A functionalized fabric as a self-decontaminating textile for trapping and degradation of organophosphorus nerve agent

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Supporting Information available

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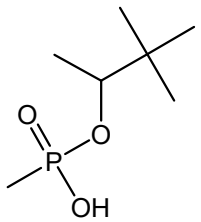
1. General

Scavenger **1** was prepared as previously described.[1]

The protocol used to determine the structure of the degradation product of soman by scavenger **1** was previously described.[2] 1D ^{1}H NMR experiments were performed on a Bruker Avance 600 instrument spectrometer equipped with a triple cryoprobe CPTCI (^{1}H, ^{31}P, ^{13}C). One dimensional ^{1}H NMR spectra was recorded at 25°C with water signal suppression (pre-saturation and excitation sculpting), during a total acquisition time of 1 min 30 sec (number of scans equal to 16 and a presaturation delay of 3 sec).



Pinacolic methylphosphonic acid (PMPA, usual name)

3,3-dimethylbutan-2-yl hydrogen methylphosphonate (IUPAC name), 616-52-4 CAS.

Structure of the degradation product of soman by scavenger 1

SEM-EDX analyses were performed on a Hitachi SU 5000 scanning microscope equipped with a FEG source, and the AZtec EDS/EBSD coupled system from Oxford Instruments (60 mm^2 SDD spectrometer and EBSD Symmetry camera).

XPS analyses were performed using an Omicron Argus X-ray photoelectron spectrometer, equipped with a monochromated AlKα radiation source (hν = 1486.6 eV) and a 280 W electron beam power. The emission of photoelectrons from the sample was analyzed at a photoelectron collection angle of 45 ° under ultra-high vacuum conditions (≤ 10−9 mBar). Spectra were carried out with a 100eV pass energy for the survey scan and 20 eV pass energy for core levels regions. Element peak intensities were corrected by Scofield factors. The peak areas were

[1] Kalakuntla RK, Wille T, Le Provost R, Letort S, Reiter G, Müller S, Thiermann H, Worek F, Gouhier G, Lafont O, Estour F. *Toxicol Lett.*, 2013, **216**, 200-205.

2 Letort S, Mathiron D, Grel T, Albaret C, Daulon S, Djedaini-Pilard F, Gouhier G, Estour F. *Chem. Commun.*, 2015**, 51**, 2601-2604.

determined after subtraction of a linear background. The spectra were fitted using Casa XPS software (Casa Software Ltd, U.K.) and applying a gaussian/lorentzian ratio g/l equal to 70/30 for deconvolution.

UV spectra were recorded on a Varian's CARY© 50 UV–vis spectrophotometer.

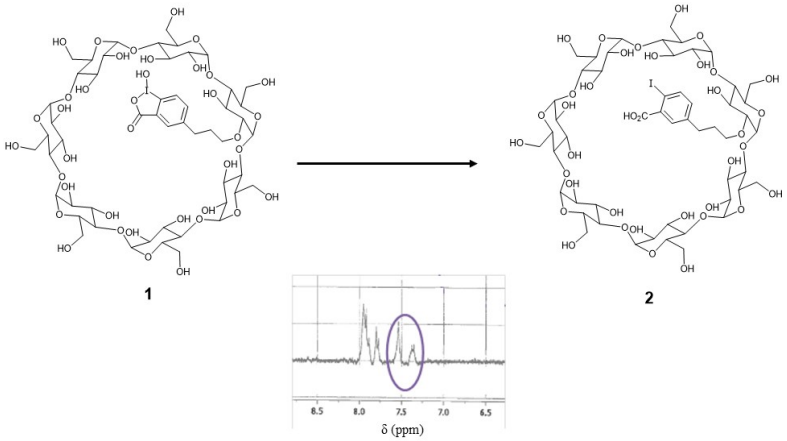
The analyses by gas chromatography were performed under the following conditions:

Injector	Splitless, 250°C, Helium as carrier gas
Column	VF-5ms (5% diphenylpolysiloxane, 95% dimethylpolysiloxane) Diameter: 0.25mm Carrier gas flow: 1.3 $mL.min^{-1}$ Temperature: 50 to 120°C ($10°C.min^{-1}$), 120 to 250°C ($15°C.min^{-1}$), 3 min step
Sensor	FPD, 280°C

2. Degradation of compound 1 by heating

- First assay: dry-heating by using a bath oil,
- Second assay: heating in aqueous solution in the presence of the reagents used for immobilization.

