrolyte stabilized nano-ZVI studies referencing α . In silica sand, He *et al.* reported an α value of 0.0019 for 11.7 nm CMC-

nano-ZVI particles and Phenrat *et al.* reported an α value in the range of 0.30–0.32 for 63 nm PSS-nano-ZVI particles⁴⁶ at nano-ZVI concentrations comparable to those of our study. Laumann *et al.* reported an α value of 0.20 for commercial PAA-nano-ZVI in porous media (sand) with a Darcy velocity of $6 \times 10^{-4} \text{ m s}^{-1}$ and a $C_0 = 200 \text{ mg l}^{-1}$. The attachment efficiency (α) of CNC-COOH/nano-ZVI calculated here is lower than that of the commercial polyelectrolyte stabilized nano-ZVI even at lower Darcy velocity ($3.2 \times 10^{-4} \text{ m s}^{-1}$) and C_0 (1 g L^{-1}). The η_0 of CNC-nano-ZVI and CNC-COOH-nano-ZVI is 0.0024 and 0.00158, respectively. The η_0 is dominated by the cumulative effect of diffusion; therefore diffusion is recognized as the dominant mechanism for nanocomposite deposition (attachment on porous media).

3.5 Reactivity of CNC supported nano-ZVI with contaminants

The reactivity of CNC-supported nano-ZVI was studied by evaluating their ability to degrade MO dye. MO degradation by nano-ZVI has been well studied and reported in the literature. This was used as a proof of concept to assess the CNC-supported nano-ZVI. Fan *et al.*²⁷ described the degradation pathway of MO by nano-ZVI in two steps: adsorption and reduction. The reaction is associated with the formation of byproducts such as sulfanilic acid, *N,N*-dimethyl-*p*-phenylenediamine and *N*-methyl-*p*-phenylenediamine.

The degradation rate of MO (800 mg L^{-1}) using nano-ZVI (0.1 g L^{-1}) as reactant was investigated using a batch test setup at 298 K (Fig. 7). Two controls were also set up for each of the two nanocellulose samples without nano-ZVI. At the end of the reaction, the bands at 463 and 270 nm became weaker and a new band at 248 nm appeared (Fig. S4, ESI[†]). The spectra revealed the MO degradation and the formation of sulfanilic acid as one of the by-products identified by the band at 248 nm.^{16,27}

Control CNC-OH and CNC-COOH without nano-ZVI did not show significant degradation or adsorption of MO. CNCs are likely to be poor adsorbents for MO due to their hydrophilic surfaces. However, in our study, we observed an increase of nano-ZVI reactivity in the presence of CNC. Cellulose nanocrystal-supported nano-ZVI showed higher reactivity towards dye removal compared to the bare-nano-ZVI. After 30 min of reaction, MO dye was degraded up to 62%, 82%, and 84% by using bare-nano-ZVI, CNC-nano-ZVI, and CNC-COOH-nano-ZVI, respectively. The modelled C_{ultimate} and calculated empirical rate constant (eqn (3)) are 302, 146 and 132 mg l^{-1} and k is equal to 0.39, 0.41, and 0.34 min^{-1} for bare-nano-ZVI, CNC-nano-ZVI and CNC-COOH-nano-ZVI, respectively. Unlike stabilization methods reported previously,^{23–25,47} the use of nanocellulose as a support material does not decrease the reactivity of nano-ZVI, but rather, increases it. For example, the use of polymer coating has been shown to reduce the nano-ZVI reactivity by limiting pollutant interaction with the nano-ZVI reactive site.¹² Polyelectrolyte with a high molecular weight induces further decrease of reactivity. The use of support materials should, in theory, preserve the availability of nano-ZVI reactive sites and consequently the nano-ZVI reactivity.

Considering a nano-ZVI size of 107, 117 and 112 nm for bare-nano-ZVI, CNC-OH-nano-ZVI and CNC-COOH-nano-ZVI, respectively, the surface specific of nano-ZVI and the number of reactive sites at nano-ZVI surface for all samples are similar. Considering a mean

surface area of 112 nm (≈ 107 , 117 and 112 nm), the theoretical surface area of nano-ZVI would be $5.8 \text{ m}^2 \text{ g}^{-1}$, representing the removal of 862, 1128 and 1152 ppm of MO per m^2 of nano-ZVI for bare-nano-ZVI, CNC-nano-ZVI and CNC-COOH-nano-ZVI, respectively. The reactivity of nano-ZVI increased about 25% in the presence of CNC. Aggregation of bare-nano-ZVI plays an important role in nano-ZVI reactivity by limiting the contaminant access to the nano-ZVI surface. The denser and bigger the aggregates are, the lower the nano-ZVI reactivity is expected to be. During our experiment, bare-nano-ZVI aggregation was observed; nevertheless, when CNC was introduced into the nano-ZVI as a supporting material, it did stabilize and disperse the nano-ZVI particles by preventing aggregation, and consequently increased the reactivity of nano-ZVI by allowing the MO access to the nano-ZVI surface.

