Electronic Supplementary Information

Anisotropic Oxidative Growth Of Goethite-Coated Sand Particles In Column Reactors During 4-Chloronitrobenzene Reduction by Fe(II)/Goethite

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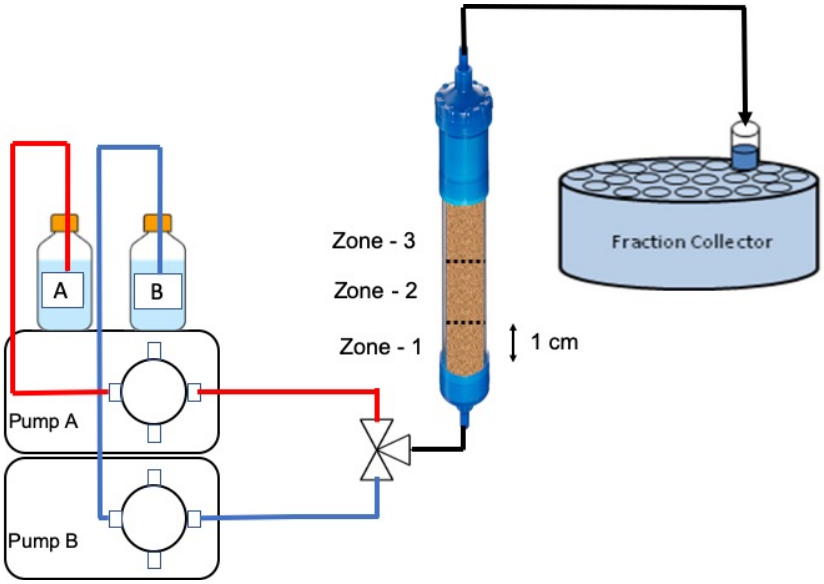
Environmental Science: Nano

Section S1: Column Schematic



Solution A: $FeCl_2$ (buffered with 10 mM $NaHCO_3$)

Solution B: 4-ClNB (buffered with 10 mM $NaHCO_3$)

Figure S1. The schematic image of column set up. The whole apparatus was placed in an anaerobic glove box to prevent any oxygen poisoning. The image is not to scale.

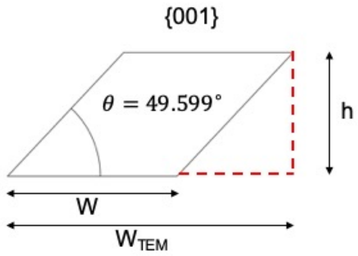
Table S1. Listing of all column experiments performed with feed conditions.

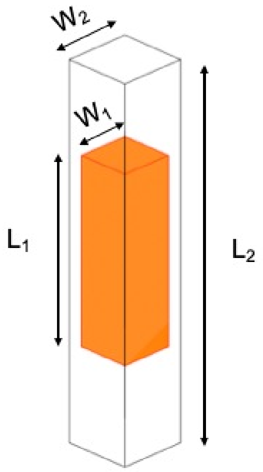
Column ID	Filling Material	Feed	Saturation	# Pore Volumes	Results
S-1	Sand	Fe(II)[a]	Saturated	4	Fig. S-6 (a)
S-2	Sand	4-ClNB[b]	Saturated	4	Fig. S-6 (b)
S-3	Sand	Fe(II), 4-ClNB	Saturated	18	Fig. S-9
SG-1	Goethite-coated sand	Fe(II)	Saturated	4	Fig. S-6 (a)
SG-2	Goethite-coated sand	4-ClNB	Saturated	4	Fig. S-6 (b)
SG-3	Goethite-coated sand	NaBr[c]	Saturated	2.5	Fig. S-7
SG-4	Goethite-coated sand	Fe(II), 4-ClNB	Saturated	18	Fig. S-9, S-11
SG-5	Goethite-coated sand	Fe(II), 4-ClNB	Saturated	220	Fig. 2, 4
SG-6	Goethite-coated sand	Fe(II), 4-ClNB	Saturated	220	Fig. S-10
SG-7	Goethite-coated sand	Fe(II), 4-ClNB	Unsaturated	220	Fig-3, 4
SG-8	Goethite-coated sand	Fe(II)	Saturated	110	Fig.S8

[a] Fe(II) concentration:1 mM
[b] 4-ClNB concentration: 0.1 mM
[c] NaBr concentration: 10 mM

Section S2: Calculation of new goethite mass formed

Calculation of the particle dimensions:





Cross-section area: $A = (W \times h)$

$W = 0.61 W_{TEM}$

$h = 0.46 W_{TEM}$

$V = (W \times h) \times L$

New goethite mass added to the column = ($V_{\text{average}} - V_{\text{average, detached}}$)$\times \rho_{goethite}$

V_{average} = $(W_{average} \times h_{average}) \times L_{average}$

$L_{average} = (L_{Z-1} + L_{Z-2} + L_{Z-3})/3$

$W_{average} = (W_{Z-1} + WL_{Z-2} + W_{Z-3})/3$

Calculation of the predicted mass of new goethite formed via an electron balance:

Method 1

1- Number of moles of organic compound (4-ClAn) production (A)

A= Area under $C_{4\text{-}ClAn}$ (mole/L) vs. V(L)

2- Number of moles of electrons used for the reaction (B)

$B = 6 \times A$

3- Mass of newly formed goethite (C)

