

Supplementary Materials

Layered Double Hydroxides with Intercalated Permanganate and Peroxydisulphate Anions for Oxidative Removal of Chlorinated Organic Solvents Contaminated Water

Karen Maria Dietmann ¹, Tobias Linke ², Miguel del Nogal Sánchez ³, José Luis Pérez Pavón ³ and Vicente Rives ^{1,*}

¹ Grupo de Investigación Reconocido – Química del Estado Sólido, Materiales y Catálisis Heterogénea (GIR-QUESCAT), Departamento de Química Inorgánica, Universidad de Salamanca, 37008 Salamanca, Spain; kdietmann@usal.es

² Institute of Earth Sciences, University of Iceland, Sturlugata 7, Reykjavík 101, Iceland; tol5@hi.is

³ Departamento de Química Analítica, Nutrición y Bromatología, Universidad de Salamanca, 37008 Salamanca, Spain; mns@usal.es (M.d.N.S.); jlpp@usal.es (J.L.P.P.)

* Correspondence: vrives@usal.es

Received: 9 April 2020; Accepted: 18 May 2020; Published: date

File S1. ICP-OES

The instrument was calibrated with in-house standards (SEL-11, Spoi17). A portion of 20 mg of the sample was dissolved in 0.77 mL of HNO₃ (65 %, Suprapur®, Merck) and then filled up to 100 mL with ultrapure water (milliQ). Then, 2 mL of this solution was filtered using 0.2 µm pore size cellulose acetate membrane filters (Advantec®, Toyo Roshi Kaisha Ltd.) and diluted with additional 10 mL of the blank solution (ultrapure water with 0.5 % HNO₃). Measurements were carried out as two triplicates for each LDH-solution. Additional dilutions were carried out if necessary.

File S2. HS-PTV-GC-MS

HS sampling was carried out with a PAL autosampler (CTC Analytics AG, Zwingen, Switzerland). The oven was kept at 80 °C for 10 min. The injection was performed by using a 2.5 mL syringe at 100 °C. A PTV inlet (CIS-4, Gerstel, Baltimore, MD, USA) with a liner (71 mm × 2 mm) packed with Tenax-TA® was used. It was operated in solvent vent mode at 20 °C for 0.10 min, increasing the temperature until 300 °C and establishing 1 min as injection time. To perform the gas chromatographic separation, an Agilent 6890 GC equipment equipped with a HP5-MS UI capillary column (30 m × 0.250 mm × 0.25 µm, J&W Scientific, Folsom, CA, USA) was used. The programme temperature started at 45 °C (2.0 min), increased at 60 °C min⁻¹ to 175 °C, and further increased at 45 °C min⁻¹ to 200 °C (1.0 min) for a total runtime of 5.72 min. The detector was a quadrupole mass spectrometer (HP 5973 N) that was used in the SIM/scan synchronous mode. Full scan was used at the examined m/z range of 25–250. In the SIM mode, two different groups (group 1: m/z 95, 97 and 130 from 0.80 to 2.70 min. Group 2: m/z 83, 97, 99 from 2.70 to 5.72 min) were used with a dwell time value of 1 ms in all cases.

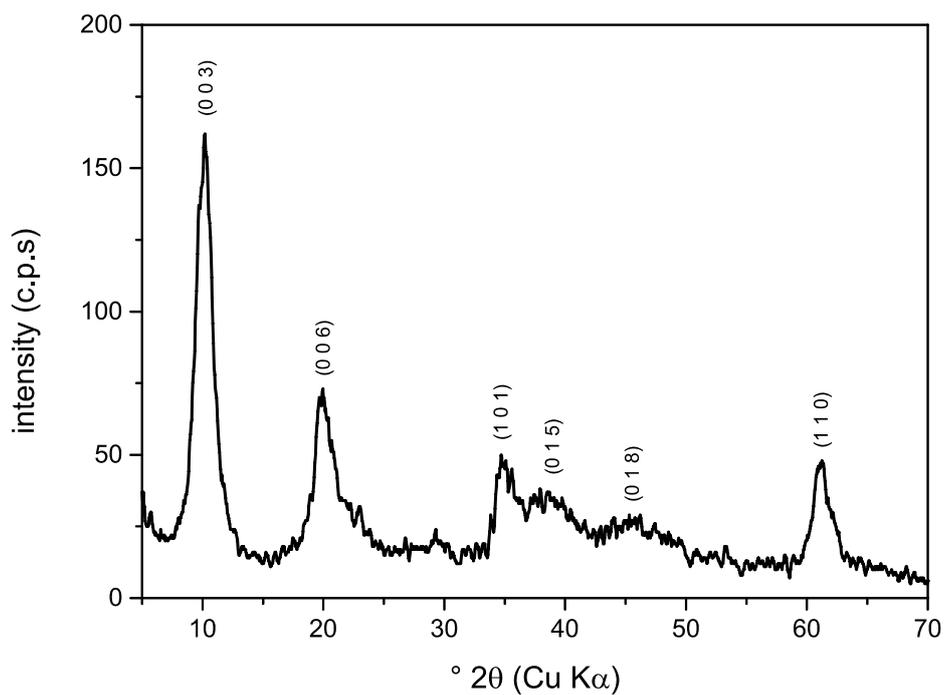


Figure S1. Powder X-Ray diffraction pattern of sample MA-MnO₄.

