Electronic supplementary information

Encapsulating nanoscale zero-valent iron with a soluble Mg(OH)₂ shell for improved mobility and controlled reactivity release

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S1. Preparation of bare NZVI (BNZVI).

BNZVI was synthesized by reduction of FeCl₃ in aqueous phase with NaBH₄^{1, 2}. In brief, a 0.4 M NaBH₄ aqueous solution was added into 71.5 mL of a 0.01 M FeCl₃ aqueous solution at a rate of 4.5 mL/min controlled by a peristaltic pump (LongerPump BT100-2J), with mechanical stirring. After 10-min injection and reaction, BNZVI particles formed in the solution were separated by magnet and washed with water and ethanol sequentially for three times. The ethanol washing were assisted with sonication (40 kHz, 100 W) in the nitrogen gas atmosphere for complete removal of any impurities.

S2. Supplemental characterizations of BNZVI and NZVI@Mg(OH)₂.



Fig. S1. Fe⁰/Fe ratios of BNZVI and NZVI@Mg(OH)₂ with different coating doses.



Fig. S2. Concentration of dissolved Mg^{2+} ions and end pH values in the suspension of NZVI@Mg(OH)₂ with different coating doses ([NZVI] = 0.1 g/L, [NaHCO₃] = 1.0 mM).

S3. Sedimentation test.

The sedimentation test was conducted to evaluate the effects of $Mg(OH)_2$ shell on suspension stability of NZVI ³. The test was conducted in a 1-cm optical cuvette with a UV-Vis spectrophotometry (Biochrom Libra S12). Briefly, the 1.0 mM NaHCO₃ solution were used to prepare a 2 mL dispersion BNZVI or NZVI@Mg(OH)₂ containing 0.1 g/L NZVI in the cuvette. Then the dispersion was sonicated for 20 sec under N₂ atmosphere. lastly, the dispersion was monitored at 508 nm to record the change of its optical absorbance (I_t) with time, which was well correlated to the change of the NZVI concentration.

Fig. S3 presents sedimentation curves of BNZVI and NZVI@Mg(OH)₂ with coating doses from 10 to 100 wt%. The sedimentation curves were obtained by plotting the normalized absorbance (I_t/I_0) as a function of time. With a constant NZVI concentration of 0.1 g/L, the I_0 of the suspension increased gradually from 1.10 to 1.55 as the coating doses increasing from 0 to 100 wt%. Decreases on I_t/I_0 indicates the aggregation and sedimentation process of nanoparticles occurring in the detection region (top region of the 2 mL dispersion). The half time of particle sedimentation (t_{half} for $I_t/I_0 = 0.5$) increased from 8.1 to 157.4 min as the Mg/Fe increased from 0 to 100 wt% (Table S1). Even after the sedimentation test, the NZVI@Mg(OH)₂ particles could still suspend in the aqueous solution, while the BNZVI particles had settled completely (Fig. S4).

The sedimentation curves of BNZVI and NZVI@Al(OH)₃ followed the pattern reported for the sedimentation of nanoparticles ³. As shown in the Fig. S3, in the beginning, the I_t/I_0 decreased slowly before an apparently critical time (t_{crit}), which means the aggregation of NZVI particles is dominated with a slow settling velocity. Then, the I_t/I_0 decreased critically after t_{crit} , indicating the settling is dominated, as NZVI clusters linked together to form chains and aggregates of a certain size and began to settle at a much faster velocity. The two portions of the sedimentation curves were fitted by Eq. S1, to describe the removal of particles by sedimentation from the detection region:

$$\frac{I_t}{I_0} = e^{-t/\tau} \tag{1}$$

where τ is the characteristic time. The fitting results were presented in Table S1. For portion I of the sedimentation curve, the τ_1 increased significantly from 35.5 to 840.3 with coating doses from 0 to 100 wt%. Meanwhile, the τ_2 increased slightly from 5.2 to 15.6. The results of characteristic times revealed that the effects of Mg(OH)₂ on the suspension stability of NZVI were mainly on the aggregation process. After the aggregates with certain size were formed, the settling velocity of BNZVI and NZVI@Mg(OH)₂ had no remarkable difference.