$C = B \times$ molecular weight of goethite (88.85 g/mol)

Method 2

1- Number of moles of organic compound (4-ClNB) fed to the column (A)

$A = \ C_{Feed}\ (mol/L) \times t \times Q(L/min)$

2- Number of moles of organic compound (4-ClNB) left the column (B)

B = Area under C(mole/L) vs. V(L)

3- Number of moles of organic compound (4-ClNB) consumed (D)

$D = A - B$

4- Number of moles of electrons used for the reaction (E) = $6 \times \ D$
5- Mass of newly formed goethite (F) = E × molecular weight of goethite (88.85 g/mol)
6- Mass of goethite coated on sand grains (G) = $m \times d \times l$

Where:

m: mass of sand grains in a column reactor

d: goethite dose in coating process (mL $_{\text{goethite stock solution}}$/g $_{\text{sand}}$)

l: mass loading of goethite in the stock solution (mg/mL)

t: elapsed time (min)

Q: feed flow rate

Section S3: Additional Data

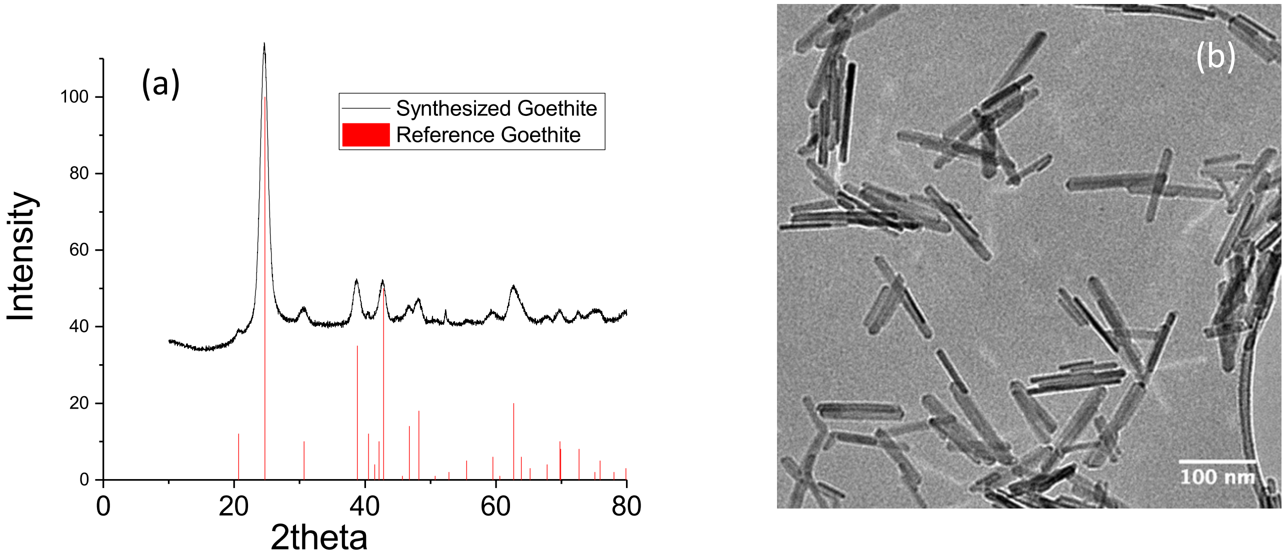


Figure S2. X-ray diffraction pattern for synthesized goethite and powder diffraction file 029-071 (a) and TEM image of as-synthesized goethite particles (b).