In the first assay, we detected by ^{1}H NMR the formation of a cyclodextrin derivative **2**:



We recovered scavenger **1** and its degradation product as a mixture at the end of the experiment. A test on methyl paraoxon (pesticide used as a model organophosphorus substrate, see task 4.3) allowed to evaluate the loss of activity of the compound **1** (see table below) in correlation with the amount of the degradation product estimated by ^{1}H NMR.

Temperature	*90°C* [a]	*110°C* [b]	*120°C* [b]	*130°C* [b]
*% of compound **1** degradation*	7%	30%	36%	47%
Loss of activity	< 10%	10%	10%	45%

[a] heating for 5 min [b] heating for 10 min

In the second assay, we only estimated the amount of the degradation product **1**:

Temperature	90°C	110°C	130°C
*% of compound **1** degradation*	— [a]	5% [a]	8% [a]
	10%[b]	10%[b]	10%[b]
	15%[c]	15%[c]	15%[c]

heating time: [a] 10 min; [b] 20 min; [c] 30 min

3. Experimental procedures for the treatment surface of textile

3.1 General approach for the padding process

The process (see figure below) consists in impregnating the textile in a bath that contains a solution of compound **1** and the crosslinking agent, followed by a padding step at a fixed pressure. The sample is then dried in an oven at high temperature.

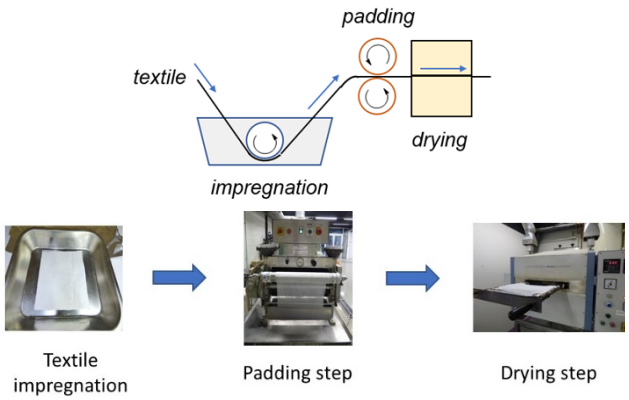


Illustration of the main steps for immobilization of CD derivatives

3.2 Immobilization assays of β-cyclodextrin

*Preparation of Solutions **I** – **IV***:

• Solution **I**: β-cyclodextrin (1.5g, 1,32 mmol) was added in 26.5 mL of distilled water, and the resulting suspension was heated to 50°C under stirring during 10 min. 1,2,3,4-butane-tetracarboxylic acid (1.5g, 6,41 mmol) was then added to the solution under stirring, followed by the addition to the mixture of sodium hypophosphite (0.45g, 5.06 mmol).

• Solution **II**: β-cyclodextrin (1.5g, 1.32 mmol) was added in 25.8 mL of distilled water, and the resulting suspension was heated to 50°C under stirring during 10 min. 1,2,3,4-butanetetracarboxylic acid (1.5g, 6.41 mmol) was then added to the solution under stirring, followed by the successive additions to the mixture of succinic acid (0.75g, 6,35 mmol) and sodium hypophosphite (0.45g, 5.06 mmol).

