Electronic supplementary material

Composite microbeads of cellulose acetate upcycled from waste for water remediation

Lorenzo Antonelli[1], Susanna Grasso[1], Massimo Giuseppe De Cesaris[1], Nina Felli[1], Chiara Dal Bosco[1], Stefano Cinti[2,*], Alessandra Gentili[1,*]

[1] *Department of Chemistry, Sapienza University, P.le Aldo Moro 5, 00185, Rome, Italy*

[2] *Department of Pharmacy, University of Naples Federico II, Naples, Italy*

* Corresponding authors:

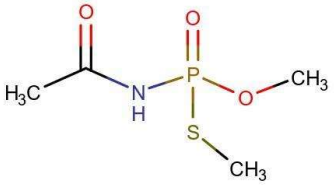
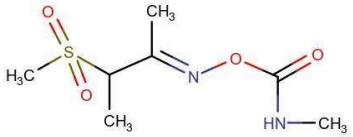
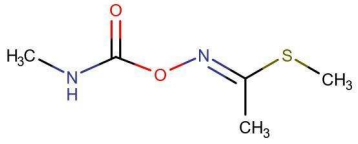
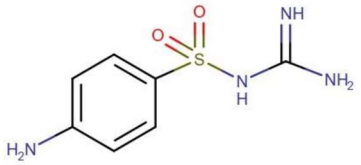
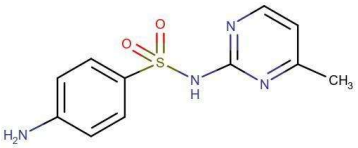
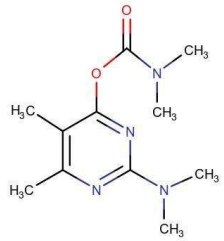
Prof. Alessandra Gentili

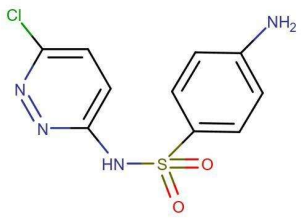
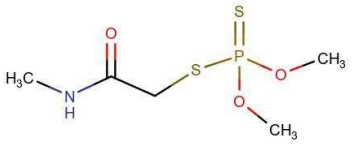
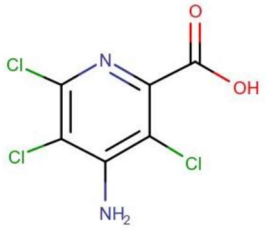
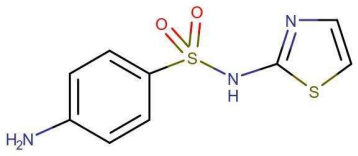
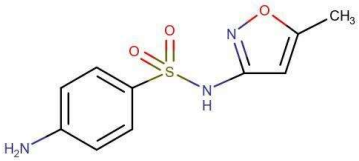
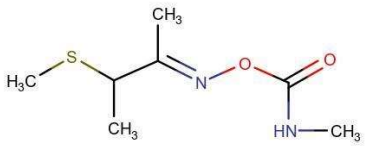
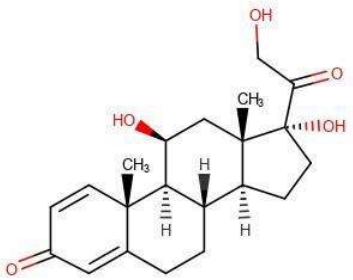
alessandra.gentili@uniroma1.it

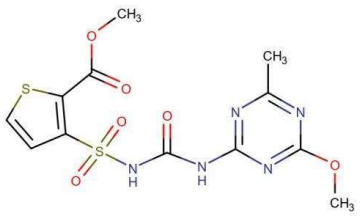
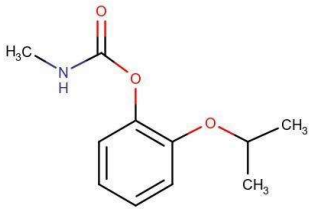
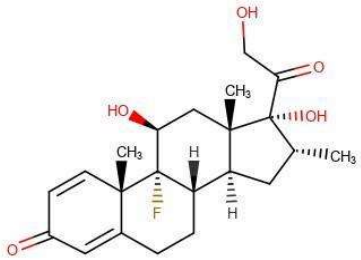
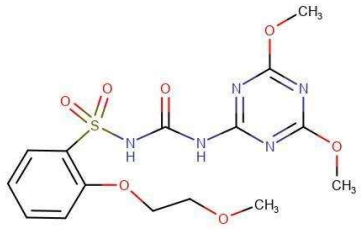
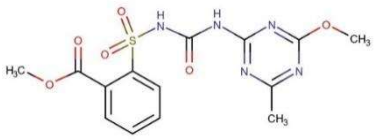
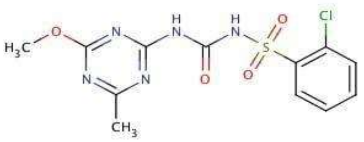
Prof. Stefano Cinti