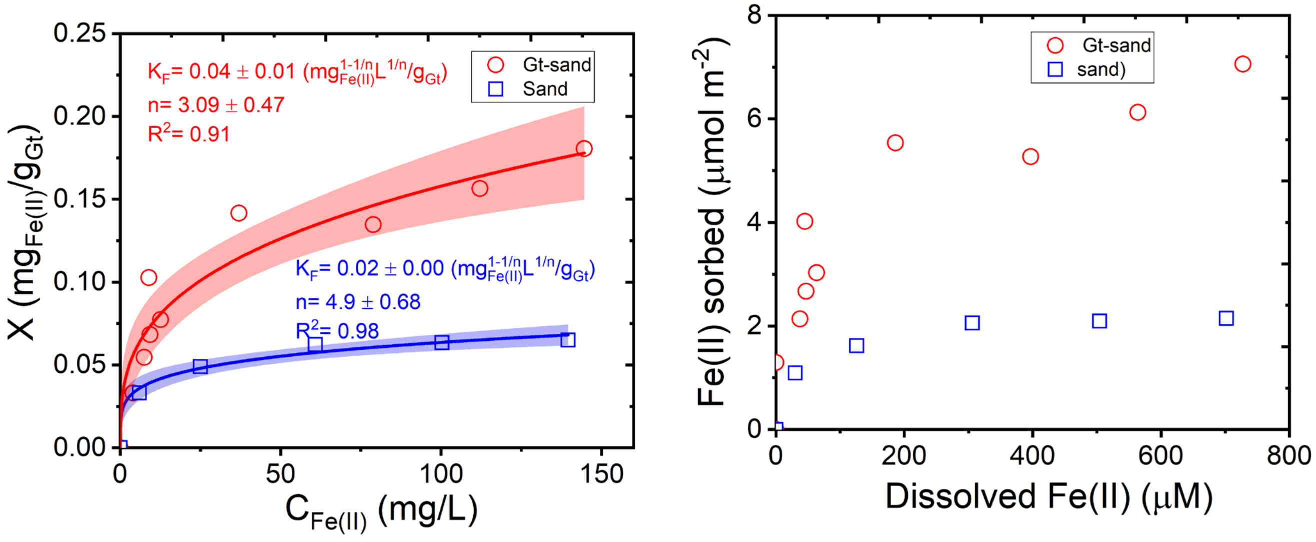


Figure S3. Left: sorption isotherms of Fe(II) on bare and goethite-coated sand (GT-sand) at pH 7 in 10 mM $NaHCO_3$ buffer. The solid lines represent fits using the Freundlich adsorption model. Errors reported with the parameters are 95% confidence intervals, and 95% confidence bands are shown in red and blue shades. Data were fit to Freundlich equation: $X = K_F C^{\frac{1}{n}}$ where X is amount of sorbate adsorbed per mass of sorbent ($mg_{Fe(II)}/g_{Gt}$); C is the equilibrium sorbate concentration ($mg_{Fe(II)}/L$). K_F and n are model parameters.

Right: The same data represented in different units for the dissolved Fe(II) and adsorbed Fe(II) to be compared to Dixit et el. results.[1]

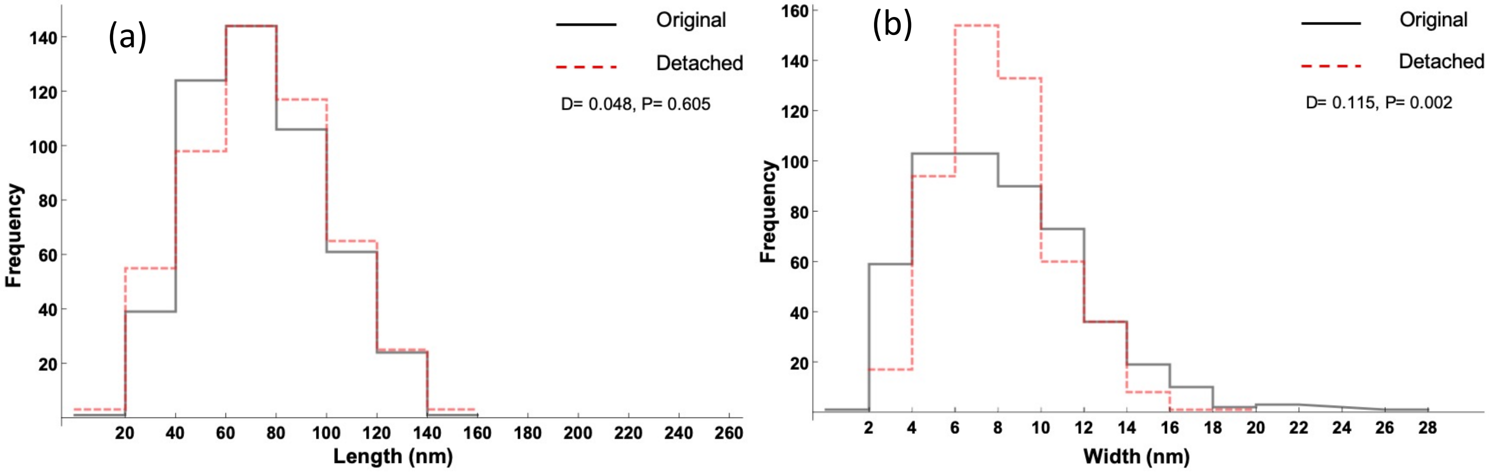


Figure S4. The distribution of goethite length (a) and width (b) of detached from sand at pH 9 compared to ones of original particles. P values show if data sets are statistically different (for P < 0.05) and D values show how histograms are different from the one for the original particles. Larger D values indicate the more difference from the detached particles.