• Solution **III**: β-cyclodextrin (1.5g, 1.32 mmol) was added in 25.8 mL of distilled water, and the resulting suspension was heated to 50°C under stirring during 10 min. 1,2,3,4-butanetetracarboxylic acid (1.5g, 6.41 mmol) was then added to the solution under stirring, followed by the successive additions to the mixture of citric acid (0.75g, 3.90 mmol) and sodium hypophosphite (0.45g, 5.06 mmol).

• Solution **IV**: β-cyclodextrin (2.4g, 2.11 mmol) was added in 24.0 mL of distilled water, and the resulting suspension was heated to 50°C under stirring during 10 min. Cyanamide (1.5g, 35.68 mmol) was then added to the solution under stirring, followed by the successive additions to the mixture of 1,2,3,4-butanetetracarboxylic acid (1.8g, 7.69 mmol) and ammonium hydrogenophosphate (0.3g, 2.61 mmol).

Immobilization step: The cotton sample (30 x 210 cm) was immersed in 30 mL of solution **I**, **II**, **III** or **IV** during 2 min under stirring. The sample was then placed into an aluminum foil.

- For samples immersed in solutions **I**, **II**, or **III**: after fulling at a pressure of 1.5 bar and a rate of 1 $m \cdot min^{-1}$ during 1 min at room temperature, the impregnated fabric was pre-dried for 5 min at 90°C. Fixation was carried out at 160°C for 5 minutes.
- For samples immersed in solutions **IV**: after fulling at a pressure of 1.5 bar and a rate of 1 $m \cdot min^{-1}$ during 1 min at room temperature, the impregnated fabric was pre-dried for 30 min at 80°C. Fixation was carried out at 120°C for 10 minutes.

Rinsing step: The fabric was rinsed twice by soaking in 200 mL of a solution prepared by addition of 1g of NaOH and 3.4 g of $NaHCO_3$ in 2 L of distilled water. The rates of immobilization (based on the mass gain) are shown in the table below.

Solution used for soaking sample	**Immobilization rate (%)**
Solution **I**	9.6
Solution **II**	12.9
Solution **III**	11.7
Solution **IV**	8.2

3.3 General procedure for immobilization of compound 1

*Preparation of Solution **V***: Compound **1** (3.0g, 2.08 mmol) was added in 23.4 mL of distilled water, and the resulting suspension was heated to 50°C under stirring during 30 min. Cyanamide (1.5g, 35.68 mmol) was then added to the solution under stirring, followed by the successive additions to the mixture of 1,2,3,4-butanetetracarboxylic acid (1.8g, 7.69 mmol) and ammonium hydrogenophosphate (0.3g, 2.61 mmol).

Immobilization step: The cotton sample (15 x 15 cm) was immersed in 30 mL of solution **V** during 2 min under stirring. The sample was then placed into an aluminum foil. After fulling at a pressure of 1.5 bar and a rate of 1 $m \cdot min^{-1}$ during 1 min at room

temperature, the impregnated fabric was pre-dried for 30 minutes at 80°C. Fixation was carried out at 120°C for 10 min.

Rinsing step: The fabric was rinsed by soaking in 200 mL of 20 mM phosphate buffer solution at pH 7.65 for 15 min at room temperature without stirring. The rate of immobilization deposited after rinsing was estimated to be 6.7g·m^{-2} by determining the mass gain of the fabric sample.

4. Characterization of the textile functionalized by compound 1

4.1 SEM-EDX analyses

Three samples **A**, **B** and **C** were analysed by scanning electron microscopy (SEM) combined with energy-dispersive X-ray (EDX) microanalysis.

- Sample **A**: textile unrinsed after the padding step
- Sample **B**: textile rinsed after the padding step
- Sample **C**: textile rinsed after the padding step and rub-aged according to the Crokmeter manual test (Standard EN NF ISO 105-X12:2016, see figure below). The device was equipped with a 16 mm-diameter pin that moves back and forth straight along a length of 104 mm with a downward force of 9N. 250 moves were performed on the sample.

