Electronic Supplementary Information (ESI)

Iron-montmorillonite clays as active sorbents for the decontamination of hazardous chemical warfare agents

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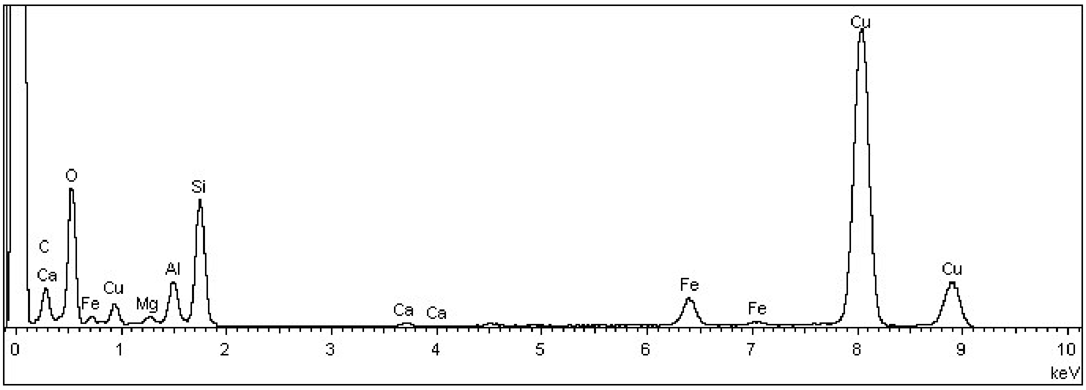

Sample	Atomic ratio (%)		
	Si	Al	Fe
H-DECON1	**65.03**	**21.53**	**13.43**

Figure S1. EDX spectrum of a representative H-DECON1 sample grain

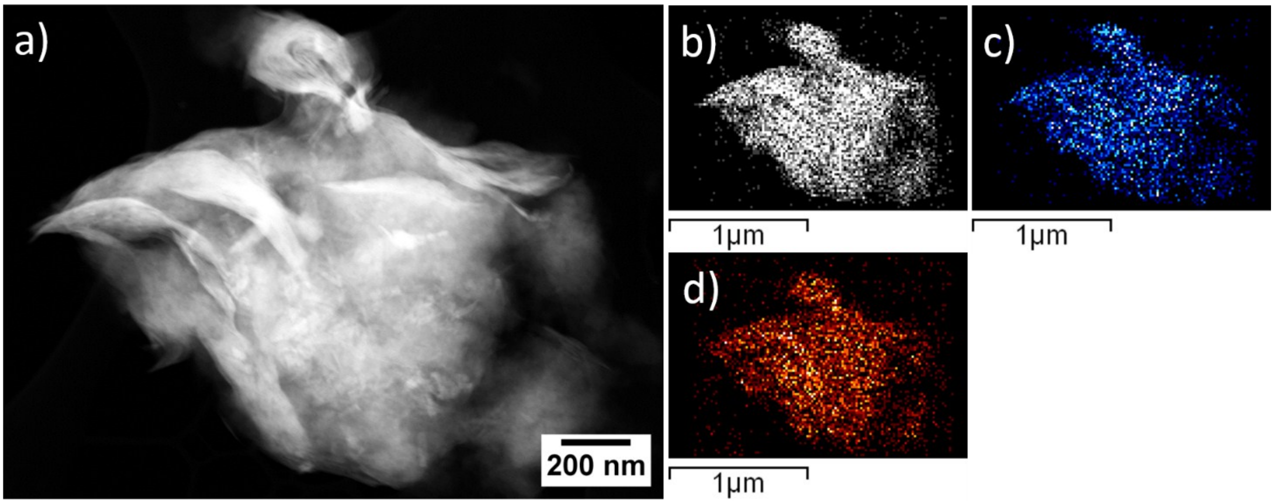

Figure S2. STEM measurements on DECON1: a) HAADF image of a sample grain; b-d) STEM-EDX mapping of the catalyst showing the iron dispersion: b) silicon map (white), c) aluminium map (blue); d) iron map (red).

