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Fast dechlorination of chlorinated ethylenes by a layered Fe(II)-Fe(III) hydroxide (green rust) composite

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Abstract Chlorinated ethylenes (CEs) are efficiently degraded by a novel green rust-carbonaceous material (GR-CM) composite. The dechlorination of tetrachloroethylene (PCE), trichloroethylene (TCE), *cis*-dichloroethylene (*cis*-DCE) and *trans*-dichloroethylene (*trans*-DCE) follow pseudo first-order kinetic with half-lives of 3.34, 4.04, 4.35 and 1.79 h, respectively, in which β-elimination is proposed as the major reductive pathway as acetylene contributed > 80% of total carbon mass of products over the reaction course. The highly reactive GR-CM composite is a promising material for remediation of CE contaminated water due to the advantages of scalability of production, low cost and eco-friendly properties.

1 Background

Green rusts (GRs) are Fe(II)-Fe(III) hydroxide salts with brucite-type layer structure, which are strong reductants for diverse reducible contaminants in soils and water including chlorinated ethylenes (CEs). Although the reduction of CEs by GRs is thermodynamically favorable, experimental results have not provided consensus on the reactivity towards CEs degradation, such as pseudo first-order kinetic constants of tetrachloroethylene (PCE) degradation varying from 0.013 h^{-1} to zero under different experimental conditions (**Table 1)**. Thus, the dechlorination reaction appears to be kinetically constrained. We have now investigated how carbonaceous material enhanced dechlorination of CEs by GR.

Table kinetic information of PCE degradation by GR from different studies

GR type	pH and buffer	k_{app} (h^{-1})[a]	References
GR_{Cl}	pH 8; HEPES buffer	$(4.9\pm1.2)\times10^{-5}$	Liang and Butler, 2009
	pH 9; no buffer	$(5.4\pm3.0)\times10^{-5}$	Choi, 2006
	pH 9; no buffer; [1mM Ag(I)][c]	$(1.9\pm0.7)\times10^{-4}$	Choi, 2006
GR_{SO4}	pH 7; bicarbonate	4.1×10^{-3}	Lee and Batchelor, 2002
	pH 8; HEPES buffer	NC[b]	Liang and Butler, 2009
	pH 9; no buffer	NC	Choi, 2006
	pH 9; no buffer; [1mM Ag(I)][c]	$(5.0\pm1.3)\times10^{-3}$	Choi, 2006
GR_{CO3}	pH 9; no buffer	$(1.0\pm0.4)\times10^{-4}$	Choi, 2006
	pH 9; no buffer; [1mM Ag(I)][c]	>0.013[d]	Choi, 2006

[a] k_{app}, apparent pseudo-first order kinetic constant;
[b] NC, not calculated due to low reaction;
[c] 1mM Ag(I) was added to the solution;
[d] 100% removal was accomplished before the first observation.

2 Methodological approach

GR suspension was freshly synthesized by the glycine-buffer method. The GR-CM composite slurry composed of 22 mM [Fe(II)] GR and 1.0 g·L^{-1} CM at pH 8.0 was obtained by mixing GR suspension with CM slurry. Batch experiments were carried out by using 10 mL headspace glass vials with 5 mL suspension and 20 μM of added CE in triplicate. Reactants and products were measured by Triplus300 combined with TRACE1300 equipped with PoraBOND U column (25 m × 0.35 mm × 7 μm) coupled to dual ECD and FID detectors.

3 Results

Fast dechlorination of PCE, TCE, *cis*-DCE and *trans*-DCE at pH 8.0 were observed by using GR-CM composite (**Fig. 1)**. All substrates with initial concentrations of 20 μM were reduced by at least 90% within 24 h, with one example of PCE shown in **Fig. 2**. Reactions follow pseudo first-order kinetic well, seen **Table 2**. Acetylene was the main product detected for all CEs, accounting for more than 80% of carbon mass in all products. Control experiments showed that neither individual CM nor GR was able to remove any of CEs over 3 months.

