

Supporting information

Soft and effective detoxification of a VX simulant in a 3D printed basic flow reactor

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General information

All reagent was purchased from Sigma Aldrich and used as provided; solvents were purchased from VWR and used without further purification. All fluidic tubing, connections, adapters were manufactured by IDEX Health and Science. Syringe pumps were manufactured by Harvard apparatus (Pump 11 Elite and PHD/ULTRA) with Air Tite plastic syringe.

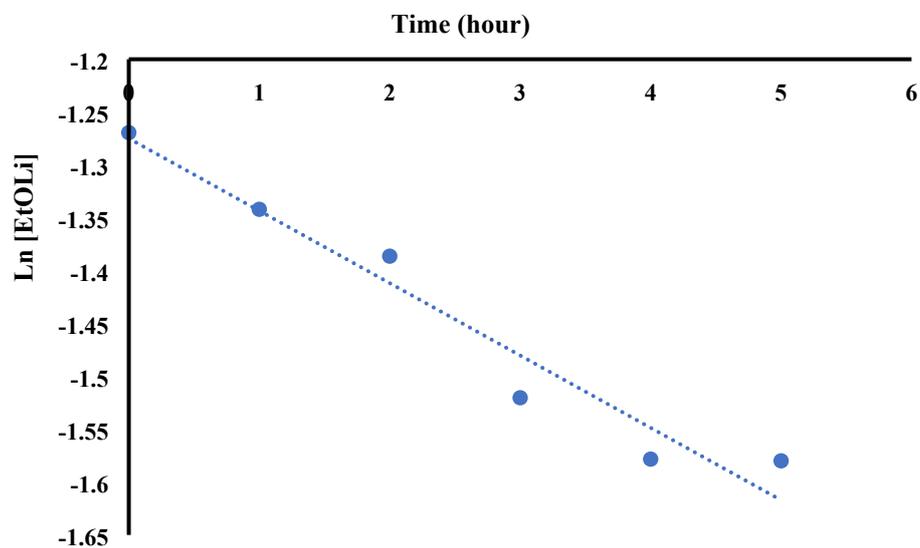
High field ^1H , ^{31}P and ^{13}C NMR studies were performed on a 300 MHz Bruker Spectrospin spectrometer. Chemical shifts (δ) are given with regard to TMS using solvent as internal reference, J coupling constants are given in Hertz.

All reactions were conducted at room temperature (23 °C) except if noted otherwise, with no particular precautions with regard to residual moisture and air. However due to the acute toxicity of CWA simulants, reactions were carried out under closed atmosphere in a very well-ventilated fume hood. All glassware and materials in contact of simulants were immersed in a bleach bath under the fume hood for one day before further washing and/or disposal.

Stability of EtOLi over time

Table 1 EtOLi measured concentration at different times

Time (h)	[EtOLi]				Ln [EtOLi]
	Run 1	Run 2	Run 3	Average	
0	0.247	0.298	0.298	0.281	-1.2694
1	0.278	0.247	0.259	0.261333	-1.342
2	0.25	0.247	0.253	0.25	-1.3863
3	0.228	0.217	0.211	0.218667	-1.5202
4	0.201	0.211	0.207	0.206333	-1.5783
5	0.208	0.204	0.206	0.206	-1.5799