Initial particle size before sedimentation grew gradually from 324.2 to 1553.6 nm with the Mg(OH)₂ coating shell (Fig. S5). Although the greater sizes would enhance the frequency of collisions between particles and promote sedimentation ⁴, the suspension stability of the NZVI@Mg(OH)₂ particles were not influenced by the size increments. Although the magnetic attraction between the NZVI@Mg(OH)₂ particles was weakened, the hysteresis behaviors were still noticeable for all coating doses, which gives the NZVI@Mg(OH)₂ ease of magnetic separation (Fig. S4c).



Fig. S3. Sedimentation curves of BNZVI and NZVI@Mg(OH)₃ with different coating doses (sedimentation conditions: [NZVI] = 0.1 g/L, $[NaHCO_3] = 1.0 \text{ mM}$).

Table S1. Analysis results of sedimentation tests of BNZVI and NZVI@Mg(OH)₂ with different coating doses (Mg/Fe). ([NZVI] = 0.1 g/L, [NaHCO₃] = 1.0 mM)

Dose, wt%	t _{half} , min	t _{crit} , min	$ au_1$	R ²	$ au_2$	R ²
0	8.1	5.7	35.5	0.9882	5.2	0.9813
10	30.4	28.6	96.3	0.8988	3.0	0.9962
20	33.8	31.0	111.6	0.2985	6.0	0.9756
50	64.2	59.8	359.7	0.6371	8.1	0.9973
100	157.4	147.3	840.3	0.07081	15.6	0.9991



Fig. S4. Suspension sedimentation of (a) BNZVI after 16.5 min and (b) 100 wt% NZVI@Mg(OH)₂ after 177.5 min ([NZVI] = 0.1 g/L, [NaHCO₃] = 1.0 mM) and (c) 100 wt% NZVI@Al(OH)₃ suspension after magnetic separation.



Fig. S5. Size distribution of BNZVI and NZVI@Mg(OH)₂ with different coating doses.

S4. Supplemental information for mobility test and modelling.



Fig. S6 Size distribution of quartz sands after sieving.



Fig. S7 Variations on ζ-potential of quartz sand and pH values with dissolution of the 100-wt% Mg(OH)₂ shell in the 1 mM NaHCO₃ solution.

The BTCs and RPs were simulated by the HYDRUS-1D computer code basing on the advection-dispersion equation:

$$\theta \frac{\partial C}{\partial t} = \theta D \frac{\partial^2 C}{\partial x^2} - q \frac{\partial C}{\partial x} - \rho \frac{\partial S}{\partial t}$$
(2)

where θ is the porosity of the saturated sand column, ρ is the bulk density of the sand [M L⁻³], M and L denote the units of mass and length, respectively, *C* is the aqueous concentration of NZVI in the effluent [M L⁻³], *t* is the time [T], T denotes unit of time, *x* is the distance from the column inlet [L], *D* is the hydrodynamic dispersion coefficient [L² T⁻¹], *q* is the Darcy water flux [L T⁻¹], and S is the solid phase concentration of NZVI [M M⁻¹].

When $\psi = 1$, the k_{sw} is the particle deposition rate coefficient and can be described as:

$$k_{sw} = \frac{3(1-\theta)}{2d_c} \eta_0 \alpha_{pc} U \tag{3}$$

where *U* is the velocity of pore water (m/s). Equations for predicting the single-collector contact efficiency (η_0) are presented as follow ⁵:

$$\eta_0 = 2.4A_S^{1/3} N_R^{-0.081} N_P^{-0.715} N_{vdW}^{0.052} + 0.55A_S N_R^{1.675} N_A^{0.125} + 0.22N_R^{-0.24} N_G^{1.11} N_{vdW}^{0.053}$$
(4)

$$A_{S} = \frac{2(1 - \gamma^{5})}{2 - 3\gamma + 3\gamma^{5} - 2\gamma^{6}}$$
(5)