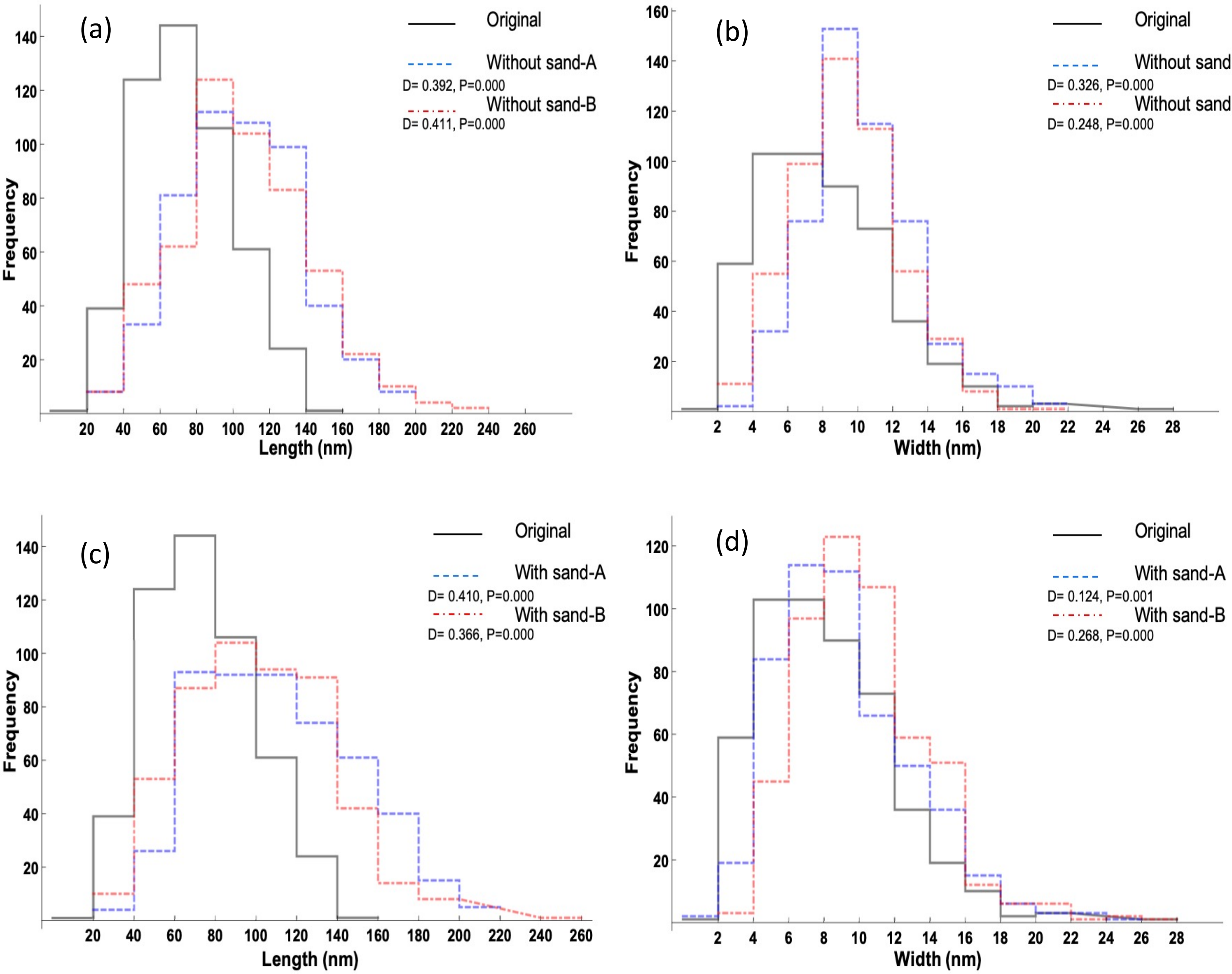


Figure S5. The distribution of goethite length (panels a and c) and width (panels b and d) of particles after reaction with 4-ClNB in different batch reactors containing water buffered with 10 mM $NaHCO_3$ (a and b) and sand-conditioned 10 mM $NaHCO_3$ buffer) (c and d) at pH 7. The reactions proceeded in the presence of 1 mM Fe (II) and 0.1 mM 4-ClNB for 5 cycles. P values show if data sets are statistically different (for $p<0.05$) and D values show how histograms are different from the one for the original particles. Larger D values indicate the more difference from the original particles. The similarity in values indicate any species dissolved from the sand do not affect particle growth.

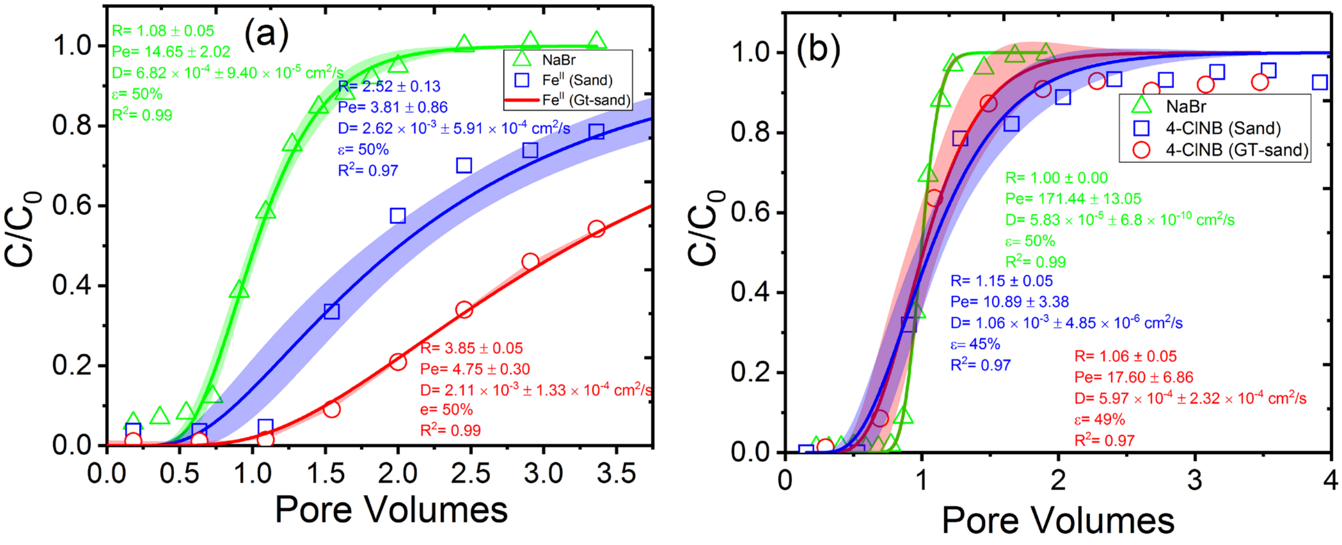


Figure S6. Concentrations of Fe(II) (a) and 4-ClNB (b) in effluent relative to influent concentrations from control column reactors (h: 3 cm, ID: 2.5 cm) for bare and goethite-coated sand (GT-sand) grains. The green symbols are the NaBr tracer breakthrough data for the column packed with the goethite-coated sand. 95% confidence bands are shown in blue, green, and red shades.