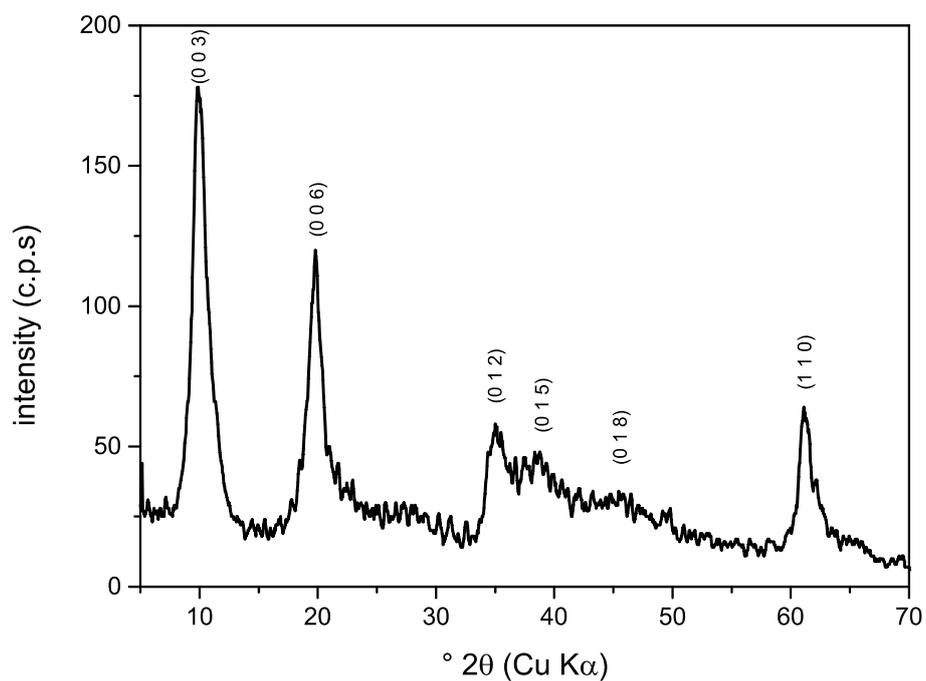


Figure S2. Powder X-Ray diffraction pattern of sample MA-S₂O₈.

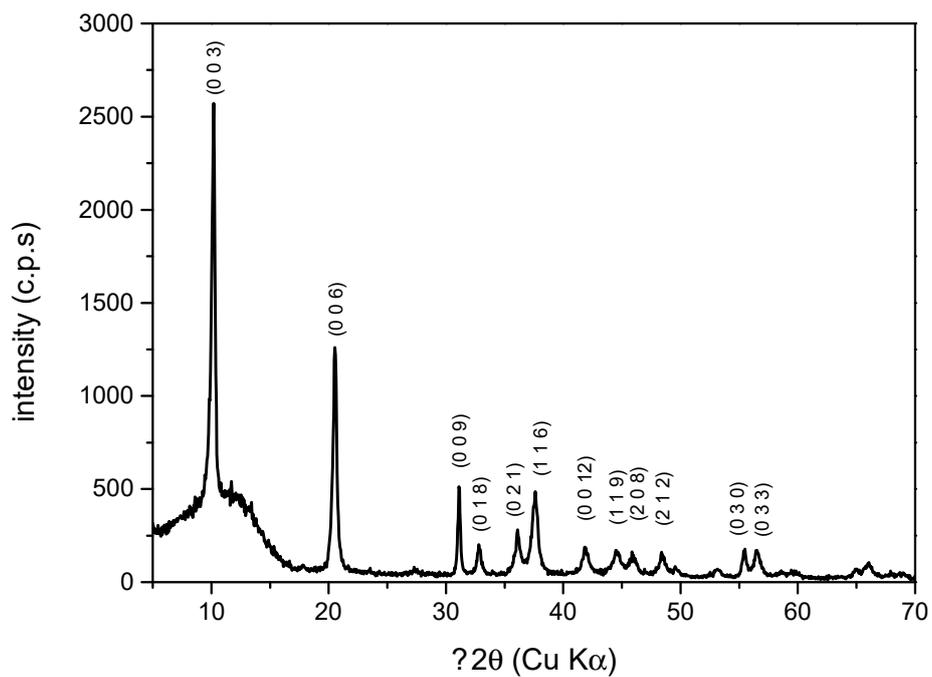


Figure S3. Powder X-Ray diffraction pattern of sample CA-MnO4.

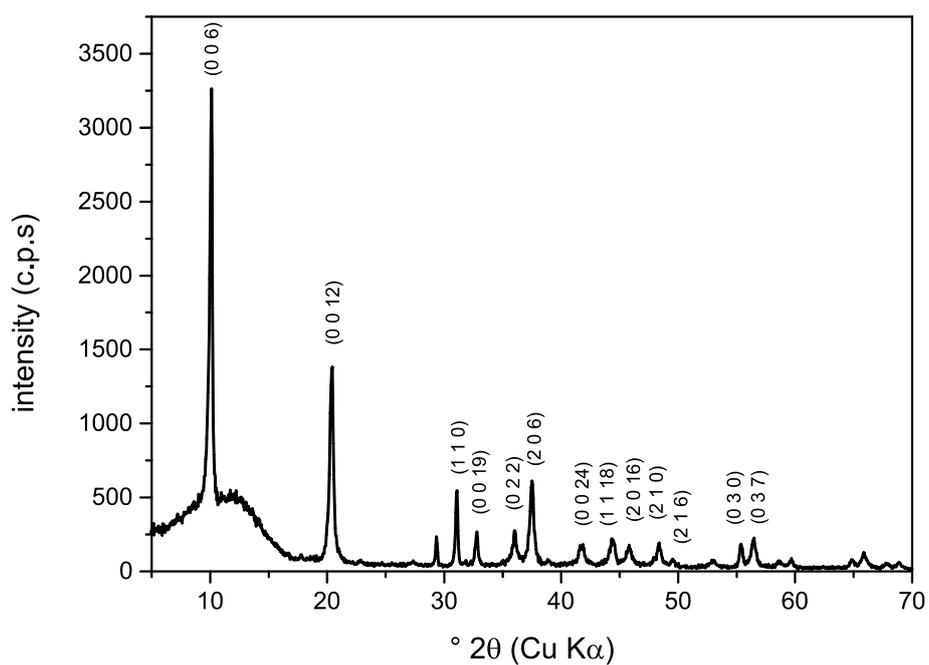


Figure S4. Powder X-Ray diffraction pattern of sample CA-S2O8.