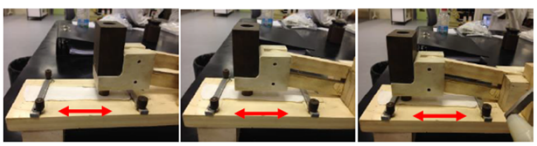
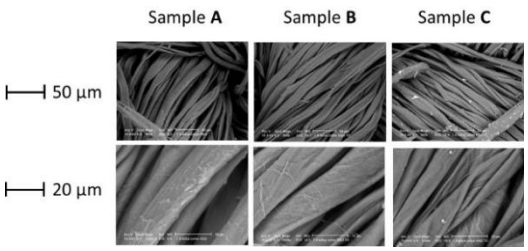


Illustration of back and forth movements for the rub-aged test

The SEM Images of the textile samples **A** (textile unrinsed after the padding step), **B** (textile rinsed) and **C** (textile rinsed and rub-aged) were shown below.



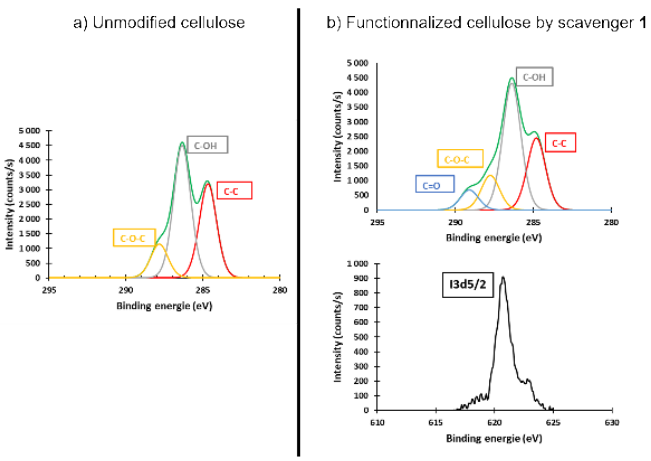
*SEM Images of the textile samples **A**, **B** and **C***

The results were compared to an untreated textile as a reference and the % of iodine was measured in each sample to highlight the presence of scavenger **1** in samples **A**, **B** and **C**.

Sample	% of iodine
Cotton reference	-
Sample **A**	1.22
Sample **B**	0.92
Sample **C**	0.88

4.2 XPS analyses

In the C1s spectrum (Figure a) below), we observe the characteristic peaks of native cellulose. Indeed, the contribution from carbon atoms can be deconvoluted into three components: C-C contributions at 284.7 eV, C-OH contributions at 286.3 eV and C-O-C contributions at 287.8 eV. The ratio between each contribution is 2.8:3.9:1 which is quite different with the theory (1:4:1). This can be explained by different treatments of cellulosic textile. Those 3 peaks are still present for the cellulose functionalized with scavenger **1** but another peak appears at 289.1 eV which is attributed to the contribution of C=O (Figure b) below). Secondly, in I3d5/2 spectrum (Figure b) below), a peak at 621 eV is detected when nothing appeared for the native cellulose proving the presence of scavenger **1** which is also confirmed by the apparition of the C=O contribution in the C1s spectrum.



Calculation from XPS measurements

Determination of the number of scavengers per unit of cellulose

The first hypothesis is that each primary OH of the cellulose has reacted with scavenger 1. This means that for each unit of cellulose, we have :

1 iodine

23 OH (21 from scavenger 1 + 2 from cellulose unit)

Then, the theoretical ratio of I/OH is 0.043 for 100 % of modified cellulose unit.

Experimentally, we obtained 0.6 % of iodine and 33.1 % of C-OH (= 0.5x66.2 %). So, the ratio of I/OH is 0.018. This result means that we modified 42 % of the cellulose units. In other words, there is 1 grafted scavenger for 2.4 cellulose units.