To test the reproducibility of the tracer and column packing, a column was wet packed with goethite-coated sand grains and conditioned with 10 mM bicarbonate solution followed by tracer analysis. Then the filing materials were removed from column and air-dried. Dried materials were wet packed again into the same column, conditioned with 10 mM bicarbonate buffer, and the tracer experiment conducted. Two columns showed the same porosity (50%) and very similar hydrodynamic dispersion coefficients (1.24 $\times 10^{-4}$ cm^2/s and 1.37$\times 10^{-4}$ cm^2/s).

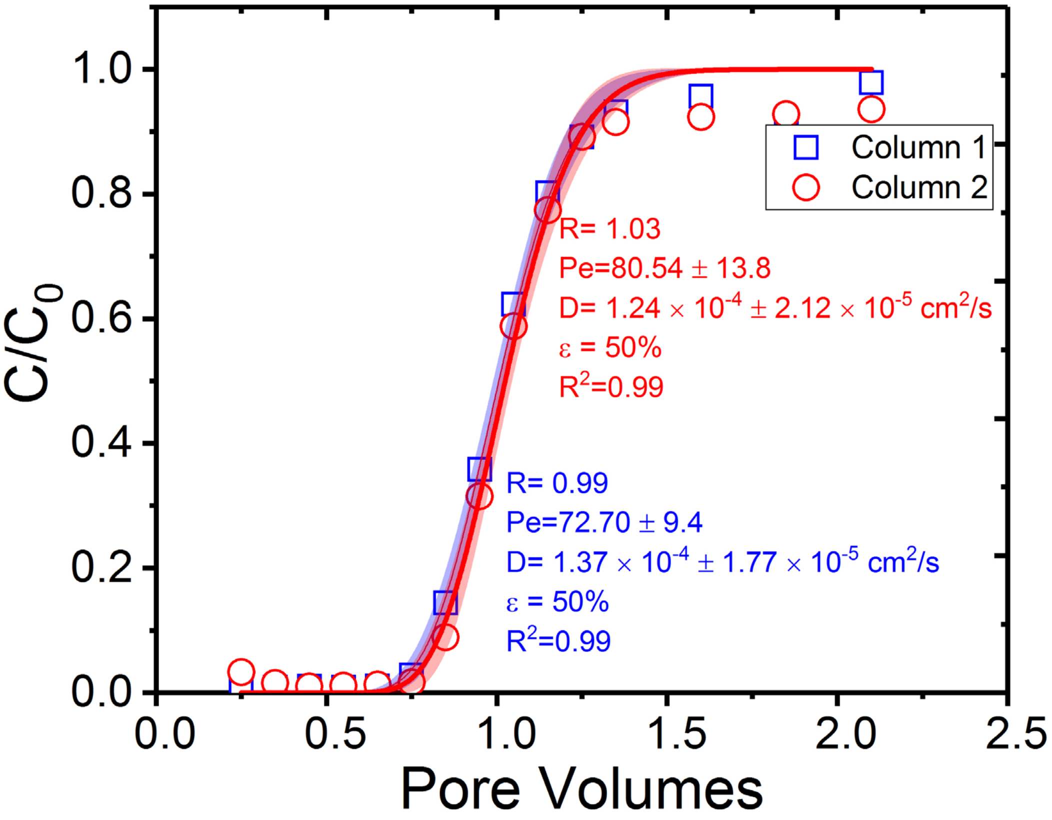


Figure S7. NaBr breakthrough curves of two columns filled twice with the same goethite-coated sand grains. For all experiments, the flow rates of NaBr were 0.5 mL/min and columns with inner diameters of 2.5 cm and heights of 3 cm were used. 95% confidence bands are shown in blue and red shades.

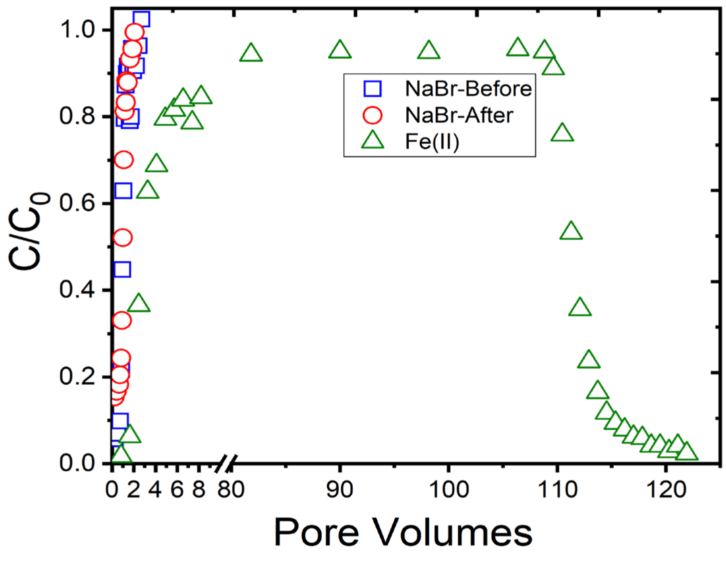


Figure S8. Concentrations of Fe(II) and NaBr in effluent relative to influent concentrations from a column reactor (h: 3 cm, ID: 2.5 cm) packed with goethite-coated sand (GT-sand) grains. The NaBr tracer breakthrough data is present for both before and after Fe(II) exposure. The Fe(II) (0.5 mM) solution was buffered in 10 mM sodium bicarbonate at pH 7 and fed into the column at a 1.0 mL/min flow rate.