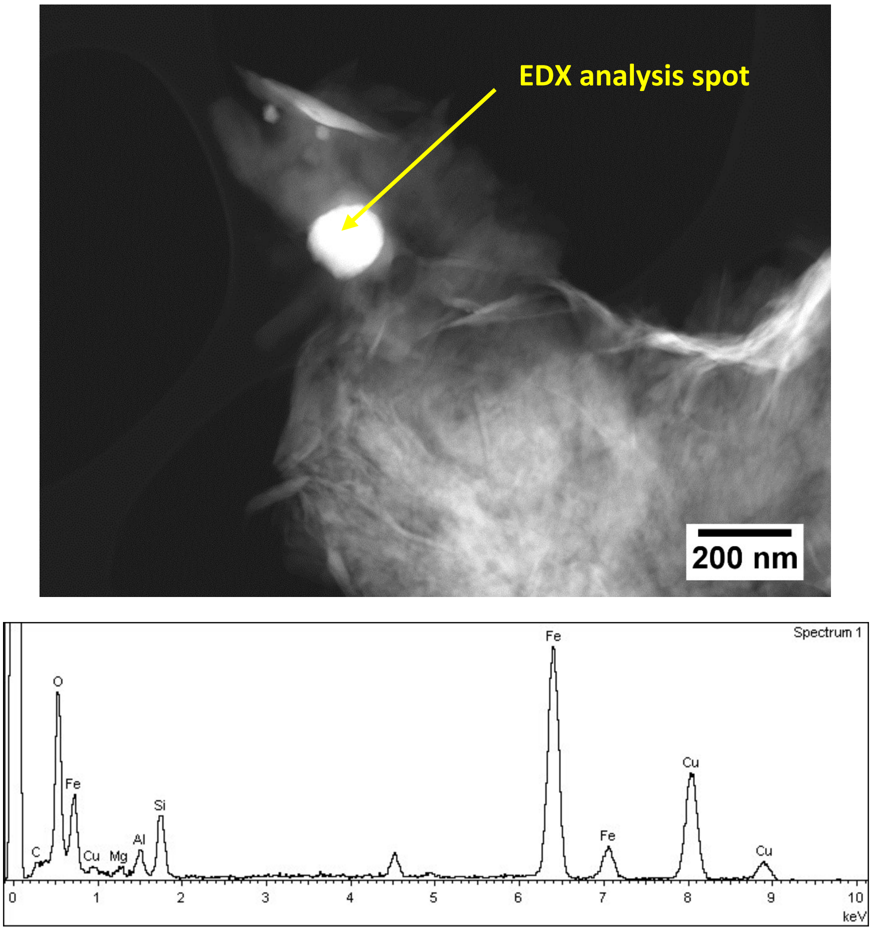

Figure S3. STEM image of DECON1 (a) and EDX spectrum (b) of the selected particle.

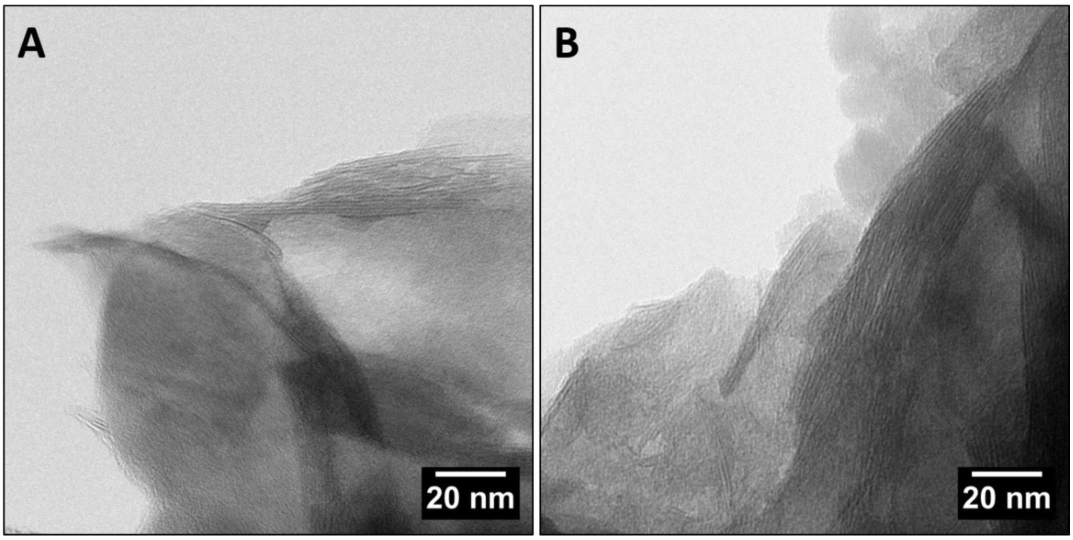

Figure S4. HRTEM representative micrograph of DECON1 (A) and H-DECON1 (B).