$$N_R = \frac{d_P}{d_C} \tag{6}$$

$$N_{Pe} = \frac{Ud_C}{D_{\infty}} \tag{7}$$

$$N_{vdW} = \frac{A}{kT} \tag{8}$$

$$N_{gr} = \frac{4\pi a_P^4 (\rho_P - \rho_f) g}{3 kT} \tag{9}$$

$$N_A = \frac{A}{12\pi\mu a_P^2 U} \tag{10}$$

$$N_{G} = \frac{2a_{P}^{2}(\rho_{P} - \rho_{f})g}{9\ \mu U}$$
(11)

where A_S is a porosity-dependent parameter; $\gamma = (1-\theta)^{1/3} = 0.809$; N_R is an aspect ratio; d_P and d_C are diameters of particle and collector, respectively; N_{Pe} is the Peclet number characterizing ratio of convective transport to diffusive transport; $D_{\infty} = kT/(6\pi\mu a_p)$, is the diffusion coefficient in an infinite medium (m²/s); a_p is the radius of particle; μ is the absolute viscosity of fluid (Pa·s); $k = 1.3805 \times 10^{-23}$ J/K is the Boltzmann constant; T is the absolute temperature (K); N_{vdW} is the van der Waals number characterizing ratio of van der Waals interaction energy to the particle's thermal energy; $A = 1 \times 10^{-20}$ J, is the Hamaker constant; N_A is the attraction number; N_G is the gravity number; ρ_f and ρ_P are densities od fluid and particle (kg/m³), respectively; g = 9.8 m/s² is gravitational acceleration.



Fig. S8. Photographs of sand columns of (a) BZNVI and (b) – (e) $NZVI@Mg(OH)_2$ with coating doses from 10 to 100 wt% at different transportation time.

Model	Coating	k _{sw}	$S_{max/}L_0$	P ²	α
Widder	dose	[min ⁻¹]	$[cm^{3}/g]$	Λ	- pc
M1	Bare	3.69	/	0.92	16.15
	10 wt%	1.73	/	0.86	8.03
	20 wt%	0.63	/	0.94	2.96
	50 wt%	0.18	/	0.72	0.81
	100 wt%	0.049	/	0.93	0.18
M2	Bare	31.75	11.84	0.95	/
	10 wt%	25.71	5.27	0.96	/
	20 wt%	9.97	1.60	0.97	/
	50 wt%	5.40	0.50	0.80	/
	100 wt%	4.23	0.21	0.98	/

Table S2. Fitted model Parameters Using model M1 and M2

1. R^2 reflects the correlation of experimental and fitted data for breakthrough curves and retention profiles; 2. $C_0 = 1$ g/L

Matariala	d _P	D_{∞}	$ ho_{ ext{P}}{}^{1}$		N	N	N	N	λī	n. () (10.2)
Materials	(×10 ⁻⁹ m)	(m^{2}/s)	(kg/m ³)	A_{S}	INR	IN _{Pe}	IN _{vdW}	IN _A	IN _G	⁷⁰ (×10 ³)
Bare	324.2	1.51×10 ⁻¹²	7860.0	22.64	8.96×10 ⁻⁴	134665.61	2.43	2.01×10-2	7.83×10-4	3.20
10 wt%	748.7	6.56×10 ⁻¹³	5417.3	22.64	2.07×10-3	310993.66	2.43	3.78×10 ⁻³	2.69×10-3	3.01
20 wt%	884.8	5.55×10 ⁻¹³	4477.0	22.64	2.44×10-3	367526.64	2.43	2.70×10-3	2.96×10-3	2.99
50 wt%	1177.6	4.17×10 ⁻¹³	3461.1	22.64	3.25×10-3	489149.37	2.43	1.53×10-3	3.71×10 ⁻³	3.17
100 wt%	1553.6	3.16×10 ⁻¹³	2971.8	22.64	4.29×10 ⁻³	645331.58	2.43	8.77×10 ⁻⁴	5.17×10-3	3.81

Table S3. Summary of dimensionless parameters governing particle filtration.

1. The particle density were calculated basing on an assumption that density of NZVI and Mg(OH)₂ were 7860 and 2360 kg/m³, respectively.



Fig. S9. Fitting curves using model M1 for (a) breakthrough and (b) retention of BNZVI and NZVI@Mg(OH)₂ with different coating doses. ([NZVI] = 1 g/L, $[NaHCO_3] = 1.0 \text{ mM}$, pore water velocity = 3.38 cm/min).