Table S2. Mass of iron present on the goethite-coated particles before and after exposure to Fe(II) harvested from different zones of the column based on the calibrated peak areas for elemental iron wavelengths at 238.204 nm, 239.562 nm, and 259.94 nm. No 4-ClNB was introduced in these experiments.

Sample	238.204 nm (mg)	239.562 nm (mg)	259.94 nm (mg)
Pre-reaction	0.69 ± 0.02	0.69 ± 0.02	0.70 ± 0.04
Post-reaction (Bottom)	0.70 ± 0.02	0.72 ± 0.02	0.73 ± 0.04
Post-reaction (Middle)	0.70 ± 0.02	0.70 ± 0.02	0.72 ± 0.03
Post-reaction (Top)	0.70 ± 0.01	0.71 ± 0.02	0.75 ± 0.02

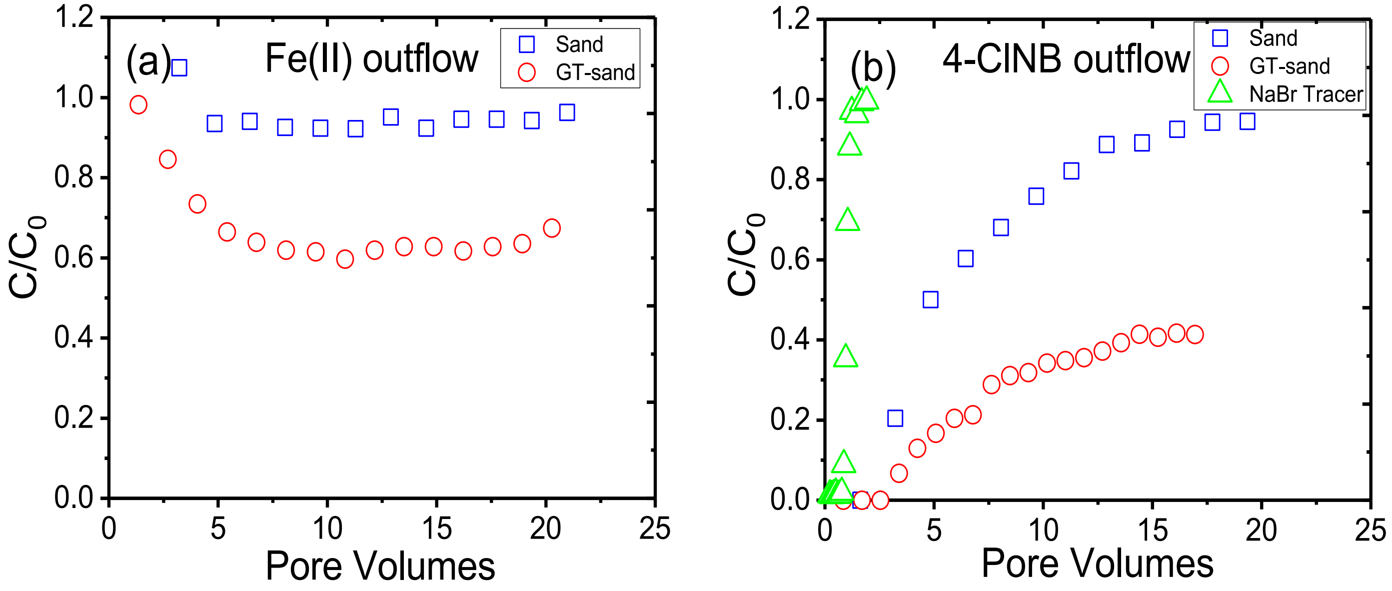


Figure S9. Concentrations of Fe(II) (a) and 4-ClNB (b) in effluent relative to influent concentrations from two identical column reactors (h: 3 cm, ID: 2.5 cm) packed with bare and goethite-coated sand (GT-sand) grains. The green symbols are the NaBr tracer breakthrough data for the column packed with the goethite-coated sand. Fe(II) (1 mM) and 4-ClNB (0.1 mM) solutions both buffered in 10 mM sodium bicarbonate at pH 7 and were separately fed into the column with 0.5 mL/min flow rate.