Table 2 Kinetic parameters and products distribution of CEs dechlorination by GR-CM

Chlorinated ethylene	k_{app} (h^{-1})[a]	$k_{ace.}$ (h^{-1})[b]	$t_{1/2}$ (h)[c]	Product distribution[d]
PCE	0.21±0.04	0.13±0.01	3.34	Final products: Acetylene (86%)
				Intermediates: methylacetylene (≤ 14%), TCE(≤ 0.9%)
TCE	0.17±0.04	0.13±0.02	4.04	Acetylene (93%) without any detectable intermediates
cis-DCE	0.16±0.01	0.14±0.02	4.35	Acetylene (85%) without detectable intermediates
trans-DCE	0.39±0.09	0.37±0.09	1.79	Acetylene (98%) without detectable intermediates

[a] k_{app}, apparent pseudo-first order kinetic constant of chlorinated ethylene dechlorination;
[b] $k_{ace.}$, apparent pseudo-first order kinetic constant of acetylene production;
[c] $t_{1/2}$, Half-life of pseudo first-order reaction, equal to ln2/k_{app};
[d] Distribution of individual products as percentage of initial amount of target chlorinated compound (or that in control samples measured at the same time).

Given the products distribution, possible reductive pathways have been depicted as **Scheme 1**: PCE was transformed to TCE via fast hydrogenolysis, following β-elimination with further rapid hydrogenolysis approach to produce acetylene as final product. As to TCE/*cis*-DCE/*trans*-DCE, they may be directly reduced to acetylene via β-elimination. Thus, β-elimination is proposed the main reductive pathway of CEs dechlorination by GR-CM composite.

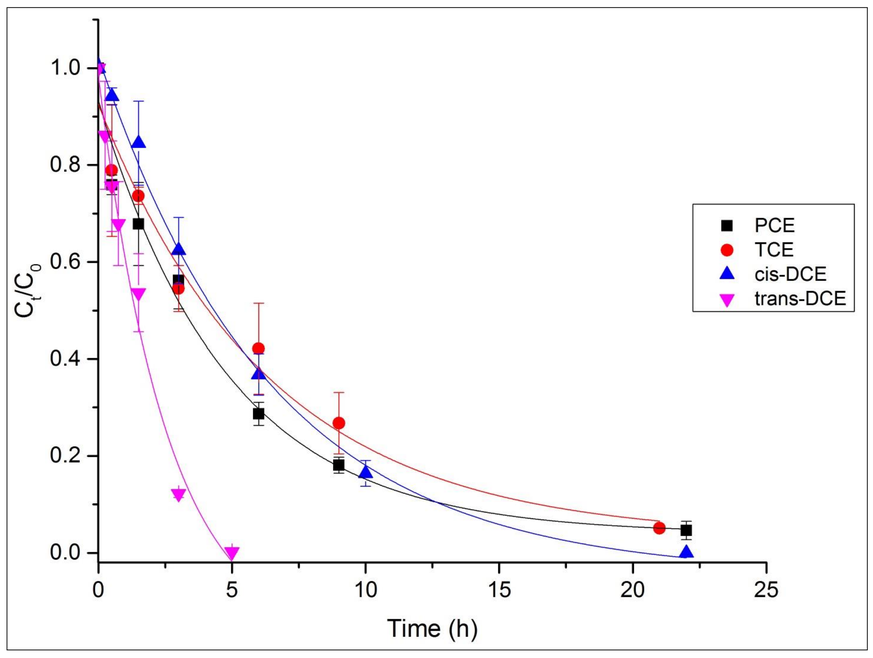


Fig. 1 Kinetics of dechlorination of PCE, TCE, *cis*-DCE and *trans*-DCE by GR-CM together with pseudo first-order kinetic fitting. Error bars represent the standard deviation (n = 3).