Direct flow neutralisation of PhX with a basic solution of EtOLi

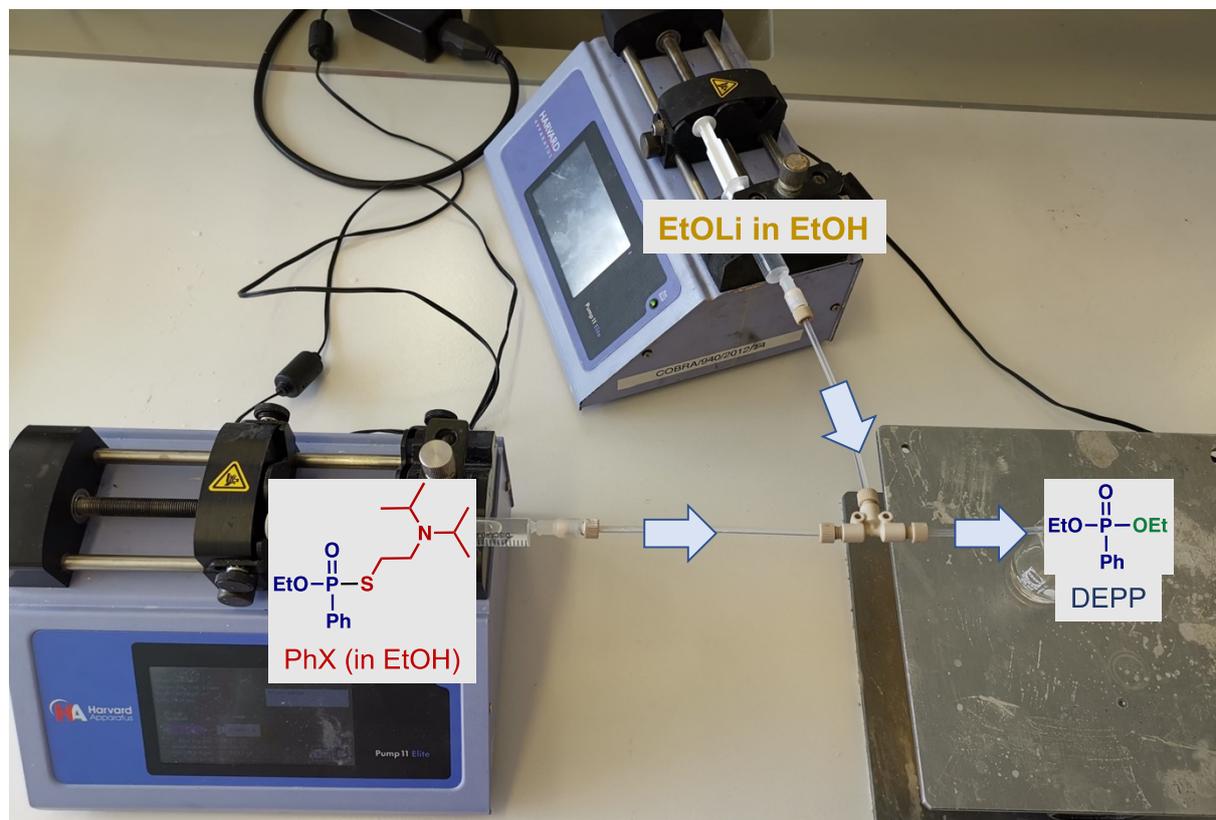


Fig. 1 Flow neutralization of PhX

Table 2. Corresponding flow rates for different reaction times

Time of reaction (min)	Flow rates ($\mu\text{L}/\text{min}$)
0	-
2.5	80
5	40
7.5	26.7
10	20
12.5	16
15	13.3
17	11.8

3D printing of the flow reactor device

The flow reactor device was printed by an extrusion-based 3D printer Stream 30 Ultra Volumic®, the used polymer is a commercially available Nylon 645 Taulman® with a diameter of 1.75 mm. A 0.25 mm extruder nozzle was used to print a built layer with a low thickness between 60 and 200 microns which allows to generate near net shaped parts and precision of impression near to 1 micron. The printing device allows us as well to configure different process parameters in order to optimize the fabrication output which depends on the size, the geometries and the type of the materials, such as the build plate temperature to prevent the warping issue, the nozzle temperature, layer height and the deposition patterns.

The main challenge when working a high melting temperature material as nylon is the warping effect that is caused by the pulling of the extruded polymer and the already cooled deposited polymer due to the temperature differences. In order to prevent the warping issue, we control the bed temperature and we use glue stick to ensure the Nylon filament is bonded to the build bed. The selected conditions were a layer height of 100 microns, the bed temperature was fixed at 50 °C and the extruder temperature at 255 °C.



Fig. 2 3D printed microreactor

CAD of the Flow reactor

The CAD of the flow reactor was done by SOLIDWORKS software. The geometry of the reactor was adjusted to avoid the collapse of the internal walls and the clogging of the flow device due to the treatment with HCl 5N, and surface modification according to Sans.¹

The microreactor is designed as 2 × 2 cm (length × diameter) cylinders, which contain 38 channels with a diameter of 1.5 mm with a total volume $V = 1.34$ mL (Fig 3a). An upper hollow part ($V = 0.64$ mL) was also designed to act as a spacer, in order to pack several reactors together in a cylindrical device.