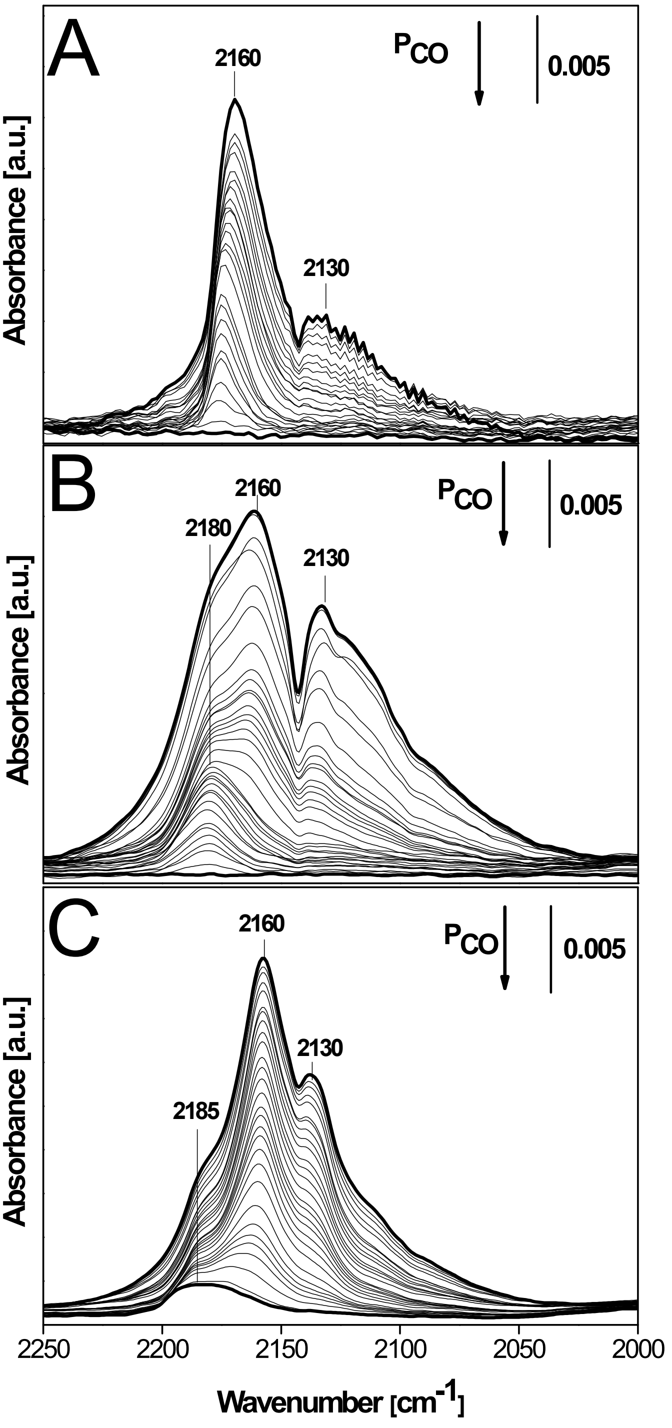

Figure S5. IR spectra of CO adsorbed at 100 K on DECON1 (A), Fe-DECON1 (B) and H-DECON1 (C). The arrows indicate a decreasing of CO pressure. Spectra are reported after subtraction of the spectrum of the bare sample (before CO interaction) used as a background.

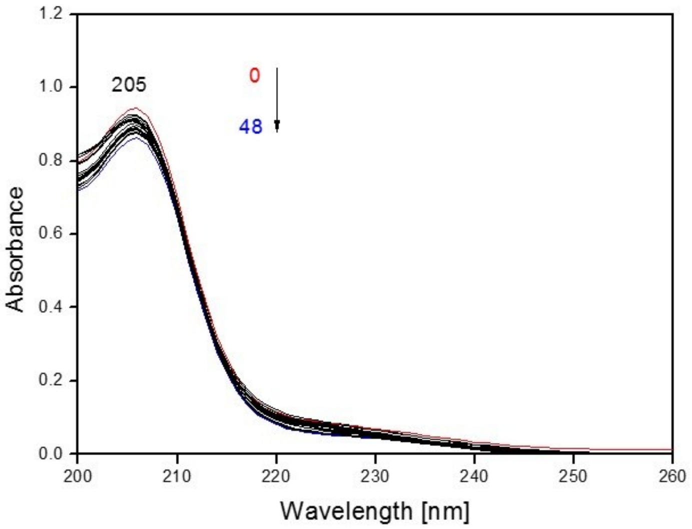

Figure S6. UV-Vis spectra of the reaction mixture in the presence of DECON1 from 0 to 48 h.

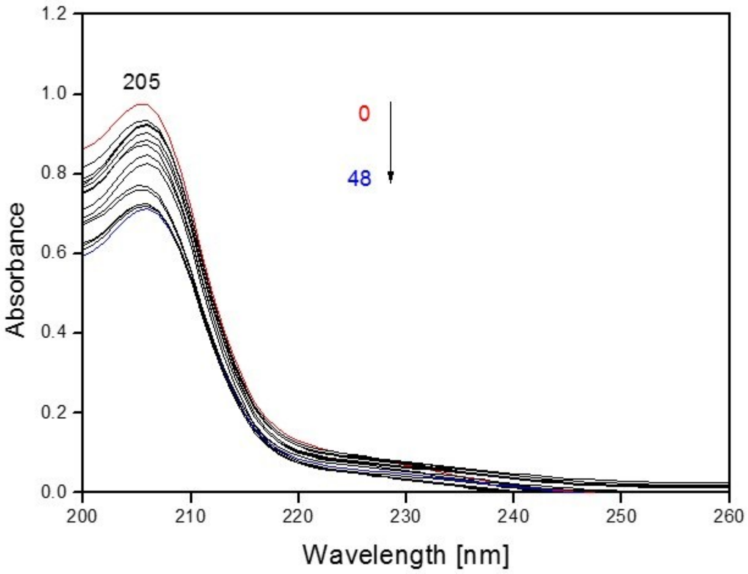

Figure S7. UV-Vis spectra of the reaction mixture in the presence of Fe-DECON1 from 0 to 48 h.

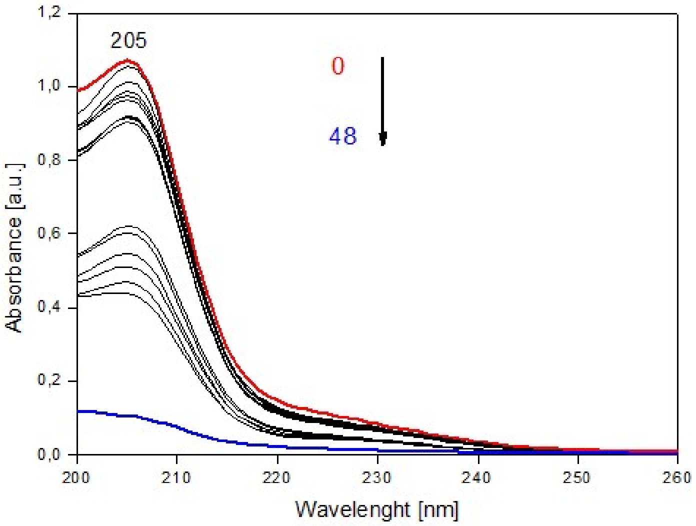

Figure S8. UV-Vis spectra of the reaction mixture in the presence of H-DECON1 from 0 to 48 h.