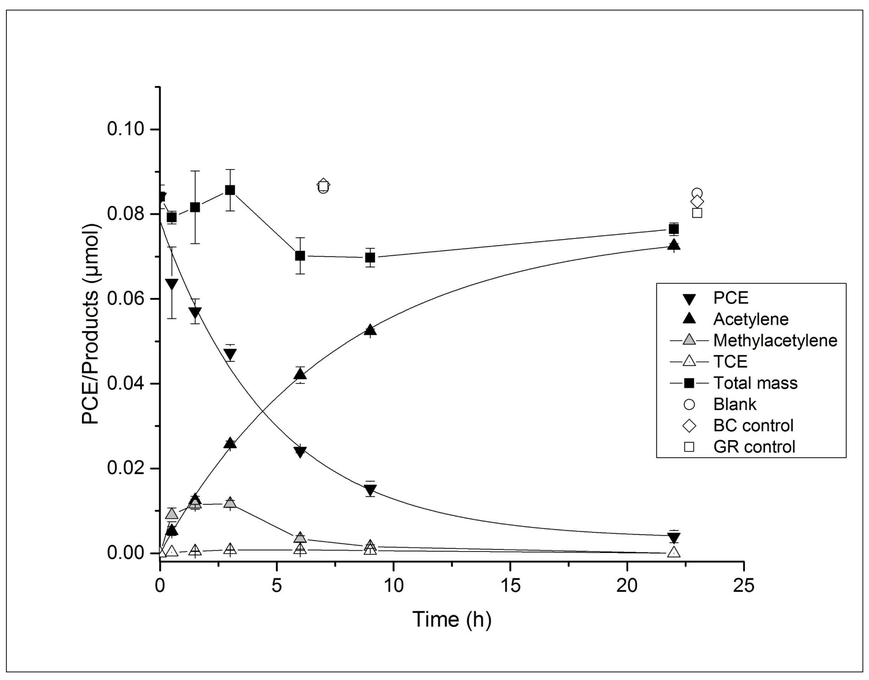
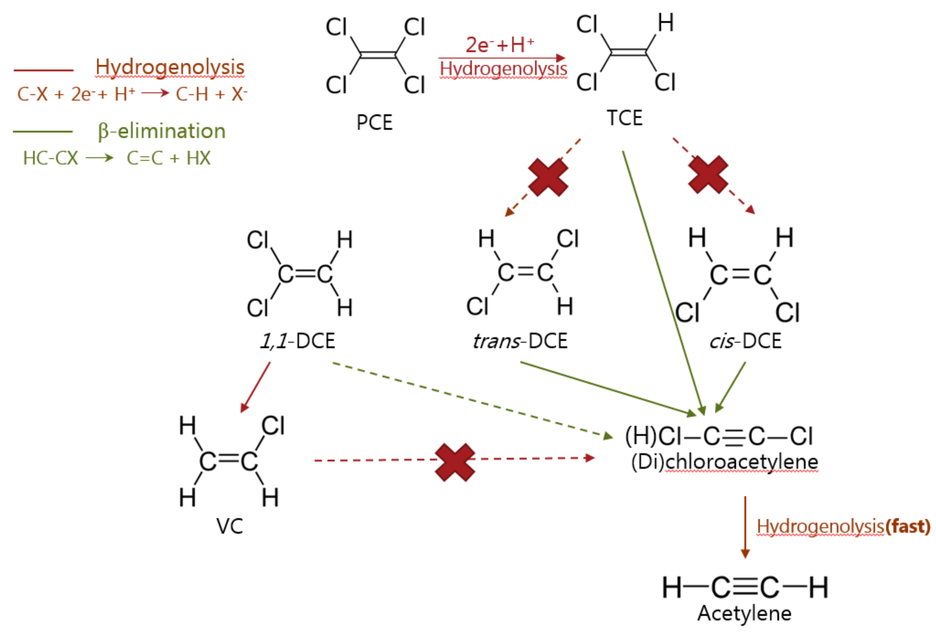


Fig. 2 Kinetics of dechlorination of individual chlorinated ethylenes and formation of corresponding products by GR-CM composite shown as C_t/C_0 vs. time.



Scheme 1 Proposed dechlorination pathway for reduction of CEs by GR-CM.