

1 Chlorinated solvent degradation in groundwater
2 by green rust - bone char composite: solute interactions and
3 chlorinated ethylene competition
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12 **Content of this supporting information**

13 This supporting information contains additional details on methods and additional data and figures to
14 support the interpretation made in the results and discussion section. In total, this SI includes 11 pages
15 with 7 figures, and 3 tables.

17 **Text S1. Synthesis of GR_{SO4} and GR_{CO3}**

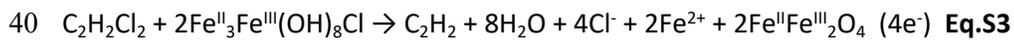
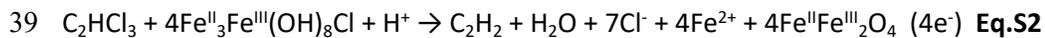
18 Syntheses of GR_{SO4} and GR_{CO3} followed similar procedures as the GR_{Cl} synthesis by Yin et al. (1). For
19 GR_{SO4}, 20 mL of 0.5 M FeSO₄ solution was added to 400 mL of 70 mM glycine inside a glass flask under
20 continuous stirring (300 rpm) with the pH kept constant at 8.0 (T ~ 22 °C) by titration with 1 M NaOH
21 using a pH-stat (Metrohm, 719 Titrino). After, 20 mL of 0.1 M Fe₂(SO₄)₃ solution was injected into the
22 synthesis flask using a 20 mL plastic syringe at a speed of 5 ml min⁻¹. The suspension was stirred for
23 another 5 min when titration terminated. GR_{CO3} synthesis was performed identical to that of GR_{Cl}
24 synthesis except that pH was kept constant by titration with 1.0 M NaCO₃ instead of 1.0 NaOH. The
25 freshly synthesized suspensions were briefly washed by two rounds of centrifugation and re-suspension
26 in deoxygenated triple-deionized water as done for GR_{Cl}. The washed GR was re-suspended in 100 ml
27 deoxygenated triple-deionized water and stirred on a magnetic stirrer at 500 rpm for 10 min prior to
28 usage.

29

31 **Text S2. Calculation of reducing capacity of GR_{Cl}**

32 In triple CE experiments with 23 mM [Fe(II)]_{GR} and 0.15 g L⁻¹ BC, the reducing capacity of GR_{Cl} is 7.6 mM
33 e⁻ assuming that GR transforms into magnetite during CE dechlorination as observed in our previous
34 study (2). Initial CE concentrations were 20 μM for PCE, TCE and cDCE, respectively, thus full degradation
35 of all added CEs requires 280 μM electron equivalents (6*20 + 4*20 + 4*20) according to Eq.S1-S3. In
36 this case, the reducing capacity of GR was 27-fold higher than the oxidation equivalents of CEs.

37



41

42 The highest CE concentration was measured in GW-C, where the initial PCE concentration (127 μM) was
43 the highest among all the tested groundwaters, and TCE (10 μM) and cDCE (19 μM) were much lower. In
44 this case, full dechlorination of all CEs would require 0.88 mM e⁻, which is still 6.4-fold lower than the
45 reducing capacity provided by the added GR (17 mM [Fe(II)]_{GR}, i.e., 5.7 mM e⁻). Therefore, we believe
46 that the observed inhibition of cDCE reduction in mixed CE systems cannot be due to insufficient GR
47 reducing capacity.