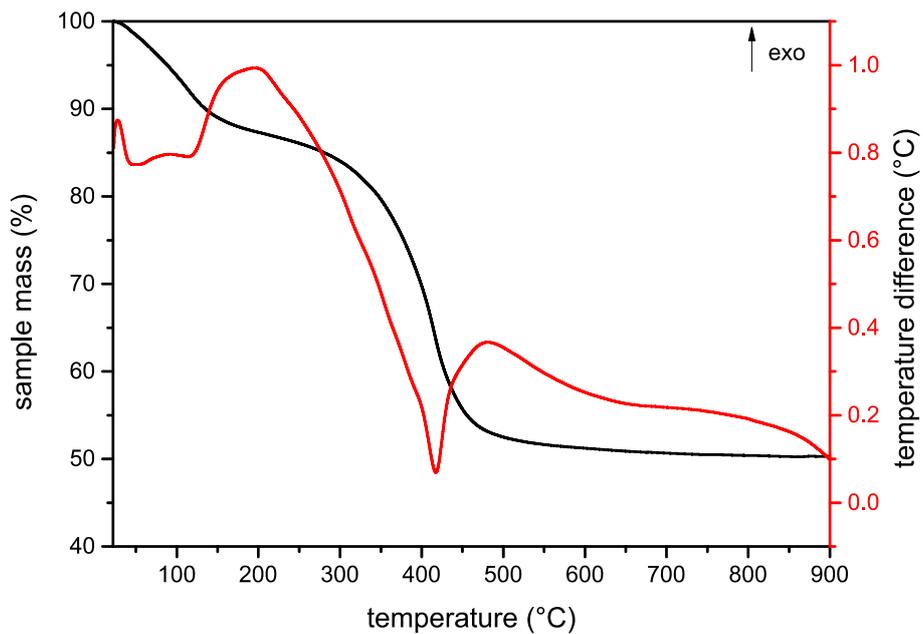


Figure S5. Thermogravimetric Analysis-Differential Thermal Analysis of sample MA-MnO4.

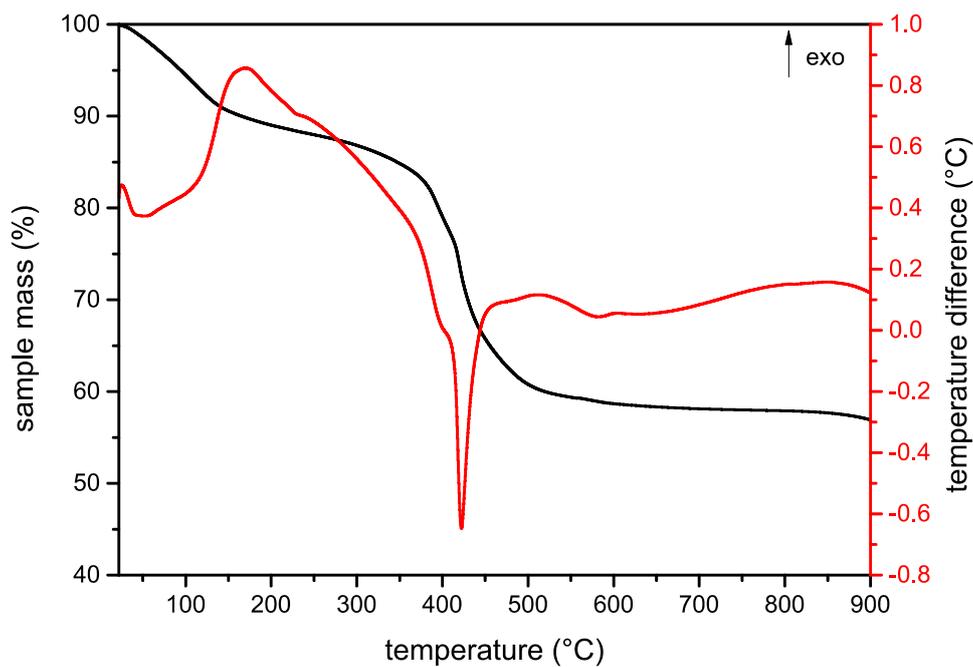


Figure S6. Thermogravimetric Analysis-Differential Thermal Analysis of sample MA-S2O8.

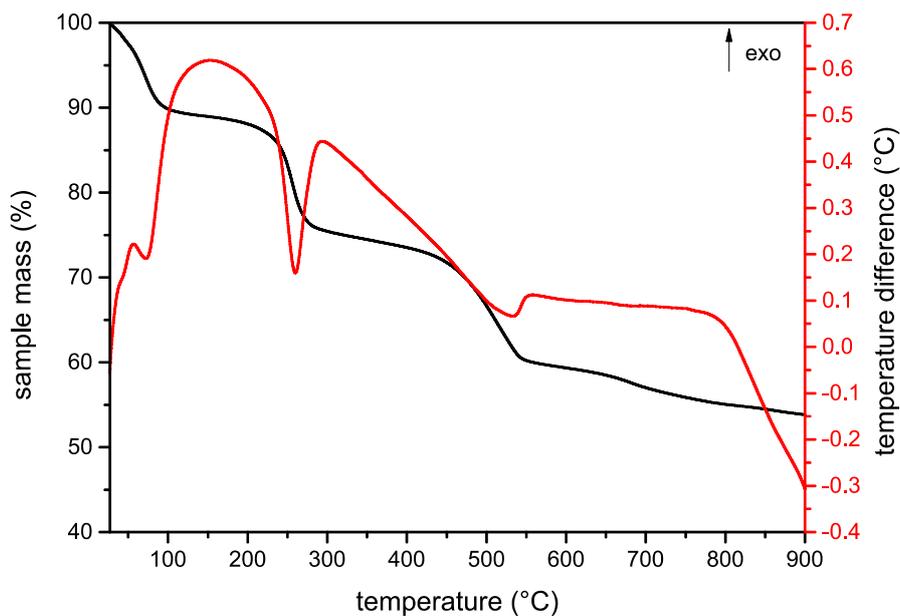


Figure S7. Thermogravimetric Analysis-Differential Thermal Analysis of sample CA-MnO4.