Determination of the percentage of remaining BTCA

Theoretically, the percentage of C=O should be the same as iodine, that is to say 0.6 %. Indeed, there is also 1 C=O per scavenger 1. However, we obtained 5.2 % (= 0.079 x 66.2) of C=O, which means that there is an excess of C=O. This excess can be due to remaining BTCA by physical adsorption. If we consider that BTCA bears 4 carboxylic acids (so 4 C=O), we can determine the remaining BTCA:

(% C=O - % I)/4 = (5.2 - 0.6) / 4 = 1.15 % of remaining BTCA.

4.3 Evaluation of the average amount of scavenger 1 immobilized on textile

Immobilization of scavenger **1** on textile was performed using the protocol described in section 2.2. The functionalized textile was then cut in samples of 5 x 5 cm. 2 samples of a size of 5 x 5 cm were assembled and sewn. Three different assemblies were prepared, one of them is composed of untreated textile and used as reference, the two others were obtained with treated textile as described in section 2.2.

*Preparation of solutions **VI** and **VII**:*

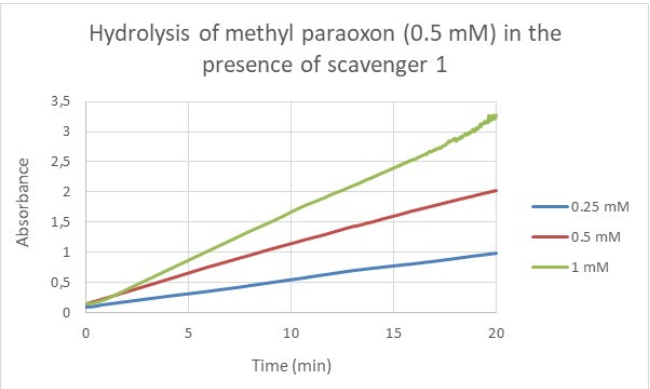
• Solution **VI**: 13 mM cetyltrimethylammonium chloride solution was obtained by dissolving 416 mg of the product in 97 mL of 20 mM phosphate buffer and 3 mL of dimethyl sulfoxide.

• Solution **VII**: A 16.67 mM methyl-paraoxon solution was obtained by dissolving 41.2mg of the product in 10 mL of anhydrous methanol. This solution was stored in a sealed vial at 0°C.

*Hydrolysis assays of methyl paraoxon in the presence of scavenger **1***

Stock solution of scavenger **1** was prepared in solution **VI**.

Kinetic assays were carried out with methyl paraoxon (0.5 mM) at 25 °C, in solution **VI**. The final concentration of methanol in the assay was 3 % v/v and that of DMSO was 2.9 % v/v. The final concentrations of scavenger **1** were 0.25 mM, 0.5 mM or 1 mM. The hydrolysis of methyl-paraoxon was monitored up to 20 min by following the release of the leaving group *para*-nitrophenol (at λ = 400 nm). From the measured absorbance, the absorbance due to spontaneous hydrolysis of methyl-paraoxon was subtracted. The spontaneous hydrolysis of methyl-paraoxon was measured under the same conditions and in the absence of scavenger **1**.



Hydrolysis assays of methyl paraoxon in the presence of assemblies

The fabric assembly was immersed in 16.2 mL of solution **VI**. The pH was adjusted between 7.35 and 7.65 by adding sodium hydrogen phosphate. The solution is maintained at a fixed temperature of 25°C. 500 µL of solution **VII** was then added and the mixture was stirred with a glass rod for 5 s. The absorbance of the solution is measured at 400 nm at regular 4-minute intervals over a maximum of 20 min (see figure below).