48

50 **Table S1. Summary of TCE dechlorination rates (k_{mass} , L g⁻¹ h⁻¹) in the presence of groundwater solutes**
 51 **and comparison to k_{mass} (TCE) in TI water shown by a decrease factor given in brackets ^a.**

Solutes	0.5 mM	1.0 mM	2.0/5.0 mM	10 mM
Cl ⁻				0.76 ± 0.04 (1.4)
SO ₄ ²⁻		1.11 ± 0.05 (1.0)		0.86 ± 0.04 (1.3)
HCO ₃ ⁻		1.17 ± 0.05 (0.9)	5 mM: 0.39 ± 0.02 (2.8)	0.16 ± 0.01 (6.7)
H ₄ SiO ₄	0.65 ± 0.05 (1.7)	0.65 ± 0.07 (1.7)	2 mM: 0.21 ± 0.04 (5.3)	

52 ^a k_{mass} (TCE) in TI water is 1.09 ± 0.06 L g⁻¹ h⁻¹, and fresh BC was used in this set of experiments. The
 53 decrease factors in brackets were obtained by dividing k_{mass} (TCE) in the reaction with TI water with
 54 measured k_{mass} (TCE) in corresponding solutions.

55

57 **Table S2. Summary of CE dechlorination rate (k_{mass} , L g⁻¹ h⁻¹) in competition experiments and**
 58 **comparison to k_{mass} (CE) in single CE experiment with TI water shown by a decrease factor given in**
 59 **brackets ^a (unless stated otherwise).**

Experimental setups	BC status	k_{mass} (PCE)	k_{mass} (TCE)	k_{mass} (cDCE)
Single CE (TI)	Stored	0.8 ± 0.1	0.52 ± 0.03 (2.1) ^b	0.14 ± 0.01
Single CE (GW)	Stored	0.14 ± 0.01(5.2)	0.20 ± 0.02 (2.6)	0.025 ± 0.07 (5.6)
PCE + TCE (TI)	Stored	0.45 ± 0.02(1.8)	0.32 ± 0.02 (1.6)	n.a. ^c
TCE + cDCE (TI)	Stored	n.a. ^c	0.61 ± 0.04 (0.85)	- ^d
PCE + cDCE (TI)	Stored	0.77 ± 0.04(1.0)	n.a. ^c	- ^d
PCE + TCE + cDCE (TI)	Stored	0.32 ± 0.05(2.5)	0.20 ± 0.03 (2.6)	- ^d
PCE + TCE + cDCE (GW-F)	Stored	0.22 ± 0.01(1.5) ^e	0.16 ± 0.01 (1.3) ^e	- ^d

60 ^a Decrease factors in brackets were obtained by comparing to the corresponding single CE experiments
 61 with stored BC, i.e., the values in the first row;

62 ^b The decrease factor in brackets was calculated by dividing the k_{mass} (TCE) obtained in the single TCE
 63 experiment in TI water in **Experiment a** (1.09 ± 0.06 L g⁻¹ h⁻¹; Table 1) with the here measured k_{mass} (TCE)
 64 (i.e., **Experiment b**) to show the impact of BC storage time;

65 ^c No data;

66 ^d No clear sign of cDCE degradation as cDCE data was not significantly different from control data;

67 ^e Decrease factors in brackets were obtained by dividing CE k_{mass} in triple CE experiments in TI water with
 68 the corresponding k_{mass} value in the CE-spiked clean groundwater, GW-F.

70 **Table S3. Summary of CE dechlorination rate (k_{mass} , L g⁻¹ h⁻¹) in contaminated groundwaters and**
 71 **comparison to triple CE experiments with CE-spiked clean groundwater shown by a decrease factor**
 72 **given in brackets^a (unless stated otherwise).**

Groundwater	BC status	k_{mass} (PCE)	k_{mass} (TCE)	k_{mass} (cDCE)
GW-A	Fresh	n.a. ^b	0.048 ± 0.005 (3.3/7.0) ^d	n.a. ^b
GW-B	Fresh	0.06 ± 0.01 (3.7) ^c	- ^e	- ^e
GW-C	Fresh	0.10 ± 0.02 (2.2) ^c	- ^e	- ^e
GW-D	Fresh	0.035 ± 0.007 (6.3)	0.050 ± 0.007 (3.2/6.7) ^d	- ^e
GW-E	Fresh	0.033 ± 0.004 (6.7)	0.021 ± 0.003 (7.6/16) ^d	- ^e