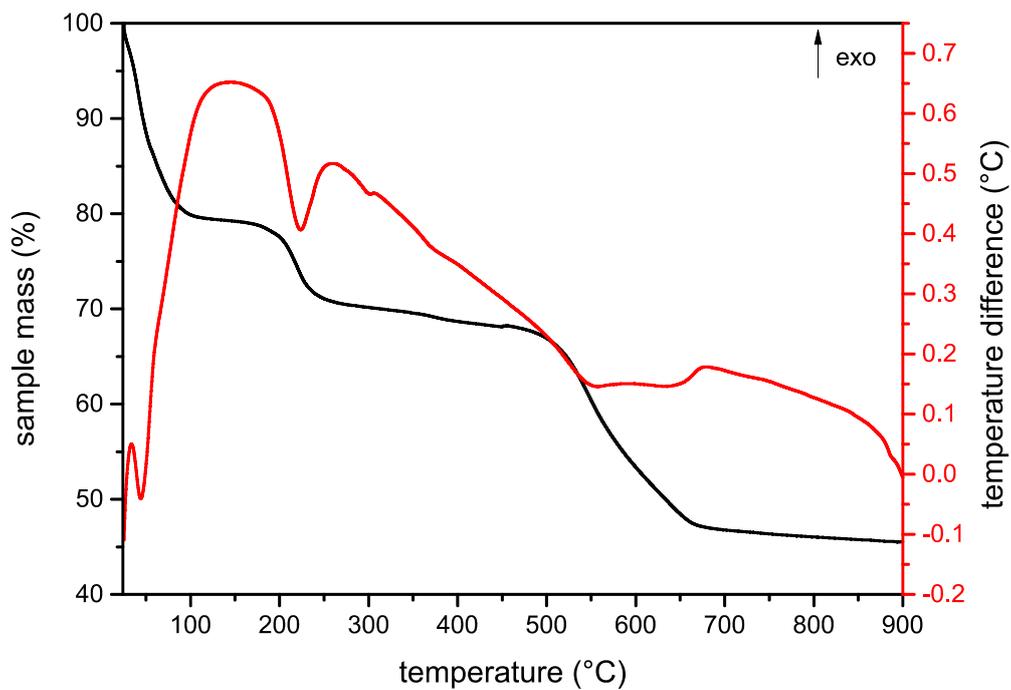


Figure S8. Thermogravimetric Analysis-Differential Thermal Analysis of sample CA-S2O8.

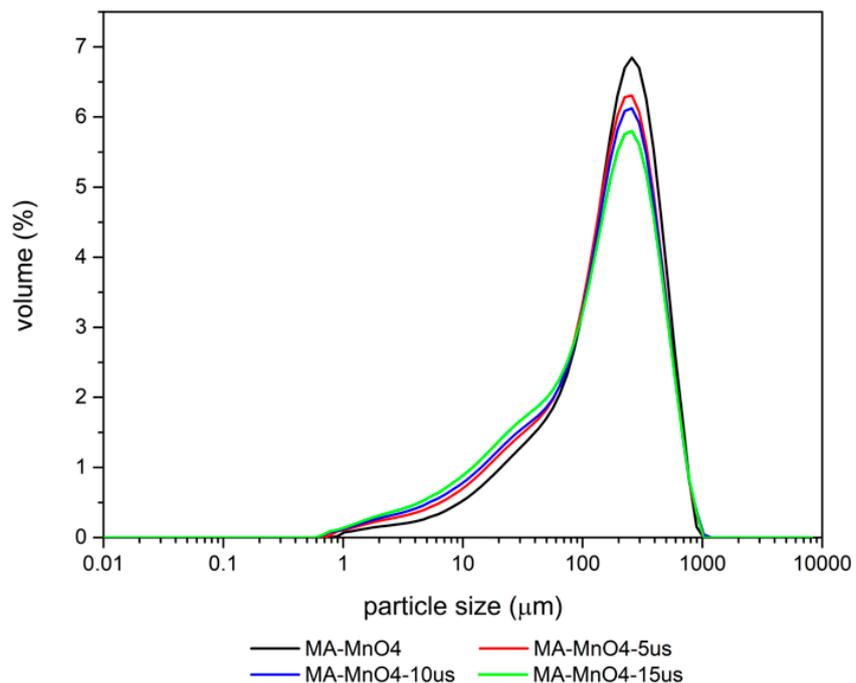


Figure S9. Particle size distribution of sample MA-MnO4 after different times (min) of ultrasound treatment.

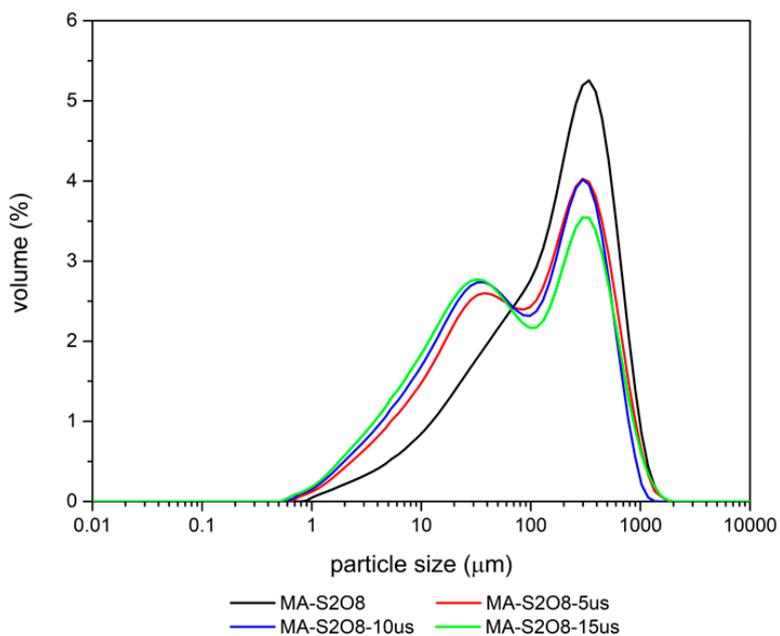


Figure S10. Particle size distribution of sample MA-S2O8 after different times (min) of ultrasound treatment.