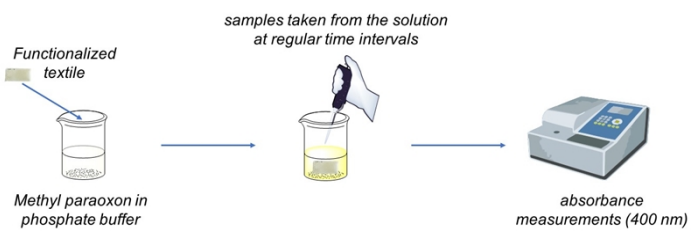
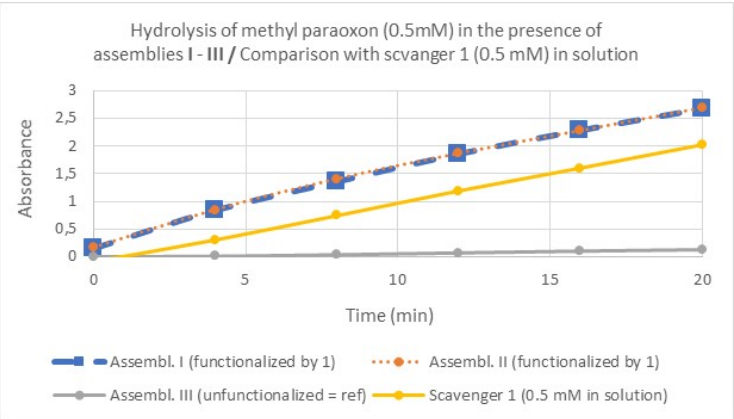


Illustration of the analysis methodology

Spontaneous hydrolysis of methyl-paraoxon was evaluated under the same conditions with unfunctionalized assembly **III**. The absorbance values obtained were deducted from the measurements to determine the actual efficiency of the functionalized assemblies **I** and **II**.



*Evaluation of the average amount of scavenger **1** on textile*

Three calibration curves were obtained at t_0 + 4 min, t_0 + 8 min and t_0 + 12 min by logarithmic regression of the absorbance values measured in kinetic experiments with scavenger **1** in solution.

t_0 + 4 min: *absorbance* = 0.3095 ln *([scavenger **1**]) + 0.7315* (R^2 = 0.9707)

t_0 + 8 min: *absorbance* = 0.648 ln *([scavenger **1**]) + 1.374* (R^2 = 0.994)

t_0 + 12 min: *absorbance* = 0.946 ln *([scavenger **1**]) + 1.9732* (R^2= 0.9991)

By using the absorbances values determined when kinetic experiments were carried out in the presence of the assemblies **I** and **II**, the concentration of scavenger **1** could be calculated from the previous regressions at fixed time intervals. The obtained values correspond to the concentration of scavenger **1** (provided by assemblies **I** and **II**) if the kinetic experiments were carried out with scavenger **1** in solution.

That leads to an average concentration of scavenger **1** of 1.1 10^{-3} mol. L^{-1}, i.e. 26.4 mg (18.4 10^{-6} mol.) of scavenger **1** immobilized in the assemblies I and II. Each assembly correspond to 2 textile samples 5 x 5 cm (50 cm^2). The average amount of scavenger **1** immobilized on assemblies I and II is then around 5.3g.m^{-2}.

5. Preparation and evaluation of sponges' efficiency

Immobilization of scavenger **1** or β-cyclodextrin on textile was performed using the protocol described for scavenger **1** in section 2.2 with cotton samples of 21 x 29.7 cm (A4). The functionalized textile was then cut in samples of 5 x 9 cm.

2 samples of a size of 5 x 9 cm were assembled and sewn. Three kind of assemblies were prepared:

- 10 sponges were prepared with textile functionalized by scavenger **1** (sponges **D**),
- 10 sponges were prepared with textile functionalized by β-CD (sponges **E**),
- 10 sponges were prepared with unfunctionalized textile (sponges **F**).

5.1 Decontamination tests

Soman is highly toxic and must be handled with extreme care and by trained personnel. The tests below were performed in an accredited center in which staff are compulsorily trained in the handling of neurotoxic agents.

Contamination protocol:

8 plates in stainless-steel of 5x5 cm size are contaminated at a rate of 5 $g \cdot m^{-2}$ by depositing 25 drops of 0.5 µL of soman.