73 ^a Decrease factors were calculated by dividing the k_{mass} (CE) obtained in triple CE experiments with GW-F
 74 with the corresponding k_{mass} in CE contaminated groundwaters;

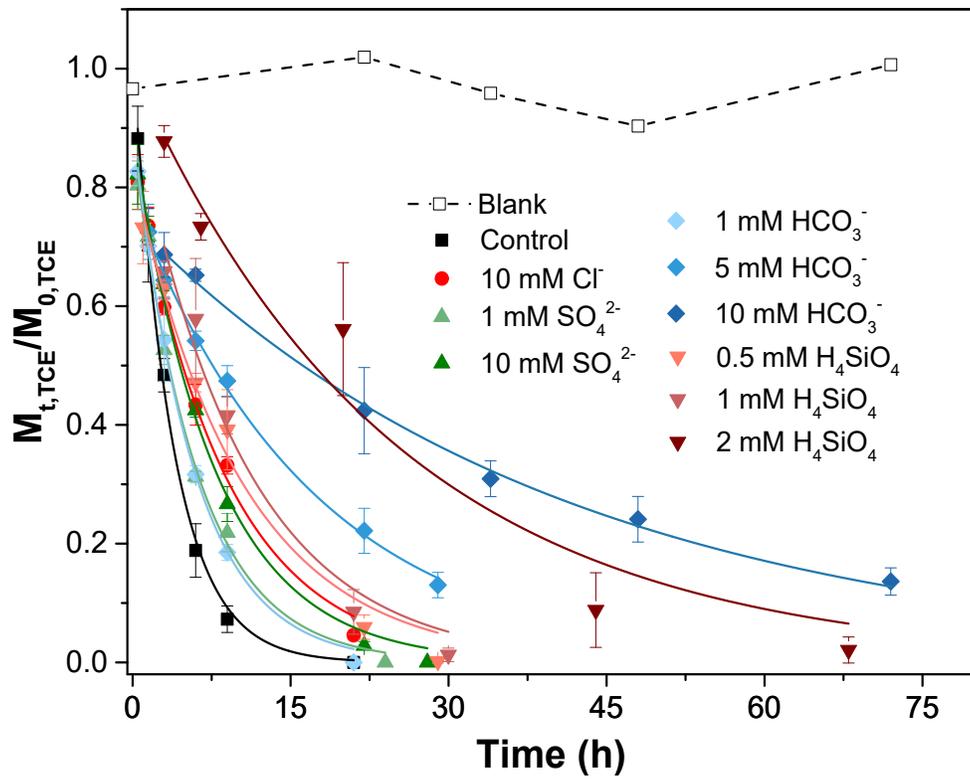
75 ^b PCE and cDCE were not detected in GW-A;

76 ^c The data were fitted by a modified first-order kinetic model ($M_t = b \times e^{-k \times t} + a$) with 'a' as an offset
 77 because the reaction substantially slowed at the end of the monitored time frame without reaching full
 78 CE degradation. Thus, "a" refers to the fraction of contaminants that remained at the end of the
 79 reaction;

80 ^d Both decrease factors refer to the comparison to the CE-spiked clean groundwater, but the value on
 81 the right includes correction for the BC aging effect (a further 2.1-fold decrease for TCE reduction, Table
 82 S2).

83 ^e No clear signs of degradation.