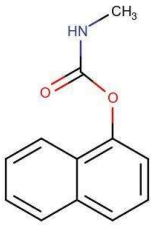
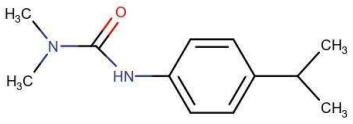
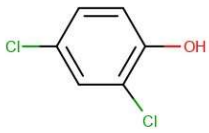
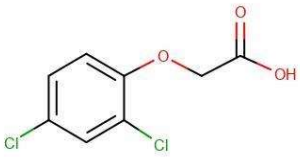
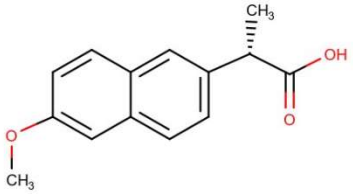
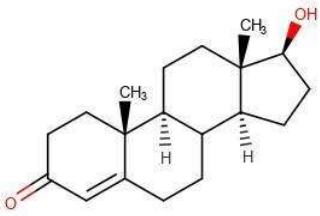
stefano.cinti@unina.it

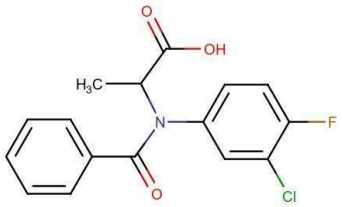
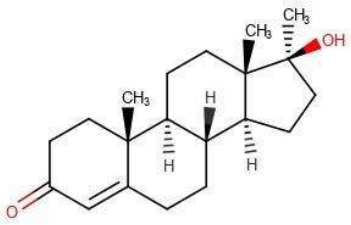
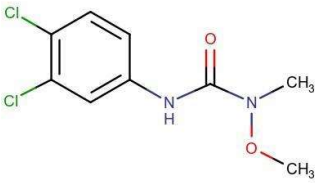
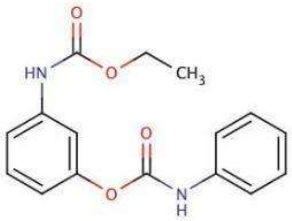
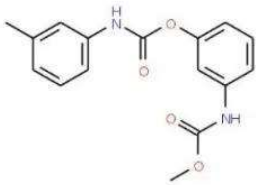
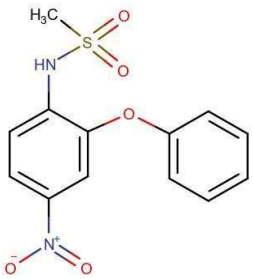
Table S1 Physicochemical properties, structure and classification of the studied analytes