Three of them were extracted for 90 minutes in 175 mL weighing bottles containing 25 mL of ethyl acetate. A 1 mL sample of the organic solution was then analyzed by gas chromatography to determine the initial contamination level at 403.8 ± 17.3 $\mu g \cdot cm^{-2}$.

The remaining five stainless steel specimens are placed in front of five uncontaminated specimens. These will be used to determine the transfer of contamination from contaminated plates to uncontaminated ones when using the sponges.

Decontamination protocol:

A sponge (5x9 cm), attached with aluminum adhesive to a 500 g metal mass, is applied for 1 to 2 s to the contaminated sample and then moved to be applied to the uncontaminated sample for 1 to 2 s. The same process is continued until all samples were completely wiped by the same sponge. As soon as the sponge application is complete, the plates in stainless-steel are put into 175 mL weighing bottles containing 25 mL ethyl acetate for 90 min (see figure below). After extraction, an aliquot was collected from each sample and analyzed by GC.

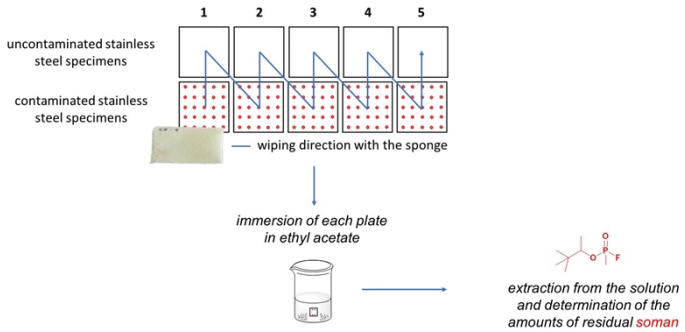


Illustration of the decontamination protocol

5 *Measurement of residual contamination on stainless steel plates previously contaminated by soman:*

The results were obtained with the are summarized in the table below.

Sample	**% decontamination of stainless-steel plates**	**Average % decontamination**
Sponges **D**	96.8	98.1 ± 1.0
	97.8	
	97.8	
	98. 7	
	99.3	
Sponges **E**	94.9	91.2 ± 3.2
	92.7	
	86.3	
	91.7	
	90.5	
Sponges **F**	91.8	95.0 ± 2.0
	94.7	
	95.7	
	95.6	
	97.3	

Measurement of contamination transfers on uncontaminated stainless-steel plates:

The results are summarized in the table below.

Sample	Extracted amounts of soman (µg·cm^{-2}) from stainless-steel plates	Average % decontamination
Sponges **D**	2.26	2.06 ± 1.15
	0.23	
	3.24	
	2.80	
	2.69	
Sponges **E**	1.33	0.91 ± 0.53
	0.46	
	0.26	
	1.10	
	1.42	
Sponges **F**	< 0.12	0.16 ± 0.08
	< 0.12	
	0.31	
	< 0.12	
	< 0.12	

5.2 Degradation kinetics of soman

Two degradation kinetics were carried out:

- the first kinetic was performed with sponges **D**, **E** or **F** having decontaminated a single 5 x 5 cm plate in stainless-steel,
- the second kinetic was performed with an assembly (**D**, **E** or **F**) having successively decontaminated five 5 x 5 cm plates in stainless-steel.

The following protocol was then implemented in both cases. After wiping contaminated plates in stainless-steel, the sponge was immersed in 20 mL of phosphate buffer (0.1 M, pH 7.4) contained in a 175 mL weighing bottle. At t = 15 min, 1 h, 3 h and 6 h, the weighing bottle was manually shaken to homogenize the buffer and 500 µL was taken, neutralized with 0.5 mL citrate buffer (0.2 M, pH 5.5) and extracted with 3 mL ethyl acetate into a 15 mL centrifuge tube. The tube was centrifuged for 1 min at 4000 rpm and an aliquot of the organic layer was taken for GC analysis.