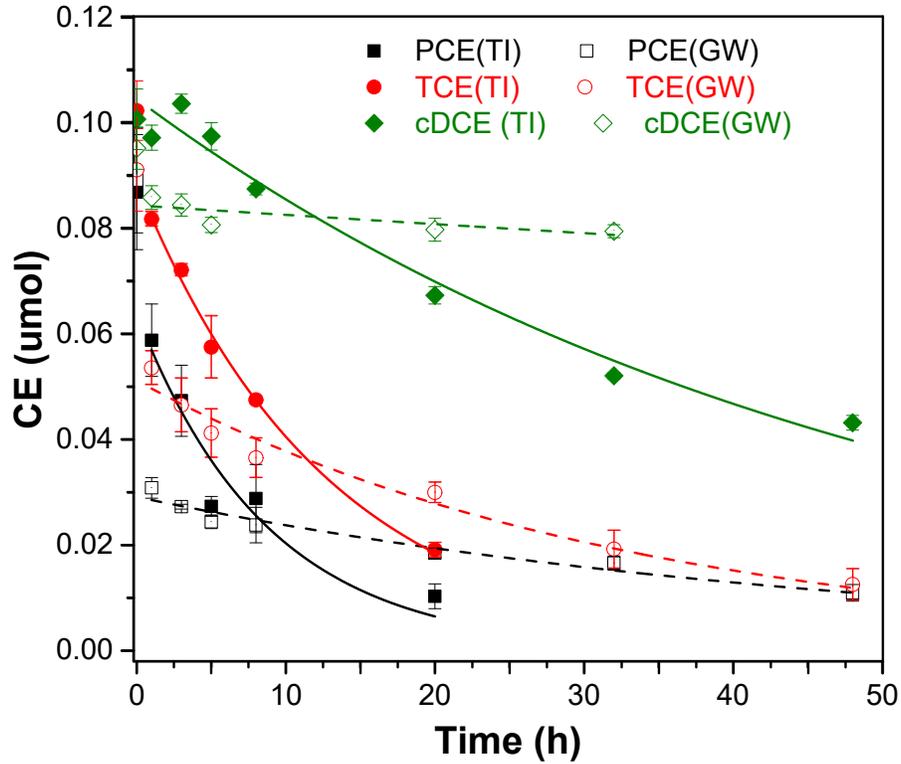
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87 **Figure S1.** Normalized TCE mass time trends ($M_{t,TCE}/M_{0,TCE}$) in reactions with 23 mM $[\text{Fe(II)}]_{\text{GR}}$ and 0.15 g
 88 L^{-1} BC in the absence and presence of different groundwater solutes at different concentrations. The
 89 solid lines show pseudo-first-order kinetic fits to the data (but excluding the data at $t = 0$).