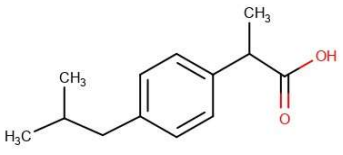
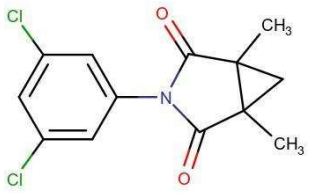
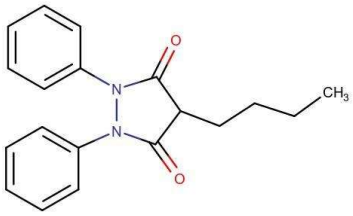
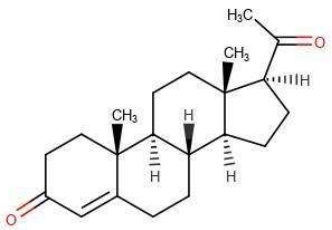
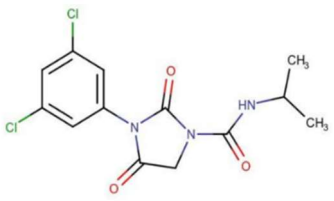
Chemical class	Analyte	logP[a,b]	pKa[a, b]	CAS number[a]	Molecular weight (g/mol)[a,b]	Structure
Insecticide	Acephate	-0.85	8.35	30560-19-1	183.2	
Herbicides	Butoxycarboxim	1.1	3.83	34681-23-7	222.26	
Insecticide	Methomyl	0.60	13.27	16752-77-5	162.21	
Antibiotico	Sulfaguanidine	-1.2	2.37	57-67-0	214.0524	
Antibiotic	Sulfamerazine	0.89	7.4	127-79-7	264.305	
Insecticide	Pirimicarb	1.7	4.34	66246-88-6	238.29	
Antibiotic	Sulfamonomethoxine	1.7	6.0	1220-83-3	264.5	

Antibiotic	Sulfachloropyridazine	1.54	6.5	80-32-0	28472	
Herbicide	Dimethoate	0.78	14.40	60-51-5	229.26	
Herbicide	Picloram	2.81	4.1	1918-02-1	239.92	
Antibiotic	Sulfathiazole	0.17	7.2	72-14-0	255.319	
Antibiotic	Sulfamethoxazole	1.58	5.6	723-46-6	253.27	
Herbicide	Butocarboxim	1.46	13.83	34681-10-2	190.26	
Hormone	Prednisolone	1.62	12.46	50-24-8	360.44	

Herbicide	Thifensulfuron-Me	2.5	2.2	79277-27-3	387.4	
Insecticide	Propoxur	1.52	12.28	114-26-1	209.24	
Hormone	Dexamethasone	1.83	12	50-02-2	392.46	
Herbicide	Cinosulfuron	1.4	2.4	94593-91-6	413.41	
Herbicide	Metsulfuron-Me	1.54	2.9	74223-64-6	381.36	
Herbicide	Chlorsulfuron	1.4	2.4	64902-72-3	413.41	

Insecticide	Carbaryl	2.36	10.4	63-25-2	201.22	
Herbicide	Atrazine	2.6	1.7	1912-24-9	215.68	
Herbicide	Isoproturon	2.87	25.6	34123-59-6	206.3	
Herbicide	Metobromuron	-0.19	2.2	3060-89-7	228.67	
Herbicide	2,4-Dichlorophenol	3.09	7.85	120-83-2	163.9	
Herbicide	2,4-Dichlorophenoxyacid	2.43	2.64	94-75-7	221.03	
Drug	Naproxen	3.18	4.28	22204-53-1	230.26	
Hormone	Testosterone	3.32	-0.88	58-22-0	288.42	

Herbicide	Flamprop	3.09	3.6	57973-67-8	321.73	
Hormone	Me-Testosterone	3.4	10.4	58-18-4	302.45	
Herbicide	Linuron	3.2	4.1	330-55-2	249.09	
Herbicide	Desmedipham	3.53	12.96	13684-56-5	300.31	
Herbicide	Phenmedipham	3.59	13.03	13684-63-4	300.31	
Drug	Nimesulide	2.6	6.56	51803-78-2	308.31	

Drug	Ibuprofen	3.5	4.45	15687-27-1	206.28	
Fungicide	Procymidone	3.8	2.1	32809-16-8	284.14	
Insecticide	Malathion	2.4	10.6	121-75-5	330.36	
Drug	Phenylbutazone	3.16	4.5	50-33-9	308.37	
Hormone	Progesterone	3.9	-	57-83-0-	314.46	
Fungicide	Iprodion	3.1	9.19	36734-19-7	330.17	

Section S1

Uv-VIS, FTIR and thermogravimetric analysis is performed on the recovered material, in order to confirm the composition of it and to certify the effectiveness of the washing procedure in removing combustion by-products and restoring a material as close as possible to the virgin polymer. The physicochemical and spectral properties of the recovered polymer were compared with those of virgin filters and filters before the washing steps.