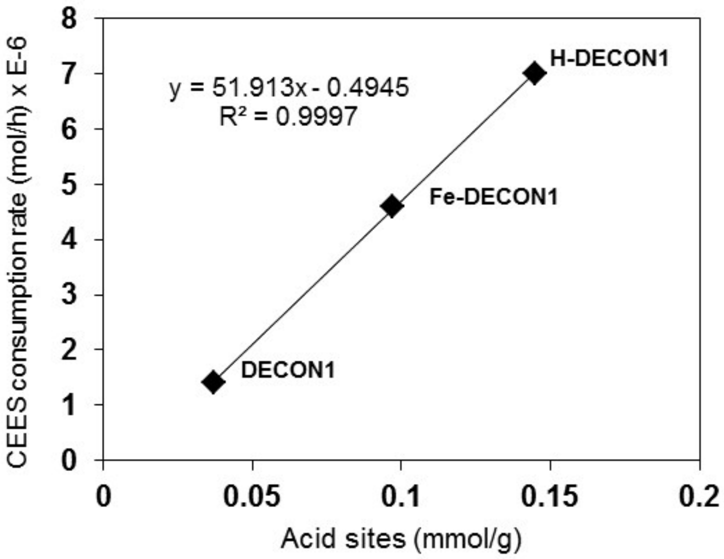

Figure S9. Linear correlation between CEES consumption rate (expressed in mol_{CEES} h^{-1}, in CEES abatement tests) and amount of acid sites (mmol g^{-1}, as obtained by NH_3-adsorption FTIR analysis). Reaction conditions as in Figure 5.

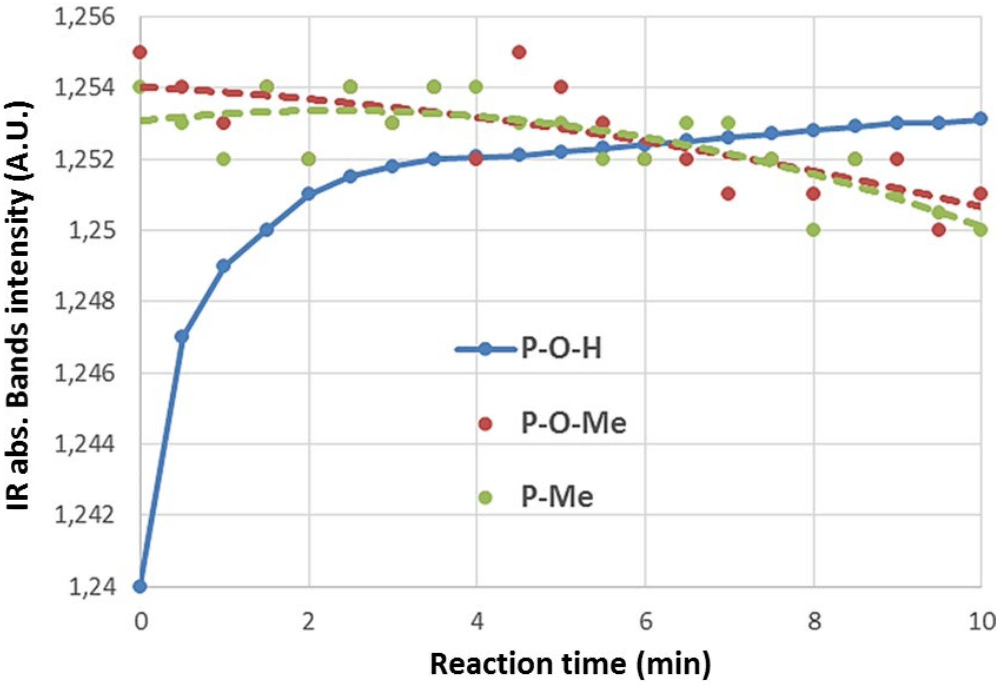

Figure S10. Time evolution of the intensity (integrated area) of selected infrared absorption bands during DMMP decontamination experiments over Fe-DECON1-PB, monitored by ATR-FTIR spectroscopy.

The DMMP decomposition profile *vs*. time was studied by attenuated total reflectance (ATR-FTIR) spectroscopy. The intensity (i.e. integrated area) of IR absorption bands located at 1315, 1022, and 1000 cm^{-1}, respectively, ascribable to P-CH_3, P-O-CH_3, and P-O-H bonds stretching vibrations[1], was recorded along reaction time. The progressive decrease of typical bands of DMMP, i.e. P-CH_3, P-O-CH_3, and the rapid formation, in few minutes, of monomethyl-methylphosphonate (P-O-H absorption band) can be observed (Fig. S10). This behavior suggests that an *in situ* catalysed hydrolysis of DMMP into monomethyl-methylphosphonate (Scheme S1) and, subsequently, into methylphosphonic acid took place at the surface of the solid.

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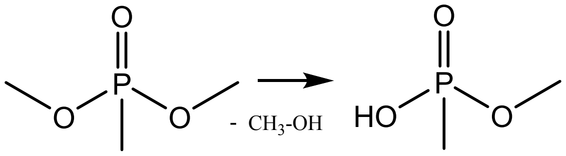
[1] K. Kim, O. G.Tsay, D. A. Atwood, D. G. Churchill, *Chem. Rev.*, 111, **2011**, 5345; K. E. O'Shea, S. Beightol, I. Garcia, M. Aguilar, D. V. Kalen, W. J. Cooper, *J. Photochem. Photobiol. A: Chem.*, 107, **1997**, 221; C. Hampton, D. Demoin,; D. A. Trubitsyn, A. V. Vorontsov, *J. Phys. Chem. B*, 109, **2005***,* 21884.



Scheme S1. Hydrolytic degradation of DMMP into monomethyl-methylphosphonate.

Experimental details for the ATR-FTIR study

ATR-FTIR analysis was performed on a FTS-60A spectrometer (Biorad) equipped with a broadband L-N_2 cooled MCT detector and a Golden Gate ATR platform with diamond crystal (Specac). The spectra were recorded using Kinetics routine. A sample of white 3 x 3 cm 100% cotton textile was contacted with 20 µl of DMMP (0.1845 mmol), 10 mg of decontamination mixture and 20 µl of high-purity deionized water (MilliQ) and was pressed onto the diamond crystal.