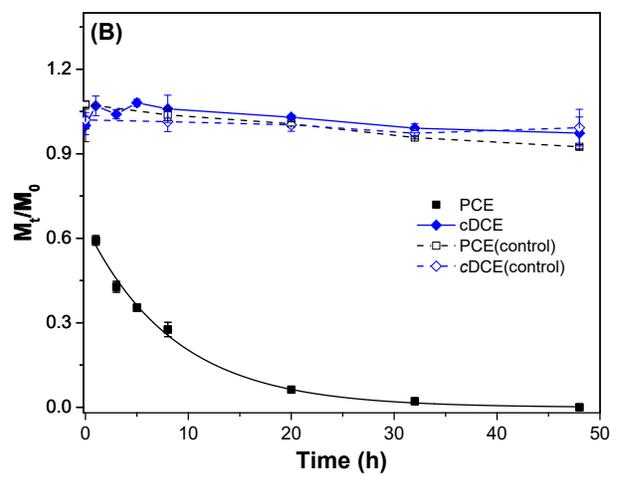
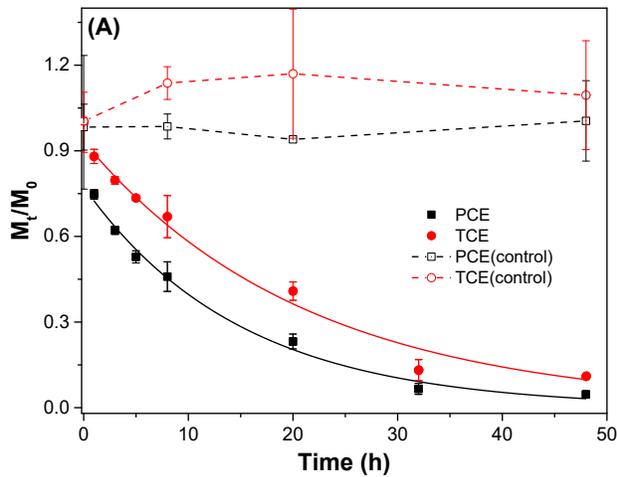
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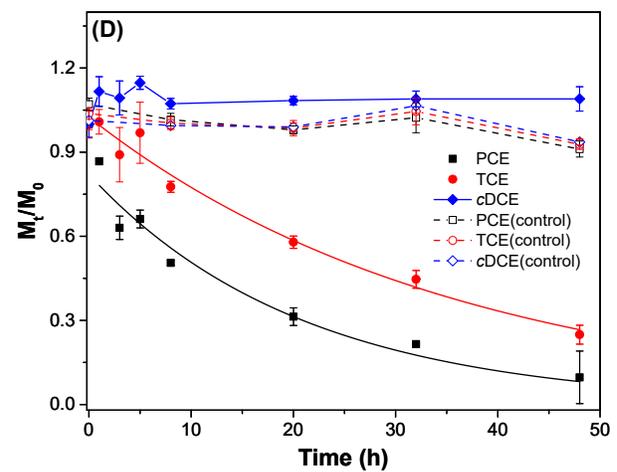
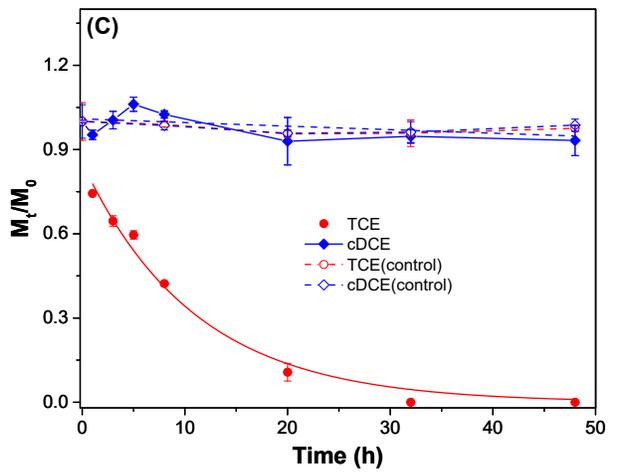
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93 **Figure S2.** Changes in CE mass as a function of time (h) in TI water (solid symbols) with the GR-BC
 94 composite (23 mM [Fe(II)]_{GR} and 0.15 g L⁻¹ BC) and in clean groundwater GW-F (open symbols) with the
 95 GR-BC composite (17 mM [Fe(II)]_{GR} and 0.5 g L⁻¹ BC). Error bars represent one standard deviation
 96 obtained from triplicate reactions, and the lines shows pseudo-first-order kinetic fits to the data.