S1.1. UV-VIS analysis

The characterization of cellulose acetate (CA) was conducted using UV–Vis spectrophotometry (model 760, PG Instruments Ltd., Leicester, UK) over the 190–450 nm spectral range, employing a 1 cm pathlength quartz cuvette. CA solutions (0.5% w/v in acetone) were prepared from pristine CA, clean cigarette filters (CFs), and unwashed CFs. The resulting spectra (Fig. S1) displayed a characteristic absorption band between 330 and 350 nm. The spectral profiles of pristine CA and clean recovered CA were nearly identical, indicating minimal alteration to the polymer structure during the cleaning process. In contrast, the spectrum of the unwashed CA exhibited significantly higher absorption and a visible yellow-orange coloration, likely attributable to the presence of conjugated species such as polycyclic aromatic hydrocarbons and aromatic amines formed during cigarette combustion.

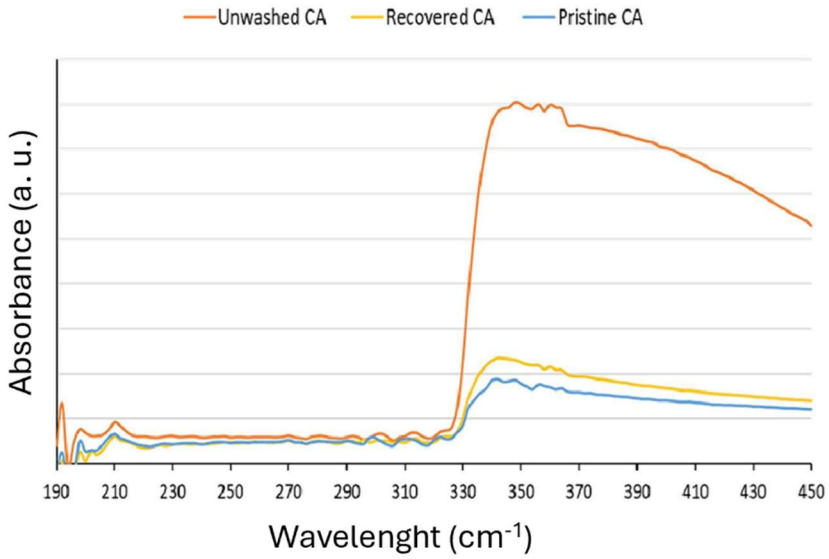


Fig. S1 UV spectra of the virgin material and CFs before and after the washing protocol

S1.2. FTIR spectroscopy evidence

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy was employed to analyse small fragments of virgin CA, regenerated CA, and unwashed CFs, using a Nicolet 6700 instrument (Thermo Fisher Scientific, Waltham, MA, USA). Spectra were recorded over the 400–4000 cm^{-1} range and are reported in Fig. S2. The following characteristic absorption bands were observed:

- **3500–3000 cm^{-1}**: O–H stretching vibrations,
- **3000–2750 cm^{-1}**: C–H stretching vibrations,

- **1750–1730 cm^{-1}**: C=O stretching of carbonyl groups,
- **1210–1163 cm^{-1}**: C–O stretching of ester linkages,
- **1120–1090 cm^{-1}**: C–O stretching of secondary alcohols,
- **<900 cm^{-1}**: fingerprint region, associated with C–H bending modes.

The spectrum of the unwashed CA displays the typical bands of cellulose acetate but also exhibits additional signals, particularly in the 1700–1500 cm^{-1} region, likely due to the presence of functional groups from combustion-derived contaminants. Following the washing procedure, the spectral profiles of the regenerated CA and the pristine material were nearly superimposable, indicating effective removal of impurities and preservation of the polymer's structural integrity.