Fig. S10. The Mg/Fe ratios of the solid phase NZVI particles (a) in the effluents of the sand columns and (b) retained within the sand columns.

S5. Time-dependent dissolution of Mg(OH)₂.

Time-dependent dissolution of $Mg(OH)_2$ was conducted by adding synthesized pure $Mg(OH)_2$ into 40 mL of 1.0 mM NaHCO₃ solution to obtain a Mg concentration of 100 mg/L.



Fig. S11. Time-dependent dissolution of synthesized pure $Mg(OH)_2$ in aqueous solution ($[Mg(OH)_2-Mg] = 0.1 \text{ g/L}$, $[NaHCO_3] = 1.0 \text{ mM}$).

S6. Supplemental results of controlled reactivity release.

Samples	Fe	Mg	Cr	О	С
(1)	1.6	21.4	0.0	61.5	15.4
(2)	4.5	12.6	2.1	66.7	14.0
(3)	10.7	6.3	4.3	62.8	15.9
(4)	42.0	0.0	0.0	48.7	9.3
(5)	9.3	0.0	14.6	54.8	21.3
(6)	0.0	22.0	0.0	64.1	13.9

Table S4. XPS element concentration (atomic %) of 50-wt% NZVI@Mg(OH)₂ and BNZVI before and after Cr(VI) removal.

Note: (1) fresh 50-wt% NZVI@Mg(OH)₂; (2) 50-wt% NZVI@Mg(OH)₂ after Cr(VI) removal with pre-washing treatment of 10 L/g and (3) 20 g/L; (4) fresh BNZVI; (5) BNZVI after Cr(VI) removal; and (6) fresh pure Mg(OH)₂.

Compounds	Binding energy, eV	FWHM, eV
Fe ⁰ 2p _{3/2}	707.1	1
$Fe^{0} 2p_{1/2}$	720.2	1.2
Fe(II) 2p _{3/2}	710.2	2.4
Fe(II) 2p _{1/2}	723.5	2.3
Fe(III)-O 2p _{3/2}	711.6	2.7
Fe(III)-O 2p _{1/2}	725.2	2.8
Fe(III)-OH 2p _{3/2}	714	2.5
Fe(III) satellite 2p _{3/2}	718.7	4

Table S5. Binding energy, FWHM and %L-G used for deconvolution of Fe 2p XPS spectra.

Table S6. XPS element concentration (atomic %) of 50-wt% NZVI@Mg(OH)₂ and BNZVI before and after Cr(VI) removal.

Samples	Fe ⁰	Fe(II)	Fe(III)
(1)	4.7	64.4	30.9
(2)	3.5	13.6	82.9
(3)	1.5	4.1	94.4
(4)	/	/	/
(5)	10.9	35.4	53.7
(6)	8.3	60.9	30.7

Note: (1) fresh 50-wt% NZVI@Mg(OH)₂; (2) 50-wt% NZVI@Mg(OH)₂ after Cr(VI) removal with pre-washing treatment of 10 L/g and (3) 20 g/L; (4) fresh BNZVI; (5) BNZVI after Cr(VI) removal; and (6) fresh pure Mg(OH)₂.



Fig. S12. Cr(VI) removal with (a) BNZVI and (b) 10 wt%, (c) 20 wt% and (d) 100 wt% NZVI@Mg(OH)₂ before and after the pre-treatment process ($[NZVI] = 0.1 \text{ g/L}, [Cr(VI)]_0 = 10 \text{ mg/L}, [NaHCO_3] = 1.0 \text{ mM}$).



Fig. S13. Dissolved Mg²⁺ concentration in the supernatant after each batch experiment of pre-treatment and Cr(VI) removal with (a) 10 wt%, (b) 20 wt%, (c) 30 wt% and (d) 100 wt% NZVI@Mg(OH)₂. Last batch at each activation volume is the batch Cr(VI) removal experiment ([NZVI] = 0.1 g/L, [Cr(VI)]₀ = 10 mg/L, [NaHCO₃] = 1.0 mM).

50
/
/
.90

Table S7. End pH values of Cr(VI) removal with NZVI@Mg(OH)₂ after pre-treatment process with various activation volume.

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