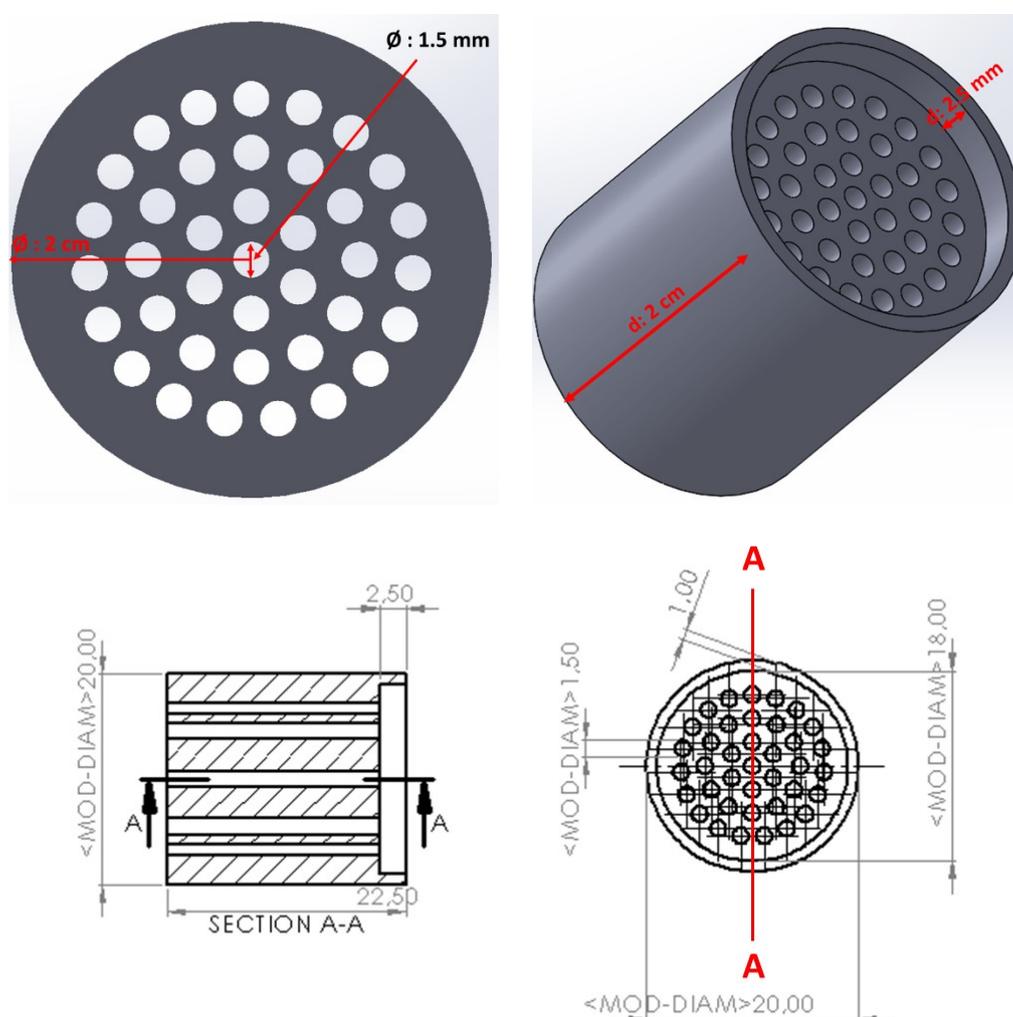