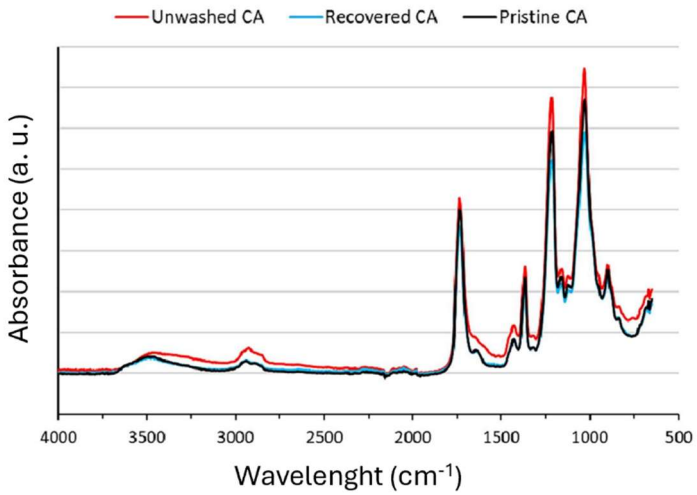


Fig. S2 FT-IR spectra of the virgin material and CFs before and after the washing protocol

S1.3. TGA analysis

Thermogravimetric analyses were performed on a Mettler TG 50 thermobalance (Mettler Toledo, Columbus, OH, USA) with a temperature ramp from 25 to 650 °C at a heating rate of 10 °C min^{-1} under an N_2 flow. The physicochemical and thermal properties of the recovered polymer were compared with those of virgin filters and CFs before the washing protocol. In all spectra (**Fig. S3**), a 3% weight loss was observed between 27°C and 127°C, attributed to water evaporation.

For the virgin polymer and for CF before the washing procedure, an additional 10% weight loss occurred between 127°C and 338°C, hypothesized to result from the degradation of plasticizing chemical additives. This weight loss was not observed in the regenerated polymer, suggesting that the washing procedure effectively removed most of the plasticizers. This hypothesis was confirmed by subjecting the virgin material to the washing protocol, after which TGA analysis revealed the complete absence of weight loss in the 127°C to 338°C range (data not shown).

The decomposition observed in all reported thermograms, characterized by a ~60% weight loss occurring between 360 °C and 390 °C, can be attributed to the thermal degradation of CA. Finally, a 13–15% weight loss was attributed to the decomposition of ash and residues at high decomposition temperatures (>400°C).

Also in this case, the analysis profile of the regenerated material is significantly over imposable with the one of the pristine polymers, except for plasticisers, whose removal offers clear practical advantages.

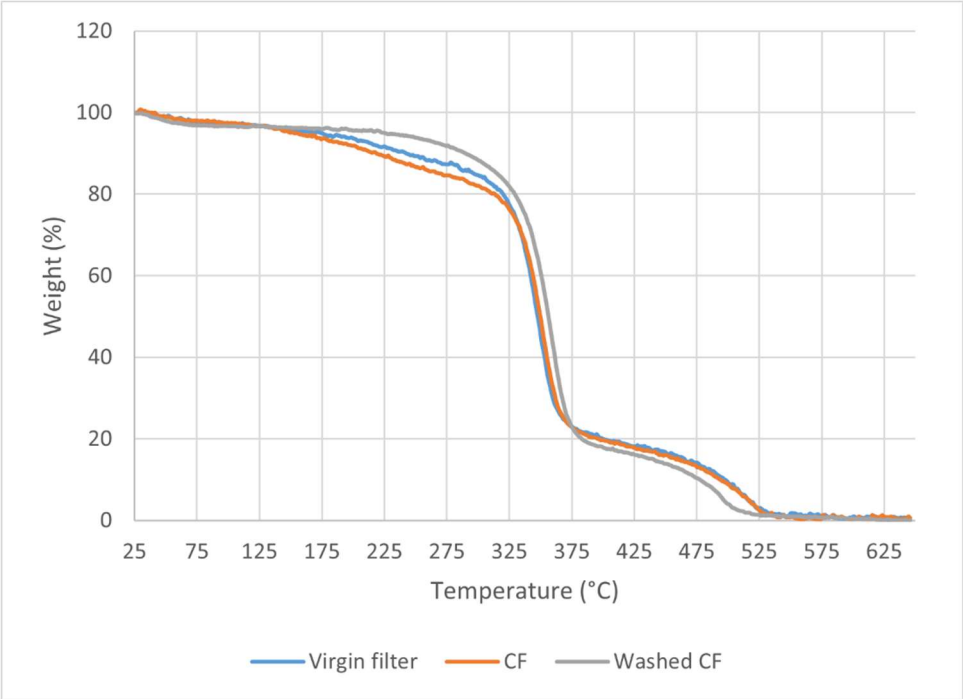


Fig. S3 Thermograms of the virgin material and the CFs before and after the washing protocol