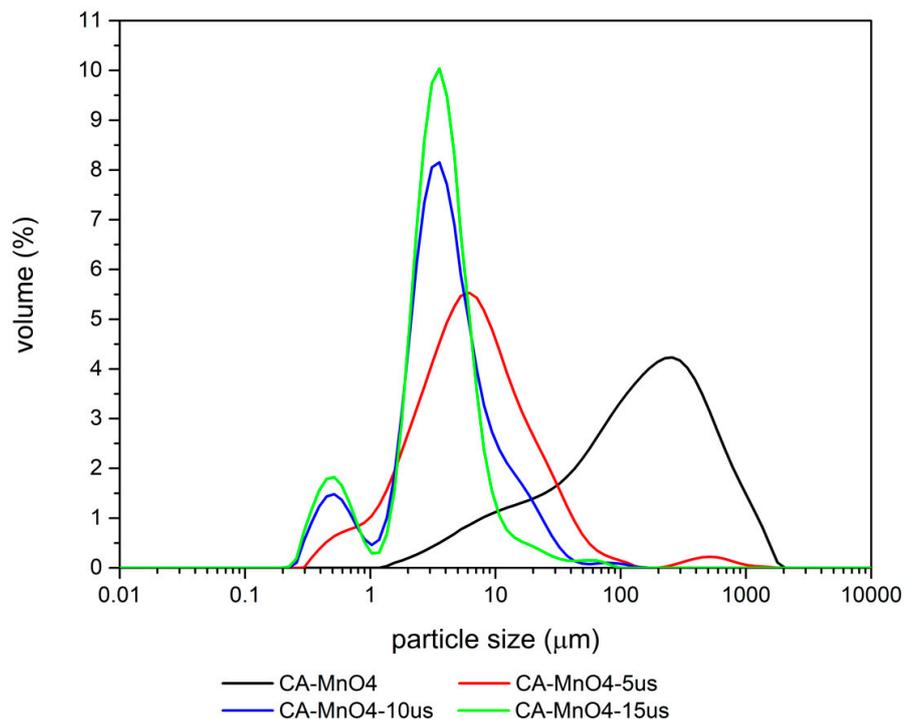


Figure S11. Particle size distribution of sample CA-MnO4 after different times (min) of ultrasound treatment.

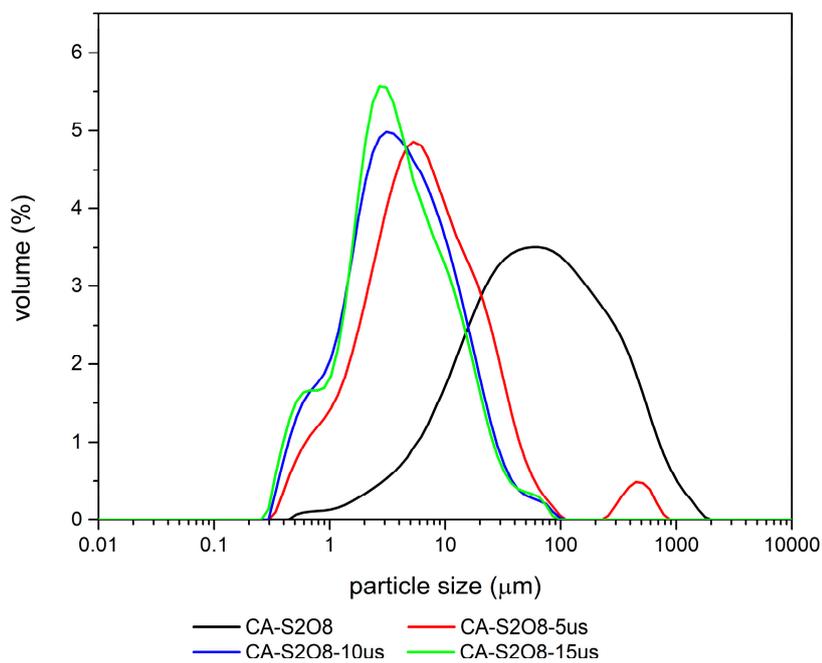


Figure S12. Particle size distribution of sample CA-S2O8 after different times (min) of ultrasound treatment.

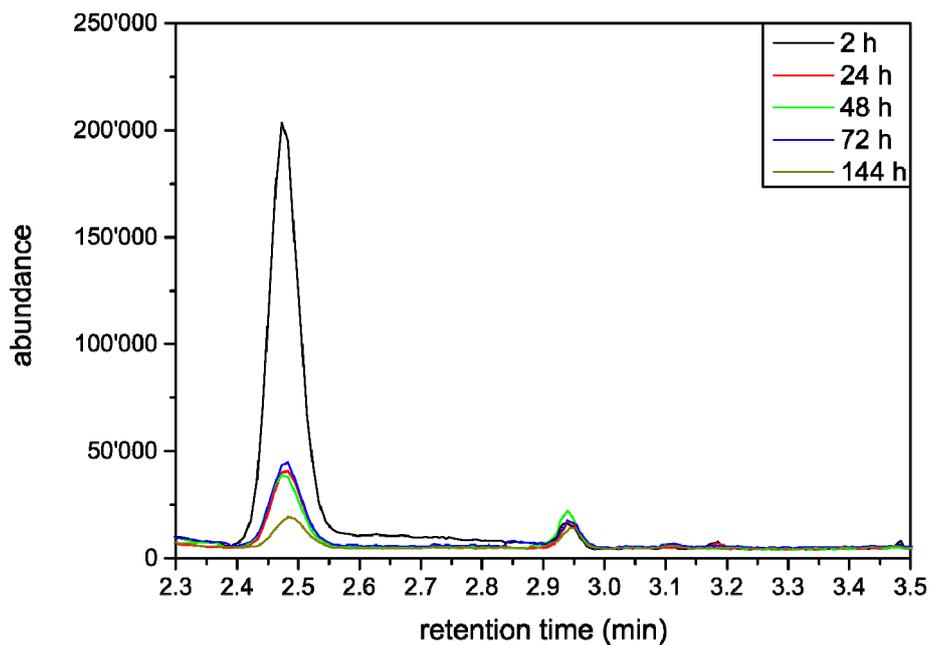


Figure S13. Result of the gas chromatography-mass spectrometry measurements of the batch experiment with 2 g MA-MnO₄ and trichloroethene.