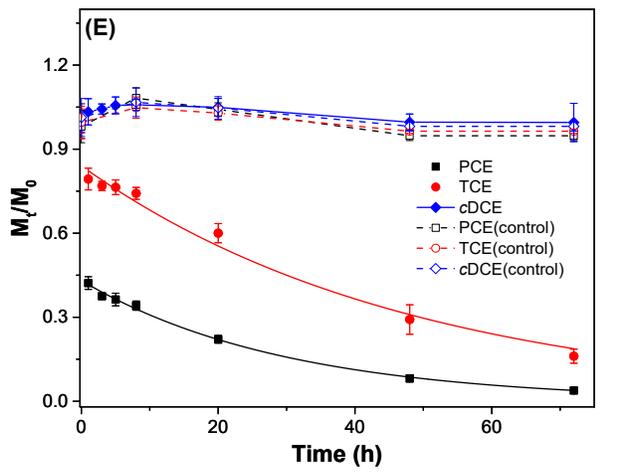
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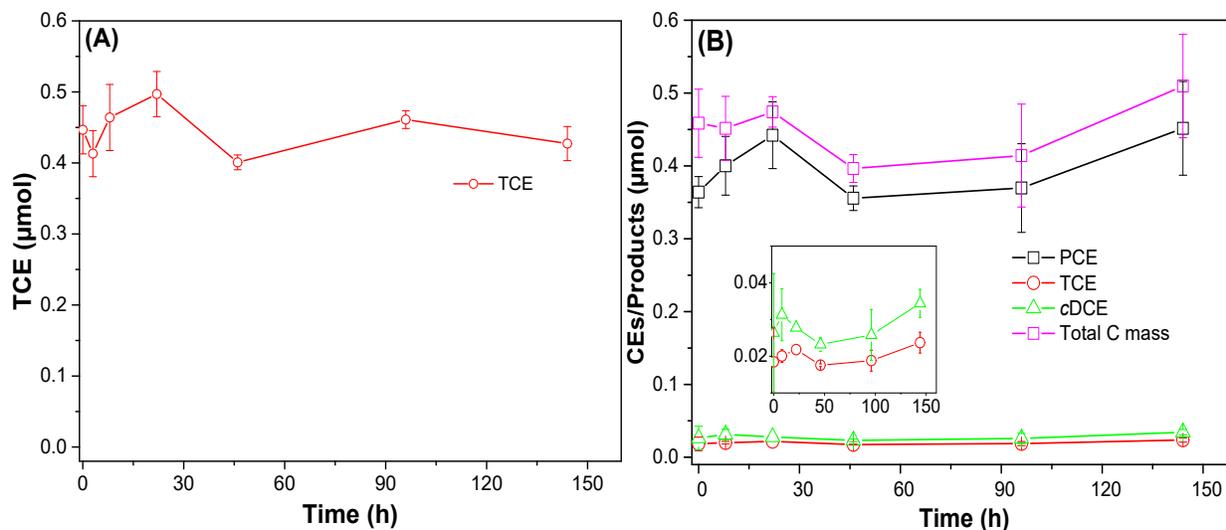


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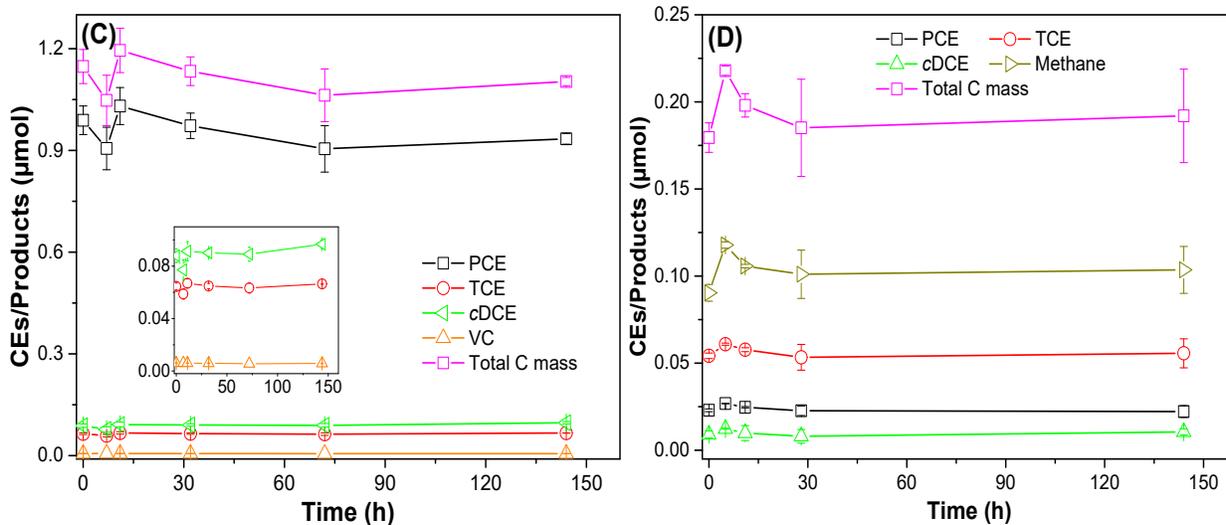