Table S2 LC-MS parameters for the identification of the thirty analytes under optimized conditions

Compound	Retention time (min)	Q1 (m/z)	Q3 (m/z)	Detection polarity (+/-)	DP (V)	EP (V)	CE (V)	CXP (V)
Acephate	2.82	184.0	143.0	+	41.0	10.0	20.0	6.0
			95.0		41.0	12.0	32.0	6.0
Butoxycarboxim	3.16	223.1	106.0	+	93.0	10.0	15.0	4.0
			166.0		84.0	8.0	15.0	8.0
Methomyl	4.03	163.0	88.0	+	15.0	4.0	13.0	3.0
			106.0		15.0	4.0	13.0	3.0
Sulfaguanidine	4.1	215.0	108.0	+	60.0	10.0	20.0	9.0
			122.0		60.0	10.0	25.0	9.0
8.0Sulfamerazine	4.23	265.0	156.0	+	41.0	8.0	25.0	8.0
			108.0		41.0	8.0	35.0	11.0
Pirimicarb	4.78	239.1	182.2	+	61.0	10.0	39.0	4.0
			72.1		53.0	34.0	39.0	4.0
Sulfamonomethoxine	6.01	281.1	92.0	+	135.0	14.0	30.0	9.0
			107.9		135.0	14.0	30.0	9.0
Sulfachloropyridazine	6.57	285.0	156.0	+	35.0	9.0	20.0	11.0

			92.0		35.0	13.0	40.0	11.0
Dimethoate	6.80	230.1	125.0	+	70.0	9.0	10.0	10.0
			171.0		76.0	12.0	15.0	8.0
Picloram	7.06	242.9	224.9	+	20.0	10.0	20.0	11.0
			196.9		20.0	10.0	31.0	15.0
Sulfathiazole	7.28	254.0	155.9	+	38.0	4.0	25.0	15.0
			92.0		66.0	10.0	37.0	6.0
Sulfamethoxazole	7.28	254.0	156.0	+	41.0	10.0	25.0	9.0
			107.9		41.0	13.0	35.0	4.0
Butocarboxim	8.07	213.0	75.0	+	60.0	7.7	41.3	9.8
			156.0		93.1	10.4	14.8	4.2
Prednisolone	9.02	361.2	147.1	+	40.0	10.0	30.0	11.0
			343.3		40.0	10.0	32.0	11.0
Thifensulfuron-Me	10.5	388.0	167.0	+	70.0	10.0	23.0	7.0
			205.0		70.0	10.0	34.0	7.0
Propoxur	10.8	210.1	111.0	+	35.0	10.0	19.0	3.0
			168.0		40.0	10.0	20.0	5.0

Dexametasone	10.9	393.4	355.3	+	50.0	10.0	18.0	11.0
			373.3		50.0	10.0	18.0	11.0
Cinosulfuron	11.0	414.2	183.0	+	50.0	10.0	20.0	11.0
			215.3		50.0	10.0	20.0	11.0
Metsulfuron-Me	11.1	382.1	167.0	+	60.0	10.0	20.0	6.0
			141.1		60.0	10.0	20.0	7.0
Chlorsulfuron	11.8	358.0	141.1	+	93.0	10.0	25.0	11.0
			167.1		93.0	10.0	25.0	11.0
Carbaryl	12.1	202.1	145.1	+	56.0	6.0	25.0	6.0
			127.1		60.0	6.0	38.0	6.0
Atrazine	12.4	216.1	104.0	+	40.6	10.0	38.3	7.1
			174.0		40.6	10.0	19.9	6.9
Isoproturon	12.7	206.7	72.1	+	25.0	10.0	15.0	11.0
			46.1		25.0	10.0	20.0	11.0
Metobromuron	13.4	258.5	169.9	+	60.0	10.0	20.0	11.0
			227.0		60.0	10.0	20.0	11.0
2,4-Dichlorophenol	13.6	160.9	125.0	-	-48.0	-8.0	-22.0	-7.0