3.6 Environmental implications

The main impediment in the use of nano-ZVI particles in subsurface environmental application is the limited mobility, which restricts the sphere of influence in the treatment process and hence, the efficiency. Nano-ZVI itself, as considered by many, is a harmless and non-toxic reactive material,^{48–50} but the slow mobility derived by affinity for sediment surfaces restricts its efficiency. Our results indicate that using crystal cellulose nanomaterials as a delivery vehicle for nano-ZVI particles addresses this concern directly by enhanced reactivity (by limiting the aggregation) and mobility. Also, cellulose nanocrystals are considered to have limited to no harmful environmental impacts, are biodegradable and are relatively easy to synthesize.^{51–53} Cellulose nanomaterials represent a new class of sustainable materials with a potential to be used in environmental applications.

Undoubtedly, real field conditions are not as optimized as lab scale studies and may reflect slightly different reactivity and mobility, but our study shows the first-hand potential of these nanocomposites as delivery vehicles. More research is required in assessing the reactivity of these nanomaterials with different organic and inorganic contaminants and also their mobility in field conditions (*i.e.* presence of natural colloids such as clay or humic acid, Darcy velocity, bacterial community, collector heterogeneity). To the best of our knowledge, this study provides the first evidence of the potential future use of CNC/nano-ZVI nanocomposites in remediation systems with improved reactivity and mobility.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Environmental significance

We report the synthesis of zero-valent iron nanoparticles (nano-ZVIs) supported by cellulose nanocrystals (CNCs) for *in situ* remediation of groundwater. In contrast to polyelectrolyte stabilization of nano-ZVI, CNC stabilization of nano-ZVI creates a porous “mesh” around the nano-ZVI surface that could increase the number of available reactive sites at the nano-ZVI interface. CNCs play a dual role as a supporting matrix by improving nano-ZVI reactivity (by limiting nano-ZVI aggregation) and mobility in porous media. The measured attachment affinity of the CNC-nano-ZVI nanocomposite to the collector surface was lower than the attachment affinity of the unsupported nano-ZVI and commercial polyelectrolyte stabilized nano-ZVI referenced. Furthermore, CNCs are naturally sourced, environmentally friendly and biodegradable, which makes them an ideal material for the design of inorganic–organic nanocomposites for the purpose of *in situ* environmental remediation, in agriculture and other applications.

Fig. 1. TEM images of (A) CNC, (B) bare-nano-ZVI with a schematic view of the typical bare-nano-ZVI chain-like cluster morphology (top left), (C) core-shell structure, (D) and (E) CNC(-COOH)-nano-ZVI with a schematic view of the typical CNC(-COOH)-nano-ZVI nanocomposite morphology (bottom left).

Fig. 2.
FT-IR spectra of (a) CNC-OH, (b) CNC-OH-Fe, (c) CNC-OH-nano-ZVI, (d) CNC-COOH, (e) CNC-COOH-Fe, and (f) CNC-COOH-nano-ZVI.

Fig. 3.
XPS spectra of Fe 2p for CNC-COOH-nano-ZVI and CNC-nano-ZVI.

Fig. 4. Experimental breakthrough curves for CNC-COOH, CNC-OH at a v_p of $3.2 \times 10^{-4} \text{ m s}^{-1}$, $C_0 = 1 \text{ g L}^{-1}$.

Fig. 5.
Zeta potential measurements of CNC-OH-nano-ZVI against the CNC/Fe wt% ratio at pH 6.8.

Fig. 6. Experimental breakthrough curves for bare-nano-ZVI, CNC-nano-ZVI, and CNC-COOH-nano-ZVI at a ν_p of $3.2 \times 10^{-4} \text{ m s}^{-1}$, $C_0 = 1 \text{ g L}^{-1}$.

	$k(\text{min}^{-1})$	r^2	C ultimate (ppm)	Amount degraded (ppm of OM/m ²)
bare-nano-ZVI	0.39	0.95	302	862
CNC-nano-ZVI	0.41	0.98	146	1128
CNC-COOH-nano-ZVI	0.34	0.95	132	1152

Fig. 7. Comparative removal of MO dye using bare-nano-ZVI, CNCOH/nano-ZVI and CNC-COOH/nano-ZVI. Conditions: amount of OM = 800 ppm, amount of nano-ZVI = 100 ppm, temperature: 298 K, agitation speed: 200 ppm, anaerobic.