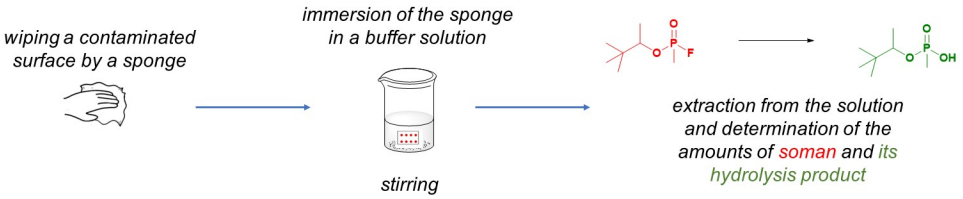


*Illustration of the protocol used for the kinetic of the degradation of soman by sponges **D** to **F***

At t = 24 h, the medium was neutralized by adding 18 mL of 0.2 M citrate buffer pH 5.5. The sponge was drained, extracted with 25 mL ethyl acetate for 90 min and then a sample of the organic phase is taken for GC analysis. The neutralized medium was homogenized and then 1 mL is taken and extracted with 3 mL of ethyl acetate into a 15 mL centrifuge tube. The tube was centrifuged for 1 min at 4000 rpm and an aliquot of the organic layer was taken for GC analysis.

The measured amounts had to be corrected by an extraction coefficient, determined according to the following protocol. A stainless-steel plate was contaminated with 25 drops of 0.5 µL of soman and then immersed in a 175 mL weighing bottle containing 20 mL of phosphate buffer (0.1 M, pH 7.4) and 20 mL of citrate buffer (0.2 M, pH 5.5). The medium was thoroughly homogenized using a 10 mL pipette. 1 mL of the mixture is taken and extracted with 3 mL of ethyl acetate into a 15 mL centrifuge tube. The tube was centrifuged for 1 min at 4000 rpm and an aliquot of the phase was taken for GC analysis.

*Kinetic with sponges **D**, **E** or **F** having decontaminated a single stainless-steel plate:*

25 cm^2 stainless-steel plates were previously contaminated with 25 drops of 0.5 µL soman. The residual contamination on these plates was measured, and the value was used to deduce the contamination absorbed by the sponges.

The results are summarized in the table below.

	*Residual soman (%) – Sponge **D***			*Residual soman (%) – Sponge **E***			*Residual soman (%) – Sponge **F***		
Time (h)	*In buffer*	*In sponge*	*Total*	*In buffer*	*In sponge*	*Total*	*In buffer*	*In sponge*	*Total*
1/4	44.9	–	–	63.7	–	–	76.0	–	–
1	14.2	–	–	46.3	–	–	49.1	–	–
3	0.17	–	–	19.5	–	–	15.5	–	–
6	< 0.13	–	–	8.3	–	–	2.8	–	–
24	< 0.13	< 0.03	< 0.16	0.32	0.62	0.95	< 0.13	< 0.03	< 0.16

*Kinetic with sponges **D**, **E** or **F** having decontaminated 5 stainless-steel plates:*

Each 25 cm^2 stainless-steel plates was previously contaminated with 25 drops of 0.5 µL soman. The residual contamination on these plates was measured, and the value was used to deduce the contamination absorbed by the sponges.

The results are summarized in the table below.

	*Residual soman (%) – Sponge **D***			*Residual soman (%) – Sponge **E***			*Residual soman (%) – Sponge **F***		
Time (h)	*In buffer*	*In sponge*	*Total*	*In buffer*	*In sponge*	*Total*	*In buffer*	*In sponge*	*Total*
1/4	81.7	–	–	81.7	–	–	74.9	–	–
1	50.5	–	–	63.9	–	–	61.7	–	–
3	13.5	–	–	29.8	–	–	23.7	–	–
6	2.5	–	–	13.4	–	–	6.7	–	–
24	< 0.03	< 0.01	< 0.03	0.70	0.78	1.48	< 0.03	< 0.01	< 0.03