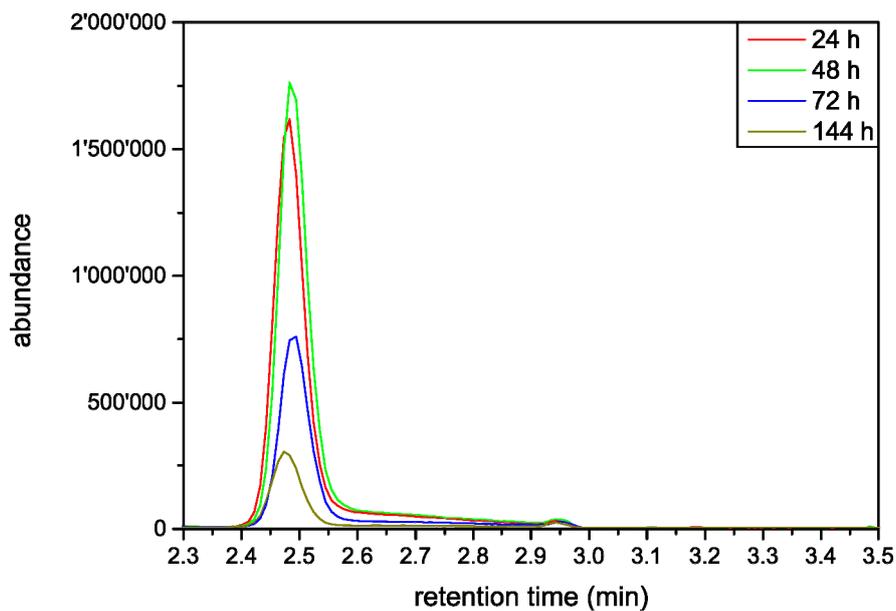


Figure S14. Result of the gas chromatography-mass spectrometry measurements of the batch experiment with 2 g MA-S₂O₈ and trichloroethene.

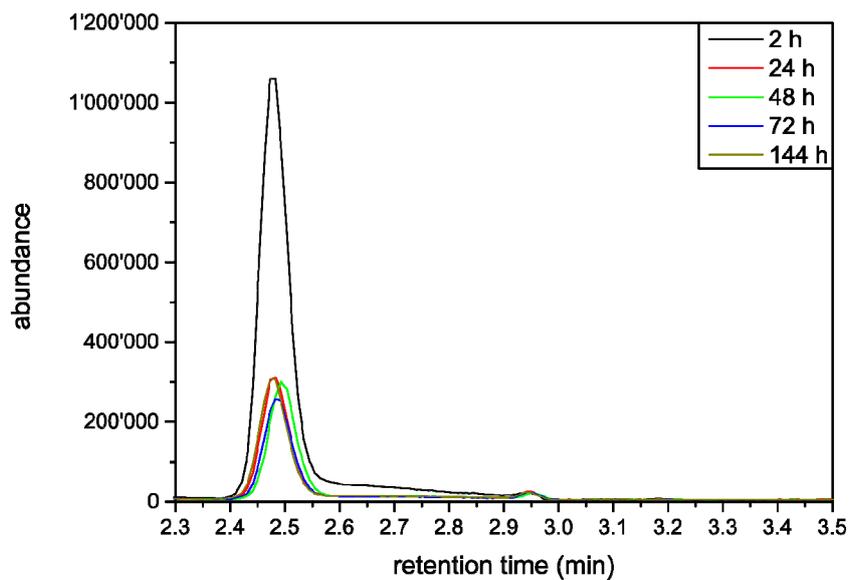


Figure S15. Result of the gas chromatography-mass spectrometry measurements of the batch experiment with 2 g CA-MnO₄ and trichloroethene.

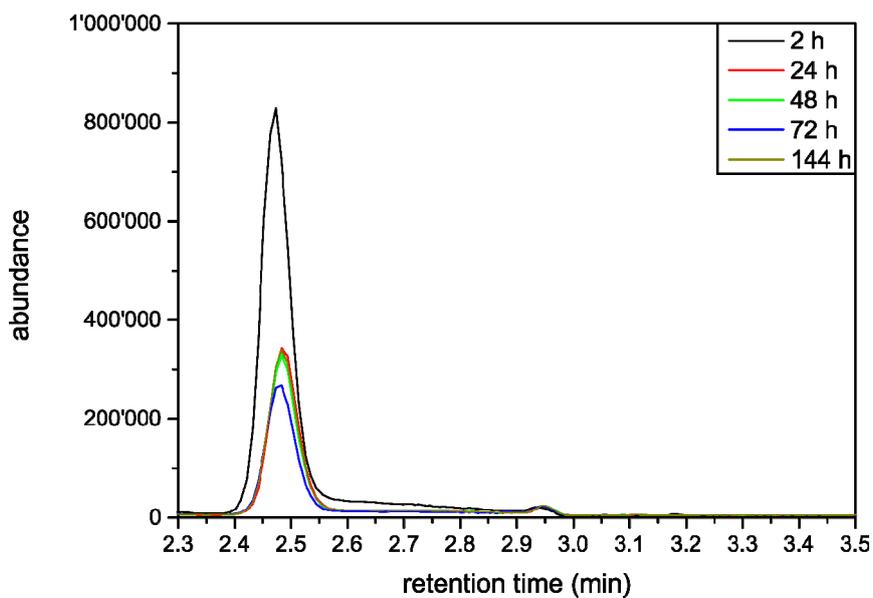


Figure S16. Result of the gas chromatography-mass spectrometry measurements of the batch experiment with 1 g CA-MnO₄ and trichloroethene.