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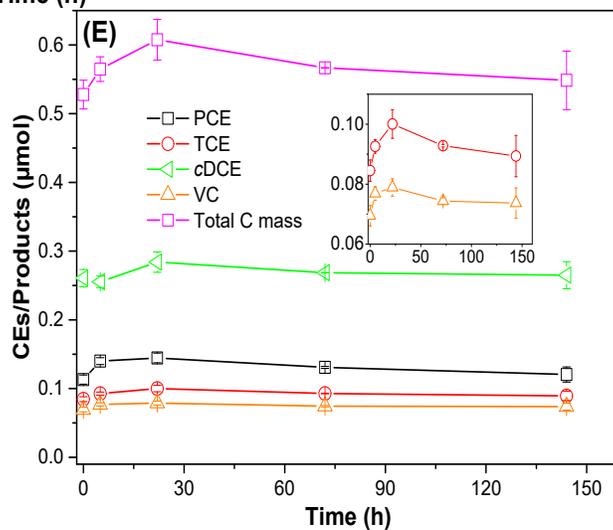
102 **Figure S3.** Normalized CE mass time trend (M_t/M_0) for CE competition experiments in TI water with the
 103 GR-BC composite (23 mM $[Fe(II)]_{GR}$ and 0.15 g L⁻¹ BC) between **(A)** PCE and TCE, **(B)** PCE and cDCE, **(C)**
 104 TCE and cDCE, and **(D)** PCE, TCE and cDCE. **(E)** Normalized CE mass time trend (M_t/M_0) for triple CE
 105 competition in clean groundwater GW-F with the GR-BC composite (17 mM $[Fe(II)]_{GR}$ and 0.5 g L⁻¹ BC).