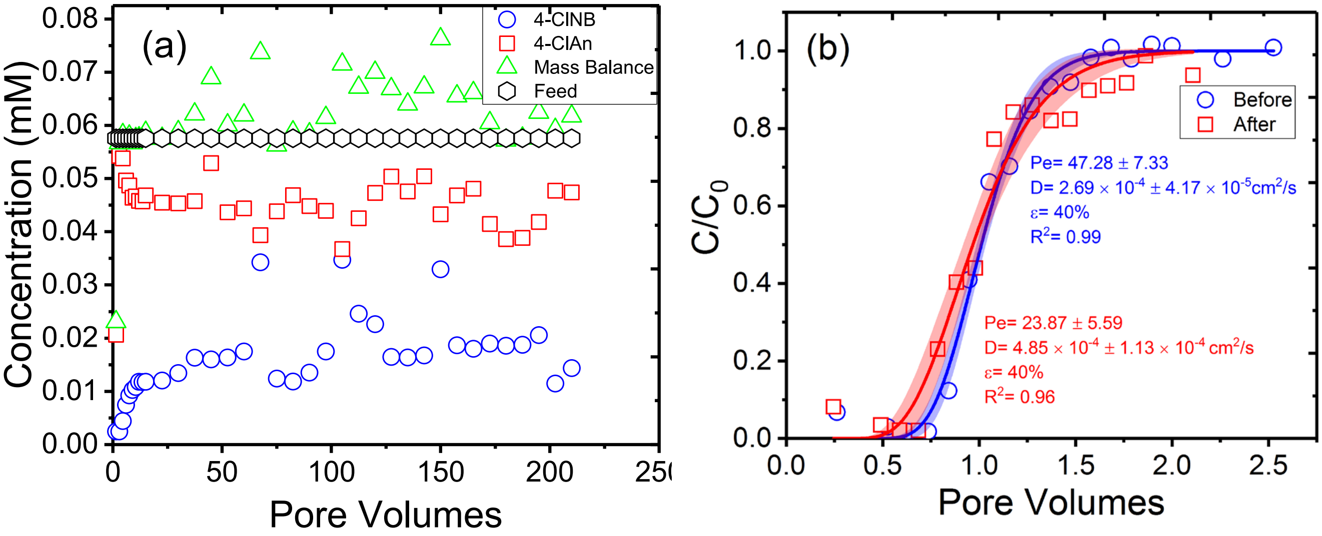


Figure S10. Concentrations of 4-ClNB in both influent (feed) and effluent, 4-ClAn in effluent, and mass balance (4-ClNB + 4-ClAn) for 220 PV (a) and tracer analysis before and after 4-ClNB reduction for 220 PV (b) 95% confidence bands are shown in red and blue shades. Prior to initiating flow of the 4-ClNB solution, 10 mM $NaHCO_3$ for 3 PV and then 1 mM Fe (II) in 10 mM $NaHCO_3$ for 3 PV were fed into each column. For all experiments, the flow rates of each Fe(II) and 4-ClNB were 0.5 mL/min and columns with inner diameters of 2.5 cm and heights of 3 cm were used.

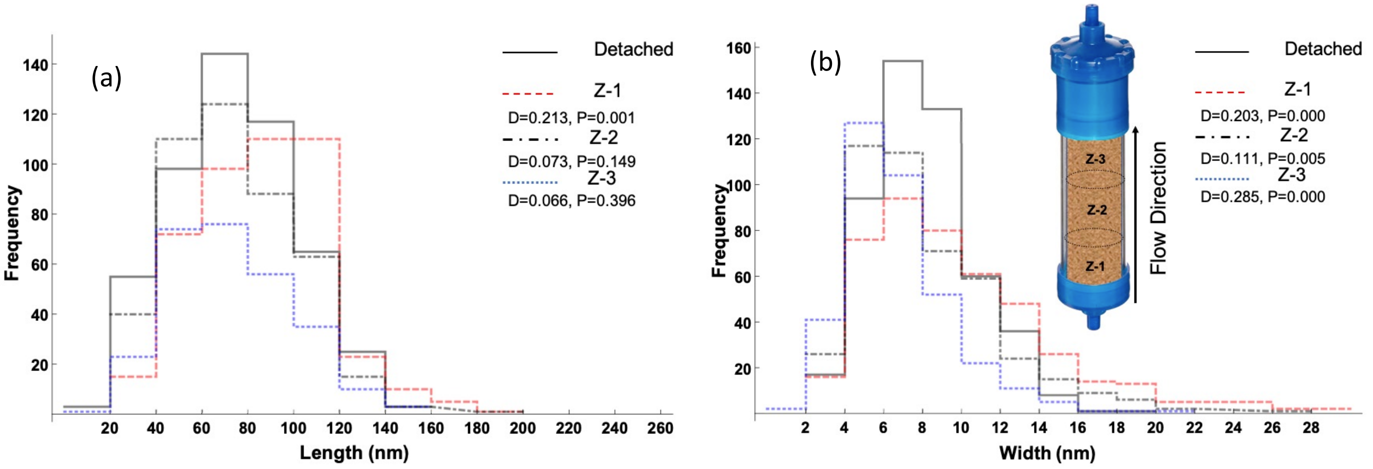


Figure S11. The distribution of goethite length (a) and width (b) after reaction with 4-ClNB in column reactor for 18 PV reaction under saturated flow condition and different oxidation zones, bottom (Z-1), middle (Z-2), and top (Z-3) compared to length and width of the detached unreacted particles. All the reactors were conditioned with 10 mM $NaHCO_3$ and fed with 1 mM Fe(II) and 0.1 mM 4-ClNB. P values show if data sets are statistically different (for $P < 0.05$) and D values show how histograms are different from the corresponding histogram of the unreacted detached particles. Larger D values indicate a greater difference from the unreacted detached particles. For all experiments, the Fe(II) and 4-ClNB flow rates were 0.5 mL/min and columns with ID: 2.5 cm and height: 3 cm were used.