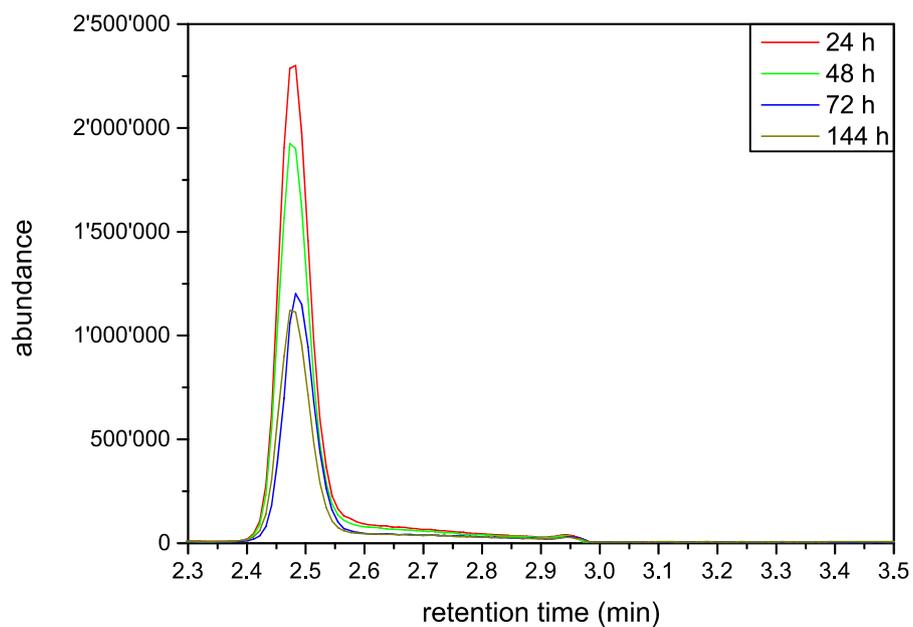


Figure S17. Result of the gas chromatography-mass spectrometry measurements of the batch experiment with 2 g CA-S2O8 and trichloroethene.

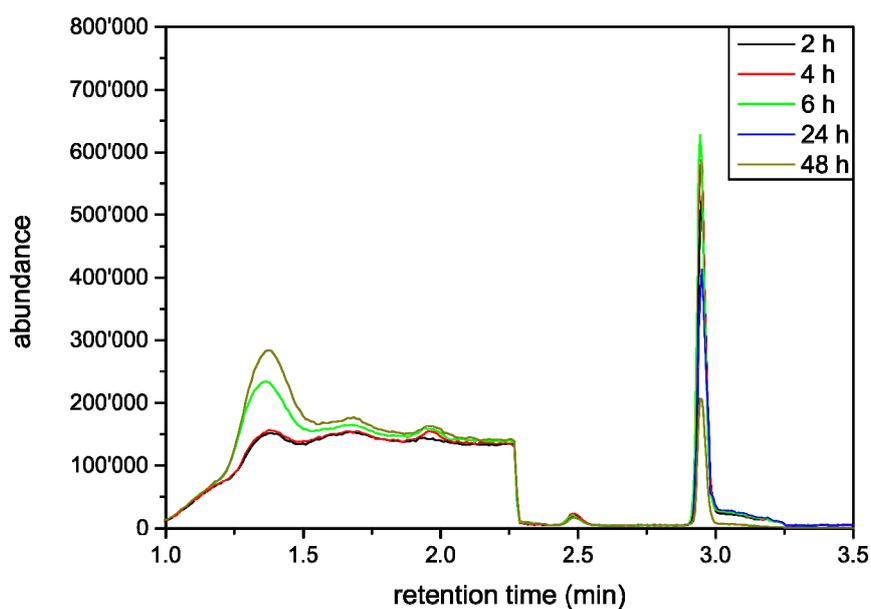


Figure S18. Result of the gas chromatography-mass spectrometry measurements of the batch experiment with 2 g MA-S2O8 and 1,1,2-trichloroethane.

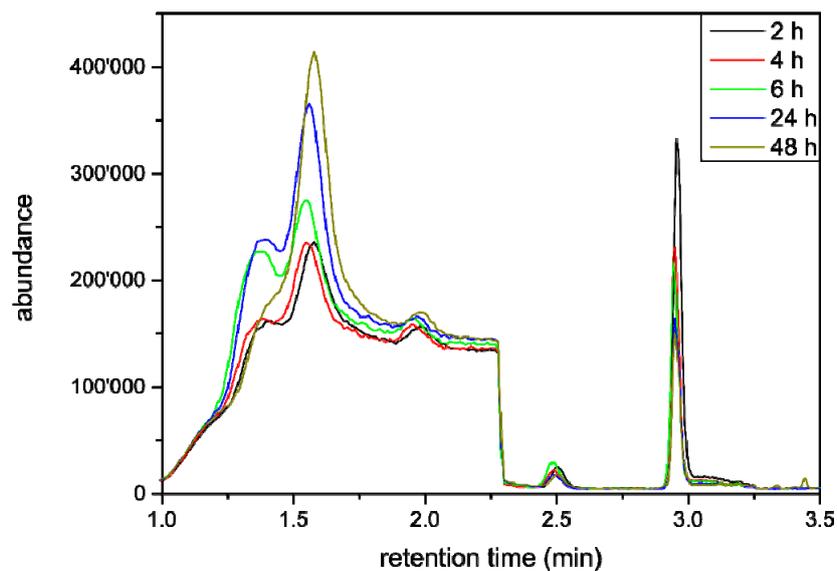


Figure S19. Result of the gas chromatography-mass spectrometry measurements of the batch experiment with 2 g CA-S₂O₈ and 1,1,2-trichloroethane.

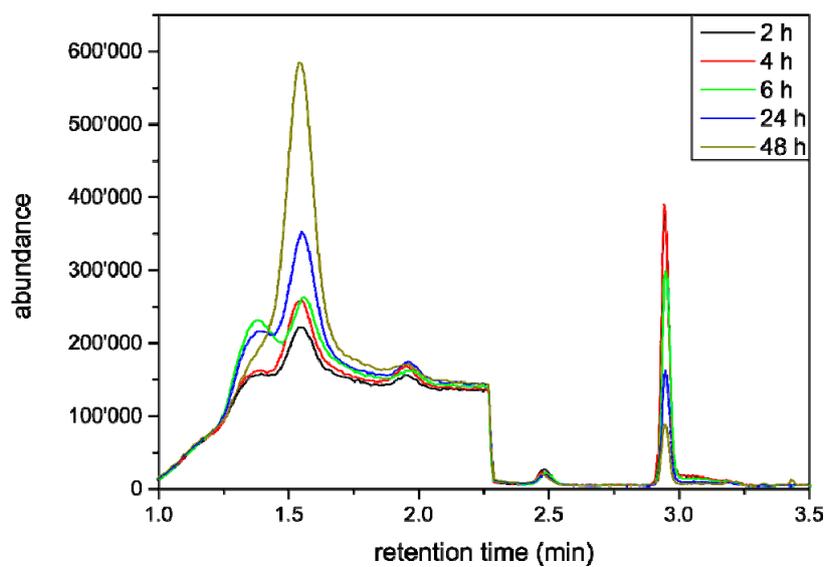


Figure S20. Result of the gas chromatography-mass spectrometry measurements of the batch experiment with 1 g CA-S₂O₈ and 1,1,2-trichloroethane.