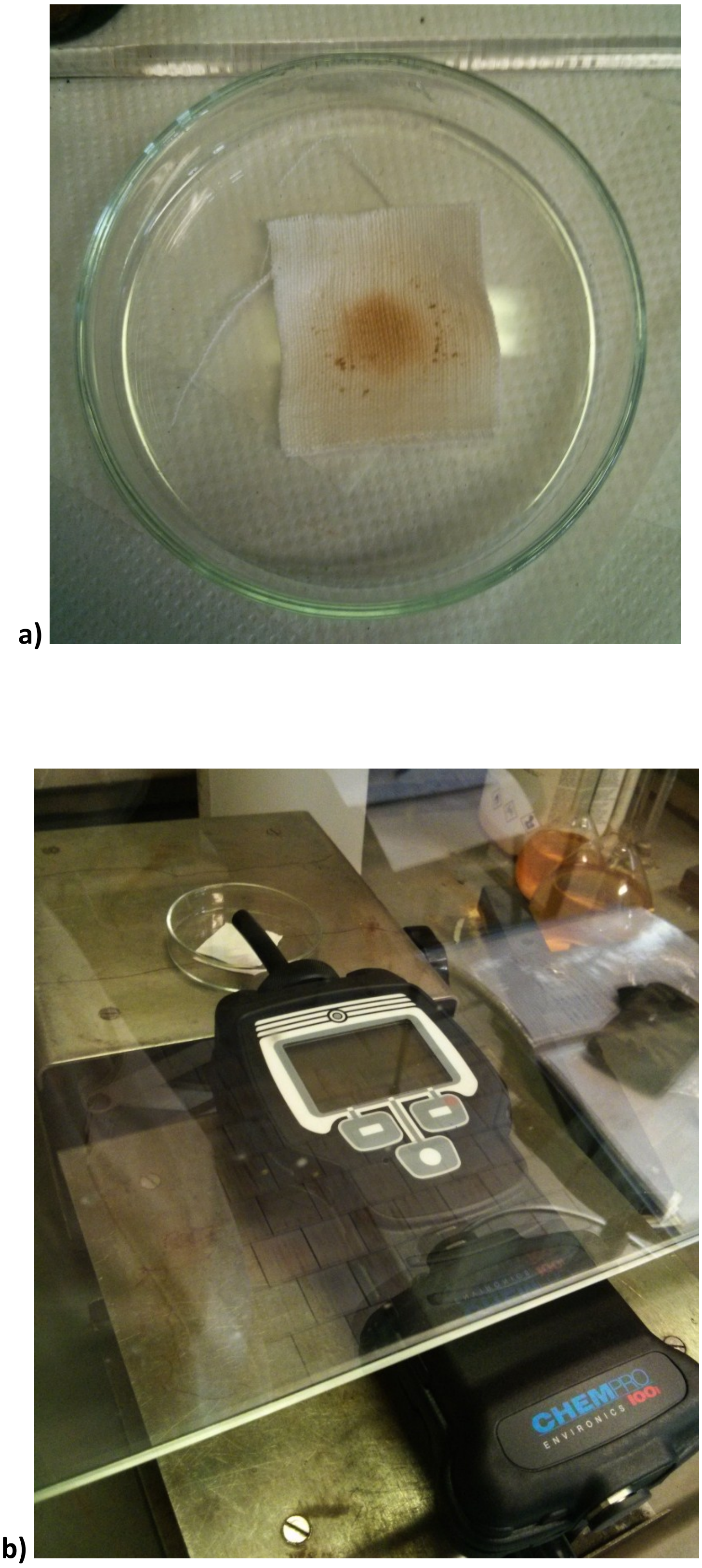


Figure S11. Experimental set-up for the catalytic oxidative decontamination of the cotton textile sample from CEES and DMMP. a) Cotton textile sample treated with Fe-DECON1 solid; b) Detection of the off-vapours by means of an on-field open-loop ion mobility spectrometer. Reaction conditions as in Experimental Section.