			88.9		-42.0	-4.0	-37.0	-5.0
2,4-Dichlorophenoxyacetic Acid	13.6	218.9	160.9	-	-46.0	-5.0	-16.0	-11.0
			124.8		-30.0	-8.0	-17.0	-7.0
Naproxen	13.8	229.1	170.0	-	-35.0	-8.0	-22.0	-5.0
			185.5		-35.0	-8.0	-21.0	-7.0
Testosterone	14.1	289.3	97.0	+	120.0	10.0	20.0	11.0
			109.1		120.0	10.0	20.0	11.0
Flamprop	14.2	321.9	105.1	-	26.0	10.0	5.0	4.0
			129.0		40.0	10.0	10.0	4.0
Me-Testosterone	15.0	303.2	97.1	+	120.0	10.0	20.0	11.0
			109.1		120.0	10.0	20.0	11.0
Linuron	15.1	249.0	182.1	+	120.0	10.0	20.0	11.0
			161.0		30.0	30.0	25.0	4.0
Desmedipham	15.3	301.1	182.1	+	56.0	10.0	20.0	11.0
			136.0		46.0	11.0	20.0	7.0
Phenmedipham	15.3	301.1	168.1	+	51.0	10.0	10.0	7.0
			136.1		81.0	10.0	12.0	10.0

Nimesulide	17.0	307.0	228.9	-	-47.0	-2.0	-17.0	-2.0
			79.1		-70.0	-6.0	-22.0	-6.0
Ibuprofen	17.0	205.2	161.0	-	-55.0	-10.0	-13.0	-15.0
			189.0		-55.0	-10.0	-13.0	-15.0
Procymidone	17.1	284.1	256.1	+	94.0	9.0	24.0	13.0
			133.0		90.0	10.0	21.0	10.0
Malathion	17.4	331.0	99.0	+	21.0	10.0	35.0	3.0
			127.0		26.0	10.0	35.0	3.0
Phenylbutazone	17.7	307.0	92.0	-	-40.0	-10.0	-20.0	-15.0
			131.0		-40.0	-10.0	-20.0	-15.0
Progesterone	18.8	315.2	97.1	+	45.0	10.0	20.0	11.0
			109.1		45.0	10.0	20.0	11.0
Iprodion	22.6	328.0	288.0	+	21.0	19.0	10.0	8.0
			245.2		46.0	21.0	10.0	42.0

Table S3 Selected parameters and explored relative values for the optimization study of the synthetic procedure. Underlined values are the selected ones, ensuring the best final result and highest throughput

Parameter	Lower value	Intermediate value	Higher value
Concentration of the organic polymeric phase (w/v %)	1.2	**5.6**	10
Amount of active carbon in the polymeric phase (% w/w)	5	10	**20**
Magnetic stirring speed (rpm)	100	**200**	300
Volume of the emulsion breaking solution (MilliQ water, mL)	7	9	**11**

Table S4 Features and performances of the developed analytical method (UPLC-ESI-MS/MS) for each of the involved analytes

Analyte	LOD (µg/L)	LOQ (µg/L)	Precision (RSD %) (n=5, 50 µg/L)	Linear range (µg/L)
Acephate	1.4	4.6	8.3	5-1000
Butoxycarboxim	5.9	19.8	9.8	20-1000
Methomyl	1.2	4.1	5.0	5-1000
Sulfaguanidine	0.6	2.1	6.7	5-1000
Sulfamerazine	1.0	3.2	8.6	5-1000
Pirimicarb	2.5	8.4	2.3	10-1000
Sulfamonomethoxine	3.2	10.5	6.1	20-1000
Sulfachloropyridazine	0.5	1.7	7.0	5-1000
Dimethoate	2.1	6.8	5.8	10-1000
Picloram	8.6	28.7	4.3	50-1000
Sulfathiazole	1.2	4.0	11.6	5-1000
Sulfamethoxazole	0.9	3.0	10.1	5-1000
Butocarboxim	5.9	19.8	5.4	20-1000
Prednisolone	9.3	30.9	4.1	50-1000
Thifensulfuron-Me	0.2	0.8	11.6	5-1000
Propoxur	3.6	11.9	8.1	20-1000
Dexametasone	2.2	7.3	11.4	10-1000
Cinosulfuron	1.9	6.2	4.8	10-1000
Metsulfuron-Me	0.3	1.1	7.5	5-1000
Chlorsulfuron	14.2	47.2	6.8	50-1000
Carbaryl	0.7	2.4	1.8	5-1000
Atrazine	10.0	33.3	8.8	50-1000
Isoproturon	0.6	1.9	10.5	5-1000
Metobromuron	3.4	11.2	7.2	20-1000
2,4-Dichlorophenol	4.0	13.4	4.8	20-1000
2,4-Dichlorophenoxyacetic Acid	2.0	6.7	3.5	10-1000
Naproxen	1.6	5.4	7.3	5-1000
Testosterone	1.0	3.3	10.8	5-1000
Flamprop	0.9	3.1	8.8	5-1000