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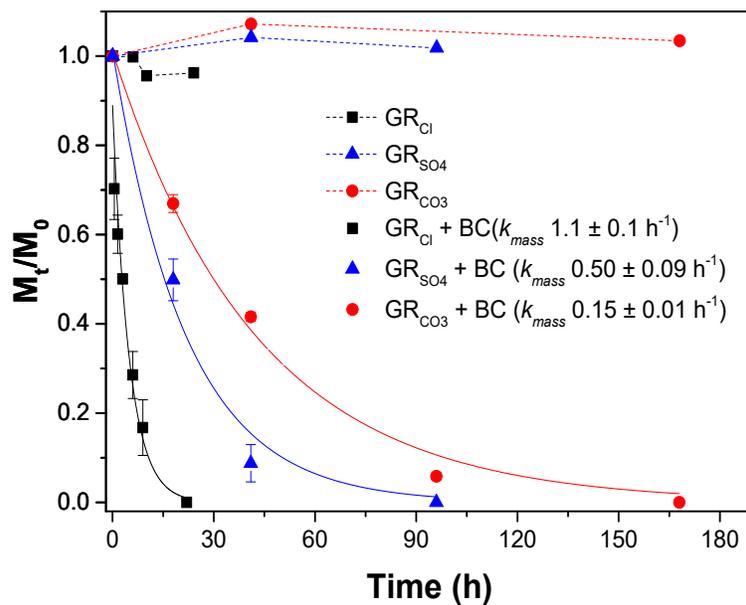
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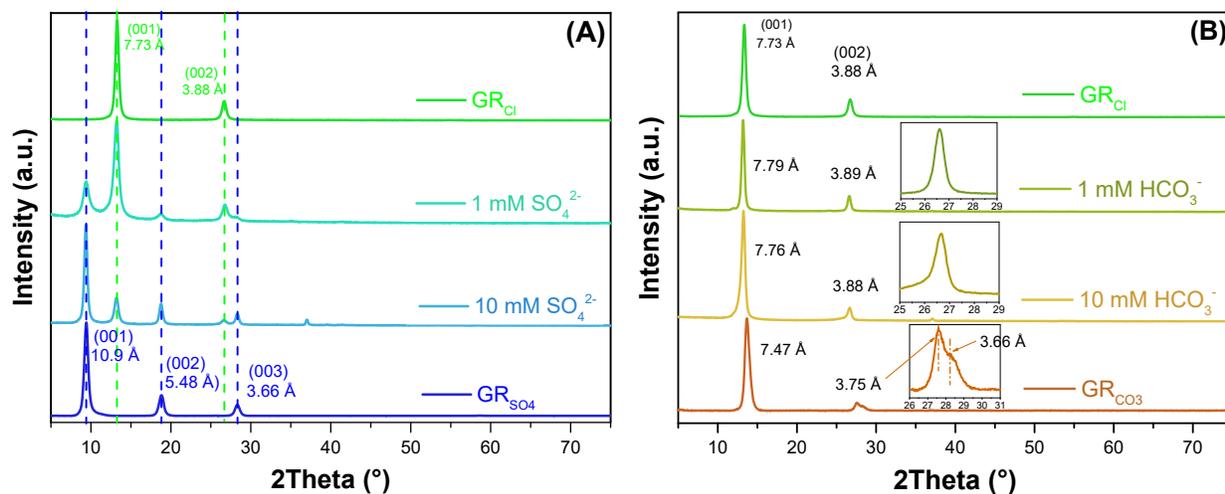
110 **Figure S4.** Time trends of CE concentrations in control experiments (no added GR-BC mixture) of **(A)**

111 **GW-A, (B) GW-B, (C) GW-C, (D) GW-D, and (E) GW-E.**



113

114 **Figure S5.** Normalized TCE mass time trends (M_t/M_0) in TI water with different GR-BC composite varying
 115 in GR type, i.e., GR_{Cl} , GR_{SO_4} and GR_{CO_3} . Solid lines show pseudo-first-order kinetic fits to the data and
 116 error bars represent one standard deviation from measurement of triplicate samples. The synthesis of
 117 GR_{SO_4} and GR_{CO_3} can be found in Text S1.



119

120 **Figure S6.** XRD patterns (Co K α radiation) of **(A)** fresh GR_{Cl}, GR_{Cl} reacted for 24 hours in 1 and 10 mM
 121 SO₄²⁻ solutions, and fresh GR_{SO4}, and **(B)** fresh GR_{Cl}, GR_{Cl} reacted for 24 hours in 1 and 10 mM HCO₃⁻
 122 solutions, and fresh GR_{CO3}. Characteristic peaks of GR_{Cl} and GR_{CO3} match the reflections of GR1 crystalline
 123 (ICDD reference code of 00-040-0127 (3) and 00-046-0098 (4)), and those of GR_{SO4} match the reflections
 124 of GR2 crystalline (ICDD reference code of 00-013-0090 (5)).



126

127 **Figure S7.** Photos of GR suspensions amended with 0, 0.01 and 0.1 M NaCl (corresponding to A, B and
128 C) after settling for (a) 1 h, (b) 16 h, (c) 40 h and (d) 64 h. A clear separation of solid and solution was
129 seen for GR in 0.1 M NaCl after 1 h, while for GR in 0.01 M NaCl, this separation only became apparent
130 after 40 hours. Sedimentation in the NaCl-free GR suspension was lowest and barely visible over the
131 monitored time frame.

132

134 **Reference**

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