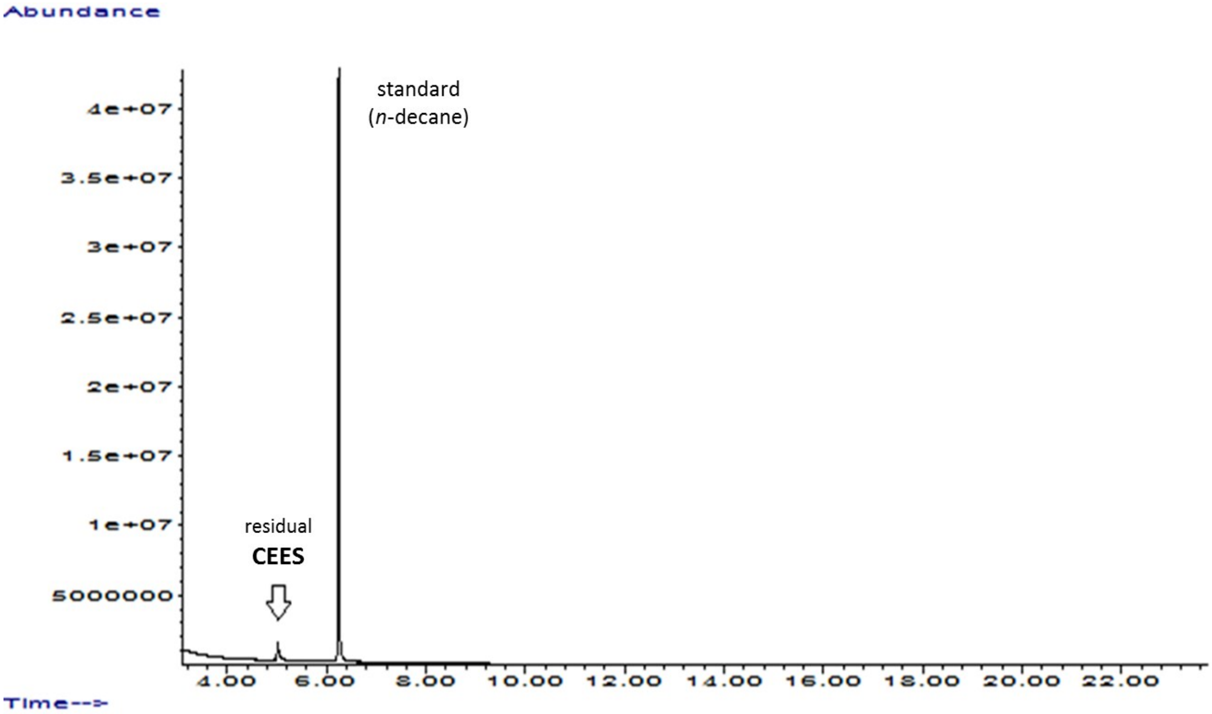


Figure S12. Chromatogram (GC-MS) of the residual contamination at the end (24 h) of the decontamination test of CEES in the presence of Fe-DECON1-PB over a cotton textile sample. Extraction with 1.5 mL of CH_2Cl_2. Reaction conditions: 0.17 mmol CEES (ca. 20 µL); 140 mg decontamination mixture; 120 µL H_2O; brushing after 1 min; room temperature.

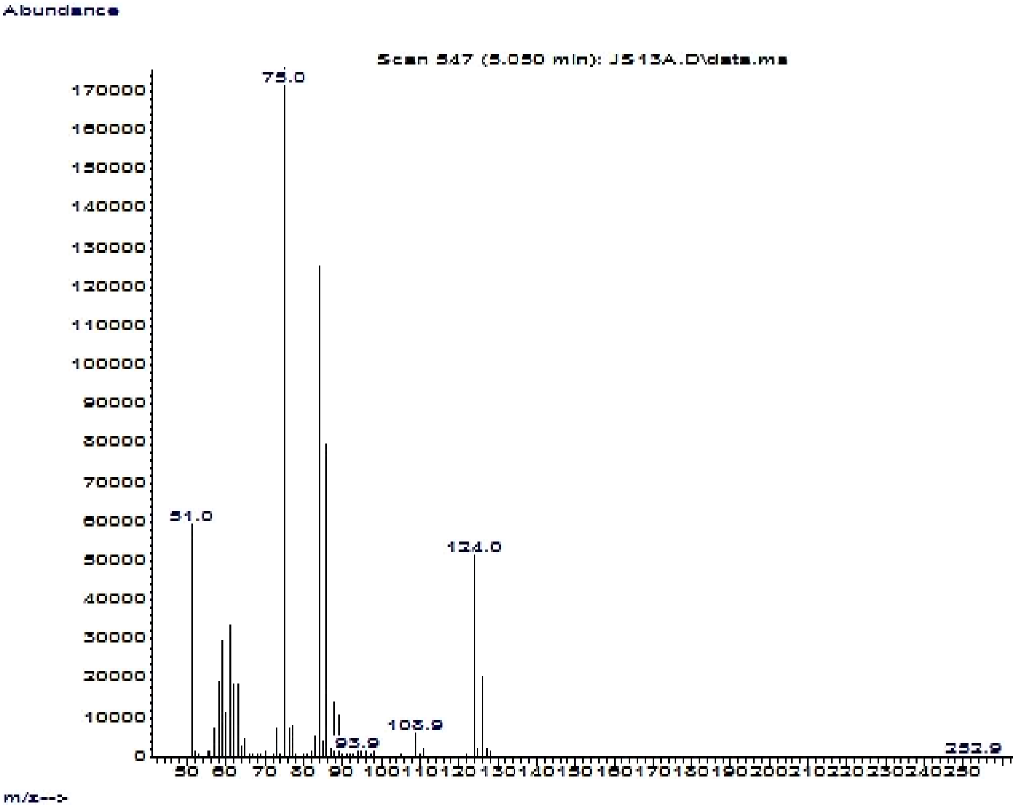


Figure S13. Mass spectrum of the chromatographic peak at 5.05 min (as reported in Figure S12) attributed to residual CEES.