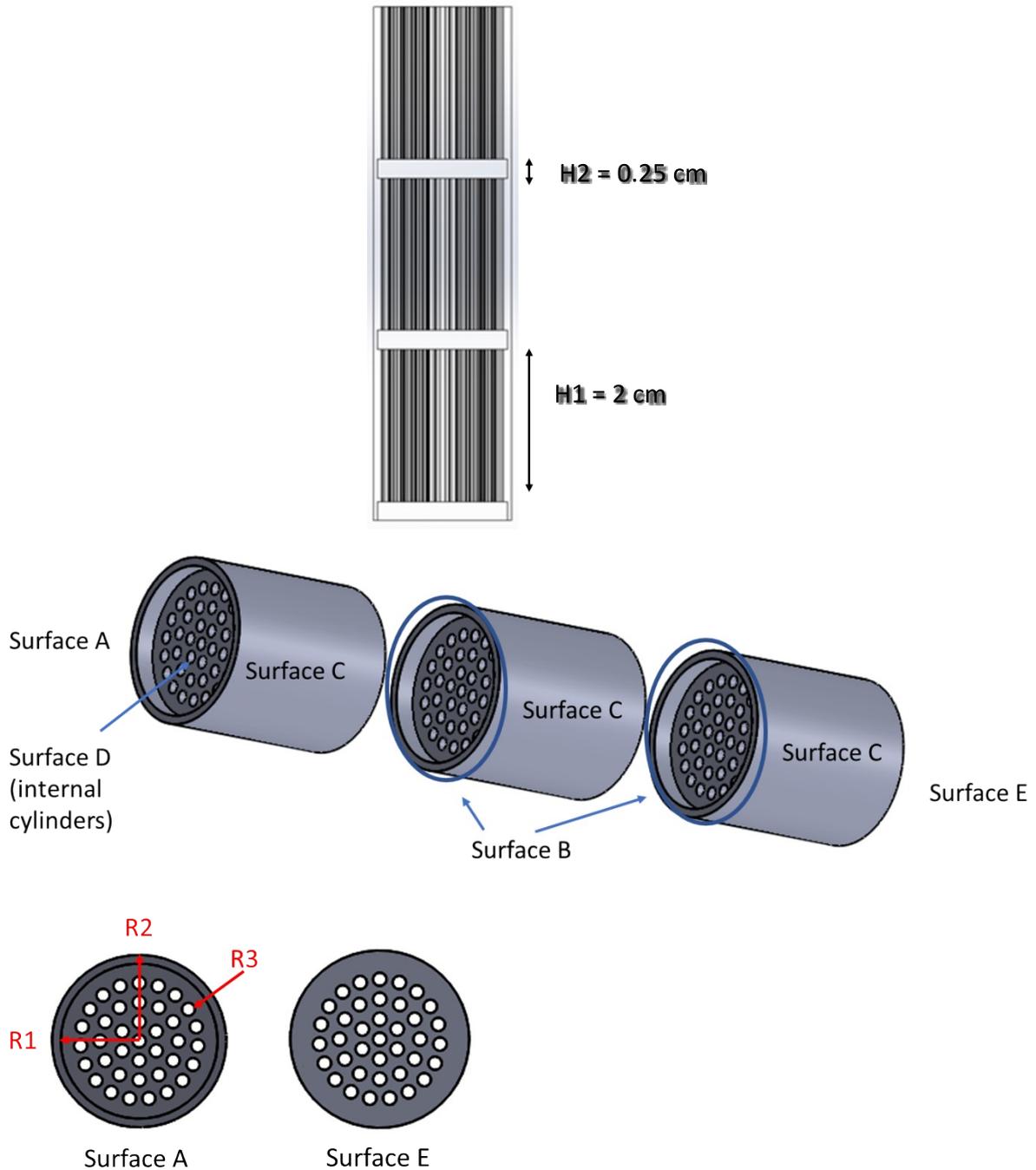