Table S1. List of chemicals used within this study.

Chemicals	Chemical Formula	Supplier	Purity
sodium hydroxides, pellets	NaOH	Panreac	98%
Aluminium oxide	Al ₂ O ₃	Fluka	99.99%
Aluminium nitrate 9-hydrate, pure	Al(NO ₃) ₃ ·9H ₂ O	PanReac AppliChem ITW Reactants	min. 98%
Magnesium nitrate 6-hydrate, for analysis	Mg(NO ₃) ₂ ·6H ₂ O	PanReac AppliChem ITW Reactants	min. 98%
Calcium nitrate tetrahydrate	Ca(NO ₃) ₂ ·4H ₂ O	Scharlab	99.5%
Potassium permanganate, puriss. P.a.	KMnO ₄	Sigma-Aldrich	≥ 99.0%
potassium bromide,	KBr	Scharlab	IR spectroscopy grade
Sodium peroxodisulfate	Na ₂ S ₂ O ₈	PanReac AppliChem ITW Reactants	98 %
oxygen, compressed	O ₂	Alphagaz, Air Liquide	> 99.995%
Trichloroethene, reagent grade, stabilized with ethanol (0.49 %)	C ₂ HCl ₃	Scharlab	99.5%
1,1,2-Trichloroethane	C ₂ H ₃ Cl ₃	Arcos Organics	98%

Table S2. Band positions (cm⁻¹) in the FTIR spectra of the permanganate intercalated samples with corresponding assignments.

Band Assignment	MA-MnO ₄	CA-MnO ₄
v(O-H)	3630–3345	3640
v ₁ ,v ₃ (H-O-H)	3630–3345	3485
δ(H ₂ O)	1632	1620
v(NO ₃ ⁻)	1385	1353
v ₁ (CO ₃)		1060
v _{as} (NO ₃ ⁻)		1023
v ₃ (MnO ₄)	904	
v ₃ (MnO ₄)	826	834
δ(Me-OH)		786
v _s (MnO ₄)		786
(Me-OH)	630	
(Me-OH)		589
(Me-OH)		527
(O-Me-O)		446

Table S3. Band positions (cm⁻¹) in the FTIR spectra of the peroxydisulfate intercalated samples with corresponding assignments.

Band Assignment	MA-S2O8	CA-S2O8
$\nu(\text{O-H})$	3575–3395	3640
$\nu_1, \nu_3(\text{H-O-H})$	3575–3395	3478
$\delta(\text{H}_2\text{O})$	1632	1622
$\nu(\text{NO}_3^-)$	1384	1384
$\nu(\text{SO}_3)$	1312	
$\nu(\text{SO}_3)$	1271	
$\nu(\text{SO}_3)$	1115	1111
$\nu_{\text{as}}(\text{S-O-O-S})$	1061	1060
$\nu_{\text{as}}(\text{NO}_3^-)$		1022
$\nu_{\text{s}}(\text{S-O-O-S})$	834	836
$\delta(\text{Me-OH})$		785
$\delta(\text{SO}_3)$	685	
$\delta(\text{SO}_3)$	667	
(Me-OH)	640	588, 529
(O-Me-O)	446	423

Table S4. Results of the HS-PTV-GC-MS measurements of batch experiments with TCE as the contaminant. Results of the blank solution are also given.

Sample	Sample Mass (g)	Reaction Time (h)	Concentration TCE (mmol/L)	Concentration TCE (%)	Amount Oxidising Agent Reacted (%)	Oxising Agent : TCE
blank		0	0.400	100.00		
		72	0.244	61		
		144	0.243	61		
MA-MnO4	2	0	0.400	100.00		
		2	0.040	10		
		24	0.008	2		
		48	0.007	2		
		72	0.007	2		
		144	0.007	2	1.3	116:1
MA-S2O8	2	0	0.400	100.00		
		2	0.369	92		
		24	0.341	85		
		48	0.159	40		
		72	0.062	16	0.4–0.9	50:1
CA-MnO4	2	0	0.400	100.00		
		2	0.226	57		
		24	0.063	16		
		48	0.061	15		
		72	0.059	15		
		144	0.053	13	1.0	131:1
CA-MnO4	1	0	0.400	100		
		2	0.169	42		
		24	0.070	17		
		48	0.066	16		
		72	0.054	14		
		144	0.049	12	1.9	66:1
CA-S2O8	2	0	0.400	100.00		
		2	0.384	96		
		24	0.283	71		
		48	0.237	59		
		72	0.228	57	<0.1	41:1

Table S5. Results of the HS-PTV-GC-MS measurements of batch experiments with 1,1,2- TCA as the contaminant. Results of the blank solution are also given.

Sample	Sample Mass (g)	Reaction Time (h)	Concentration TCA (mmol/ L)	Concentration TCA (%)	Amount Oxidising Agent Reacted (%)	Oxising Agent : TCE
blank		0	0.400	100		
		6	0.383	96		
		24	0.319	80		
MA-S2O8	2	0	0.400	100		
		2	0.398	100		
		4	0.347	87		
		6	0.332	83		
		24	0.306	76		
		48	0.279	70	<0.3	50:1
CA-S2O8	2	0	0.400	100		
		2	0.218	54		
		4	0.152	38		
		6	0.139	35		
		24	0.107	27		
		48	0.054	14	1.5	41:1
CA-S2O8	1	0	0.400	100		
		2	0.253	63		
		4	0.251	63		
		6	0.206	51		
		24	0.106	26		
		48	0.054	14	1.4	20:1



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).