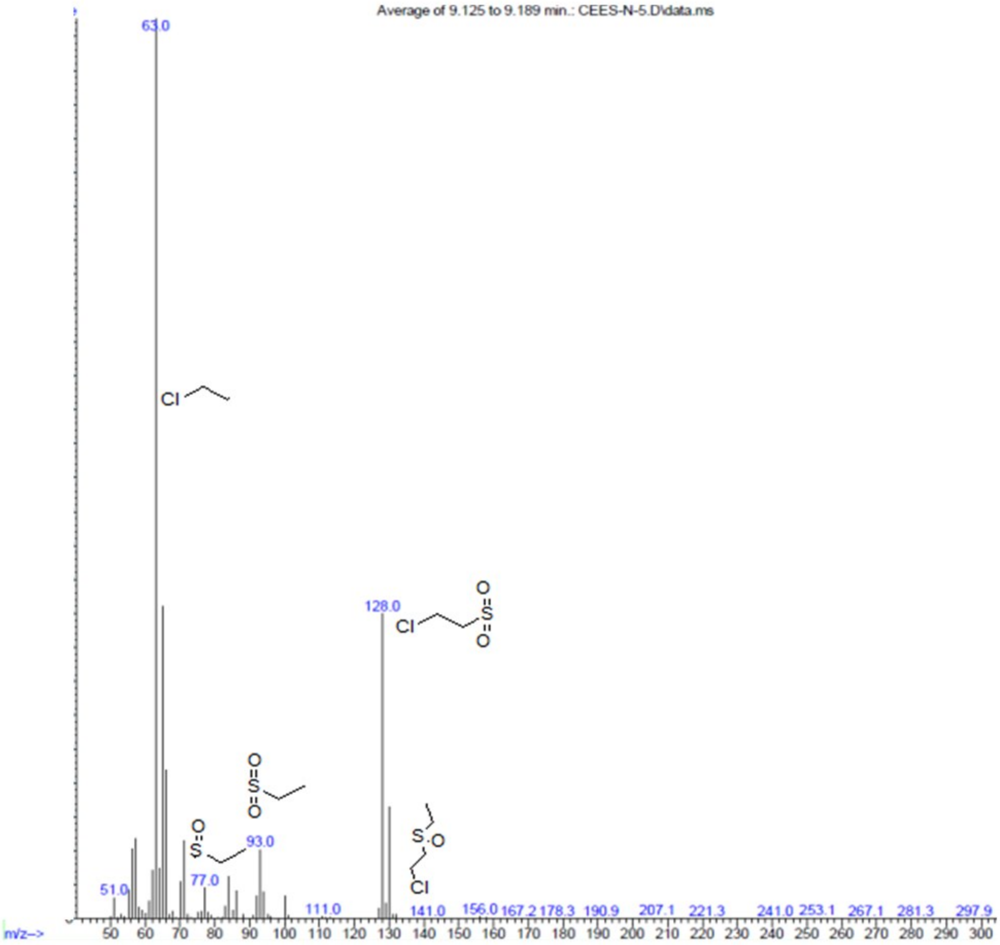


Figure S14. Mass spectrum of the chromatographic peak attributed to minor traces of CEESO$_2$ (eluted around 9.15 min on the GC-MS apparatus).

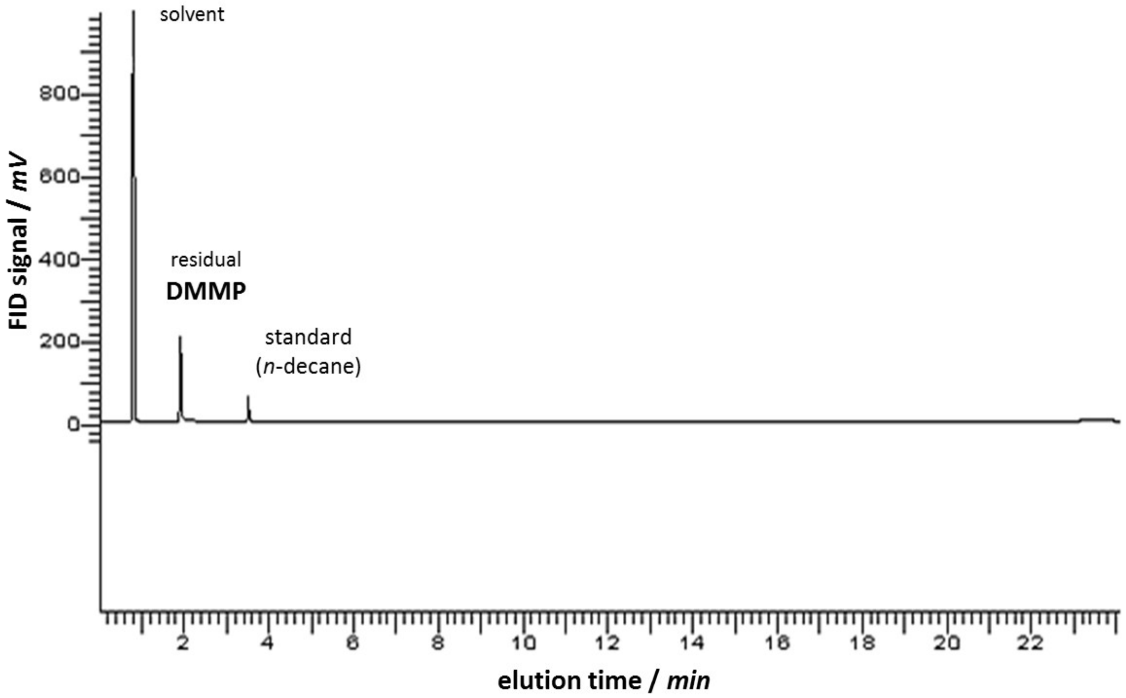


Figure S15. Chromatogram (GC-FID) of the residual contamination at the end (24 h) of the decontamination test of DMMP in the presence of Fe-DECON1-PB over a cotton textile sample. Extraction with 1.5 mL of CH_2Cl_2. Reaction conditions: 0.17 mmol DMMP (ca. 20 µL); 140 mg decontamination mixture; 120 µL H_2O; brushing after 1 min; room temperature.