Me-Testosterone	1.7	5.6	5.8	5-1000
Linuron	1.1	3.8	8.6	5-1000
Desmedipham	1.5	4.9	3.8	5-1000
Phenmedipham	1.2	4.0	4.4	5-1000
Nimesulide	0.9	3.0	3.5	5-1000
Ibuprofen	3.4	11.4	5.4	20-1000
Procimidone	5.7	19.0	2.2	20-1000
Malathion	6.3	20.9	2.0	20-1000
Phenylbutazone	1.0	3.3	9.7	5-1000
Progesterone	1.1	3.7	8.8	5-1000
Iprodion	1.4	4.8	10.0	5-1000

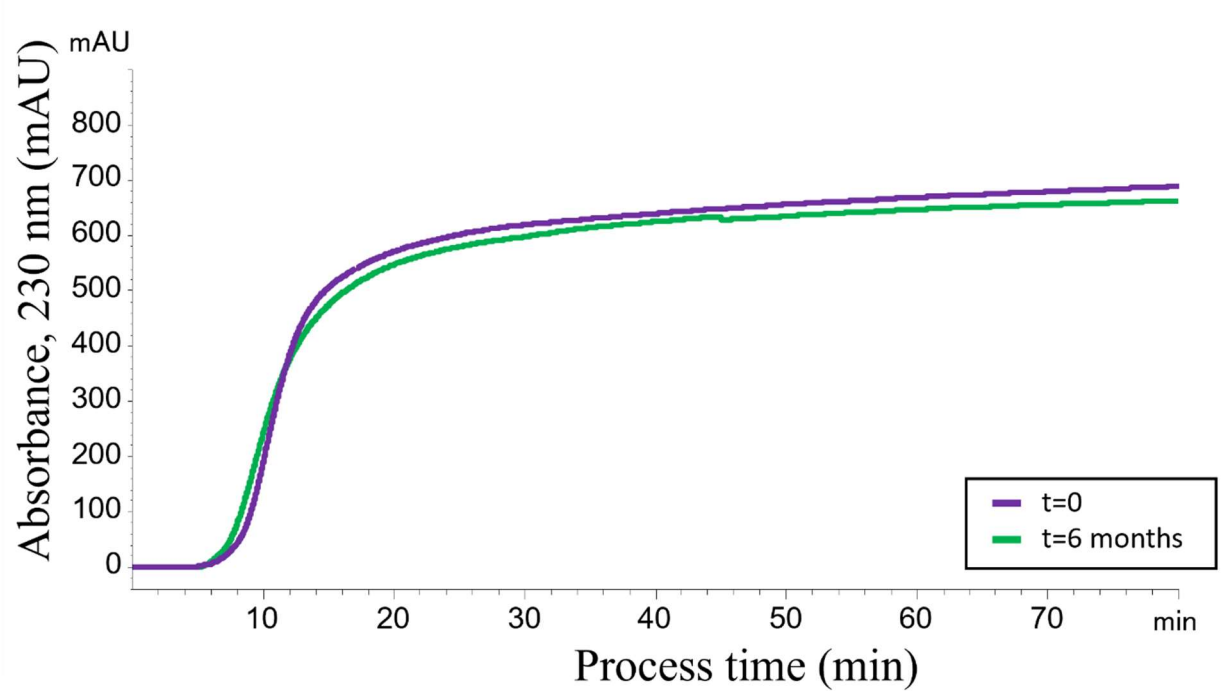


Figure S4 Integrated breakthrough curve comparison obtained respectively with a freshly prepared material and with material prepared six months before. Each curve is the average of triplicate trials. The final results are almost over imposable, with a statistical deviation of the results lower than 15%