For the column used in Figure S8, goethite particles were digested from sand surfaces by dispersing 1 g of goethite-coated sand using concentrated HCl (VWR Chemicals) for 1 hour at a 0.5 mg/mL concentration. Sand samples lost their yellow color during digestion and the solution turned yellow. The post-digestion liquid was separated from the solid sand and diluted 100-fold using ultrapure water. A 1 mL aliquot of this diluted sample was further diluted with 10 mL of 1% nitric acid. These samples were measured for iron concentration using a Thermo Scientific iCAP 7400 Inductively-Couple Plasma Optical Emission Spectrometer in radial mode. Peak areas were recorded for three elemental iron wavelengths: 259.940, 238.204, and 239.562 nm, in five replicates. Peak areas were compared against a series of standards to determine concentrations. Calibration samples were prepared using Fe(NO3)3•9H2O (Fisher Scientific) in solutions of of 0.105 M nitric acid (Sigma Aldrich) and 0.015 M hydrochloric acid to match the acid background from iron digestion. Results are presented in Table S1.

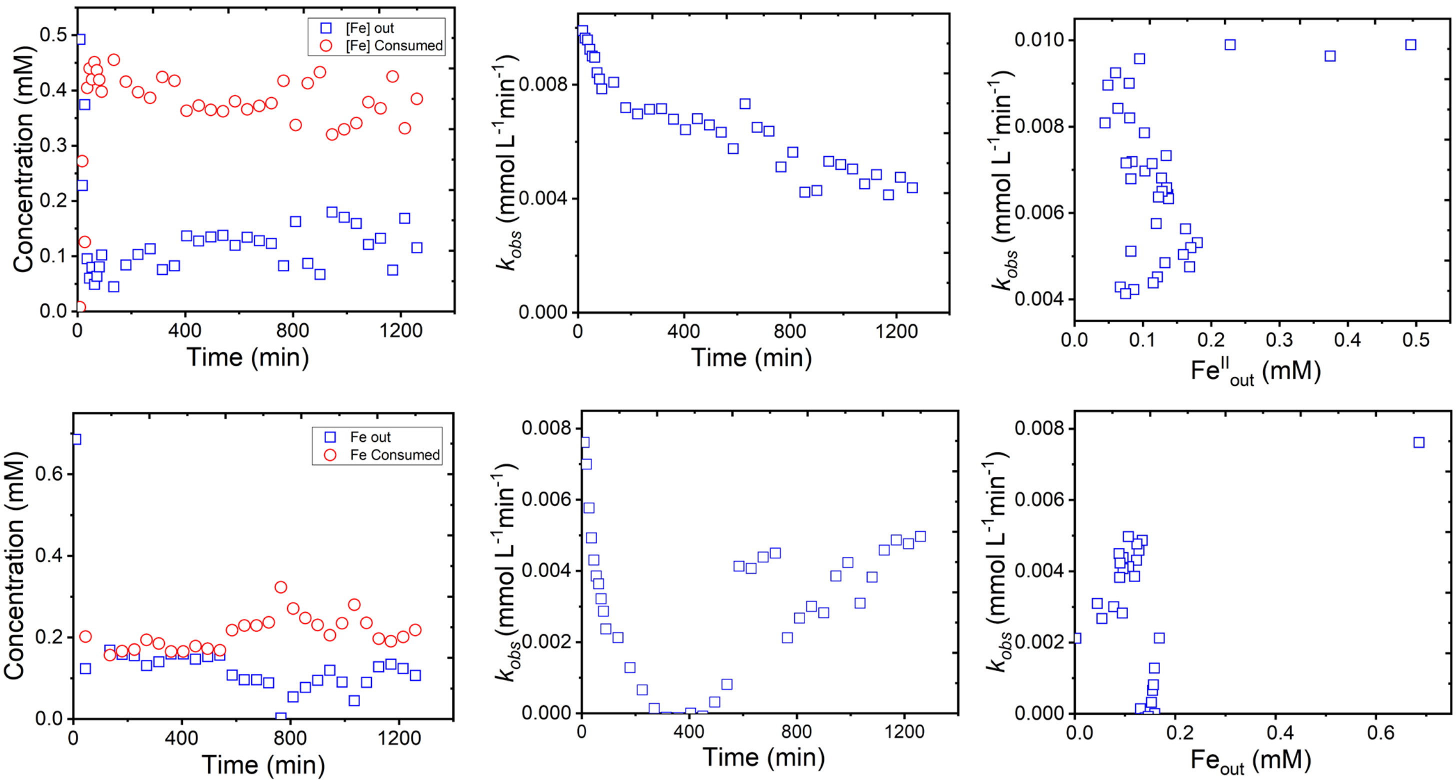


Figure S12. Fe(II) in effluent (out) and Fe(II) consumed (determined by difference with the feed) versus time, k_{obs} (as determined by equation 3) versus time, and k_{obs} versus Fe(II) out. The top set of panels are for the saturated column and the bottom set of panels are for the unsaturated column.

Reference

1. Dixit, S. & Hering, J. G. Sorption of Fe(II) and As(III) on goethite in single- and dual-sorbate systems. *Chem. Geol.* **228**, 6–15 (2006).