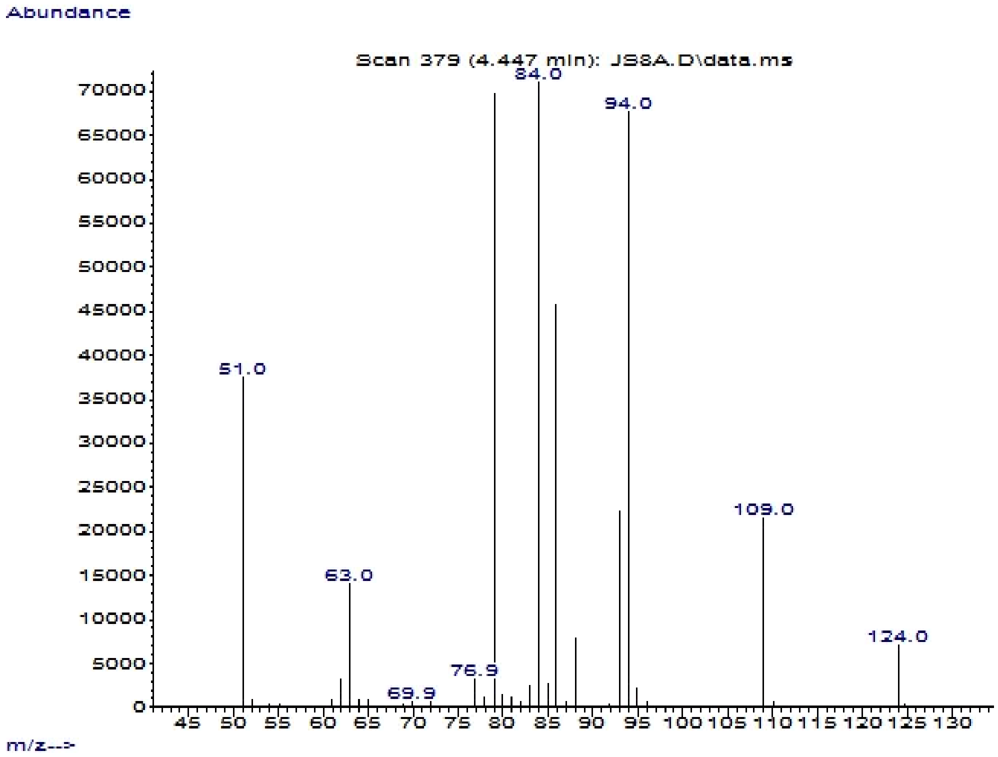


Figure S16. Mass spectrum of the chromatographic peak attributed to residual DMMP (eluted at 4.447 min on the GC-MS apparatus).

Experimental details for the catalytic decontamination tests of HD agent

The residual contamination on the PTFE coupon was extracted after 24 h with 10 mL of *n*-heptane and the extract was analysed by gas-chromatography (GC-FID, Agilent 6890N) under the following conditions: 30 m x 0.32 mm Agilent HP-5 column, split mode, split ratio 10:1, injection volume 1 µL, N_2 carrier gas, FID detector, temperature programme: 60°C 2 min, 10°C/min, 150°C 4 min. Internal standard (added to the analysis mixture for quantification purposes): *n*-decane.

The residual contamination was measured with respect to a control coupon, over which no decontamination powder was added (100% value).

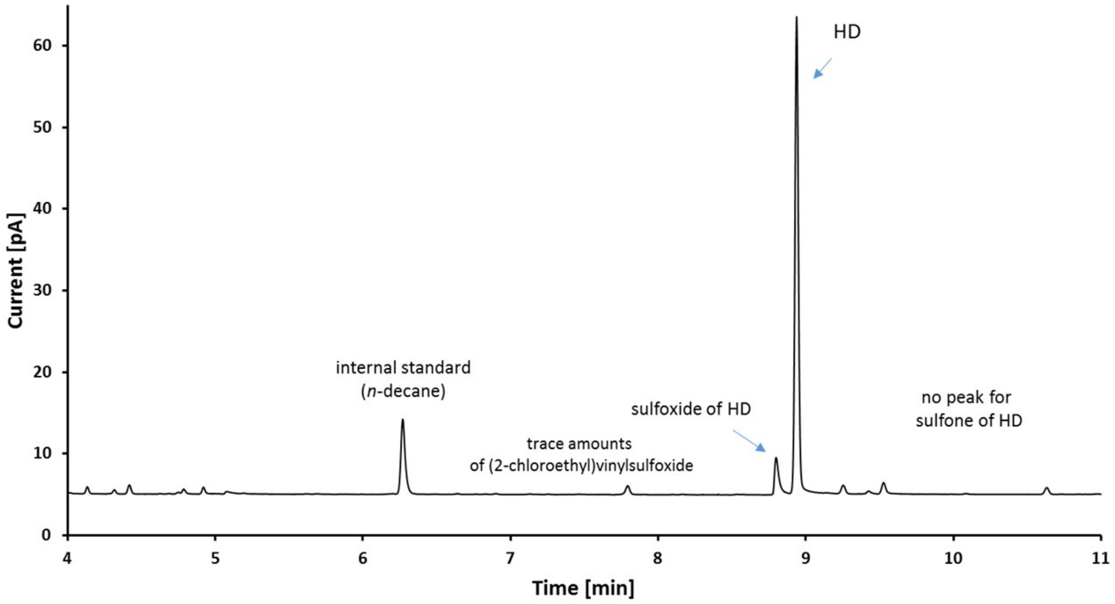


Figure S17. Chromatogram (GC-FID) of the residual contamination at the end (24 h) of the decontamination test of sulfur mustard, HD agent, in the presence of Fe-DECON1-PB over a PTFE coupon (4 cm^2). Extraction with CH_2Cl_2. Reaction conditions: 10 µL HD agent; 143 mg decontamination mixture; 120 µL H_2O; room temperature.

Figure S17 shows the chromatographic analysis of the residual species on the surface of the PTFE coupon at the end of the 24 h decontamination test, after being treated with Fe-DECON1-PB, as a decontamination powder. The residual HD peak corresponds to 20% ± 5% of the initial HD amount. No peaks of the over-oxidised compound (sulfone of HD agent) were present. The residual peak of the sulfoxide does not account for the 80% of the degraded HD, since most of the produced sulfoxide was strongly adsorbed into the Fe-DECON1 clay structure and therefore was not released nor extracted by dichloromethane.