Fig. 3 CAD of the flow microreactor

¹ E. Peris, O. Okafor, E. Kulcinskaja, R. Goodridge, S. V. Luis, E. Garcia-Verdugo, E. O'Reilly and V. Sans, *Green Chem.*, 2017, **19**, 5345–5349.



Nylon surface area of the 3 packed reactors =

Surface area A + 2 × Surface area B + 3 × Surface area C + 3 × Surface area D (internal surface of the inside cylinders) + surface Area E = 166.55 cm²

$$\text{Surface area A: } (\pi R_2^2 - \pi R_1^2) + (\pi R_1^2 - 38 \times \pi R_3^2) + (2 \times \pi \times R_1 \times H_2) = 3.89 \text{ cm}^2$$

$$\text{Surface area B: } 2 \times (\pi R_1^2 - 38 \times \pi R_3^2) + (2 \times \pi \times R_1 \times H_2) = 5.17 \text{ cm}^2$$

$$\text{Surface area C: } 2 \times \pi \times R_2 \times (H_1 + H_2) = 14.14 \text{ cm}^2$$

$$\text{Surface area D: } 38 \times (2 \times \pi \times R_3 \times H_1) = 35.81 \text{ cm}^2$$

$$\text{Surface area E: } \pi R_2^2 - 38 \times \pi R_3^2 = 2.47 \text{ cm}^2$$

S-2-(diisopropylamino)ethyl O-ethyl phenylphosphonothioate (PhX)

Obtained from ethyl phenylphosphinate and diisopropylethanolamine as a viscous, slightly yellow oil according to the literature.²

¹H NMR (300 MHz, CDCl₃) δ = 7.92 - 7.81 (m, 2H), 7.56-7.40 (m, 3H), 4.23 – 32.89 (m, 2H), 2.93 (sept, *J*=6.6, 2H), 2.75 – 2.59 (m, 2H), 2.57 – 2.45 (m, 2H), 1.37 (t, *J*=7.1, 3H), 0.91 (dd, *J*=6.6, 1.4, 12 H)

¹³C {¹H} NMR (75 MHz, CDCl₃) δ **133.7 (d, *J* = 148.8)** **132.06 (d, *J* = 3.2)**, **130.89 (d, *J* = 10.8)**, **128.15 (d, *J* = 14.7)**, **61.67 (d, *J* = 6.8)**, **48.47 (s)**, **45.86 (d, *J* = 4.7)**, **30.98 (d, *J* = 2.1)**, **20.51 (t, *J* = 6.1)**, **16.08 (d, *J* = 6.7)**.

³¹P NMR (121 MHz, CDCl₃) δ = 45.4 (m)

HRMS calc *m/z*: 330.1657 Da ([M+H]⁺), found 330.1657 (0.0 ppm)

Diethyl phenylphosphonate DEPP

Obtained from the neutralization of PhX with EtOLi, viscous colorless liquid.

¹H NMR (300 MHz, CDCl₃) δ 7.94 – 7.63 (m, 2H), 7.53 – 7.10 (m, 3H), 4.21 – 3.80 (m, 4H), 1.23 (t, *J* = 7.1, 6H)

¹³C {¹H} NMR (75 MHz, CDCl₃) δ 132.14 (d, *J* = 2.6), 131.44 (d, *J* = 9.9), 128.21 (d, *J* = 15.0), 128.04 (d, *J* = 10.8), 61.83 (d, *J* = 5.4 Hz), 16.02 (d, *J* = 6.4).

³¹P NMR (121 MHz, CDCl₃) δ = 19.8 (m)

HRMS calc *m/z*: 215.0837 Da ([M+H]⁺), found 215.0833 (1.8 ppm)

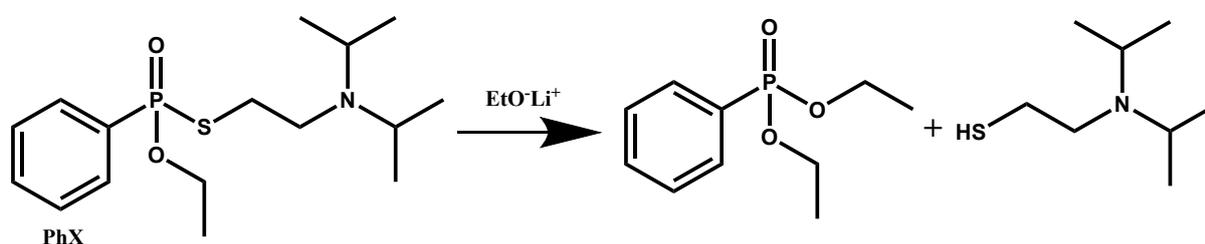


Fig. 4 Schema for the neutralisation of PhX with EtOLi

² P.-Y. Renard, H. Schwebel, P. Vayron, L. Josien, A. Valleix and C. Mioskowski, *Chem. – Eur. J.*, 2002, **8**, 2910–2916.

High field NMR Spectra

