

1 **Supplementary materials**

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3 **Synthesis and evaluation of a chitosan nanomaterial as efficient sorbent for**
4 **determination of fungicide residues in waters and wine by liquid**
5 **chromatography high resolution mass spectrometry**

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7 Lorenzo Martello ^a, Androniki Rapti^b, Dimitrios N. Bikiaris ^b, Dimitra A. Lambropoulou ^{a, c, *}

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9 a. Environmental Pollution Control Laboratory, Department of Chemistry, Aristotle
10 University of Thessaloniki, 54124, Thessaloniki, Greece

11 b. Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle
12 University of Thessaloniki, 54124, Thessaloniki, Greece

13 c. Centre for Interdisciplinary Research and Innovation (CIRI-AUTH), Balkan Center,
14 Thessaloniki, 10th km-Thermi Rd, 57001, Thessaloniki, Greece

15 * Corresponding author at **dlambro@chem.auth.gr**

Table S 1: Parameters of BET analysis

Thickness method	DeBoer
Slope	0.768
Intercept	-0.637
Correlation coefficient	0.999385
Micropore volume	0.000 cc/g
External surface area	10 m ² /g
Micropore area	0.0 m ² /g

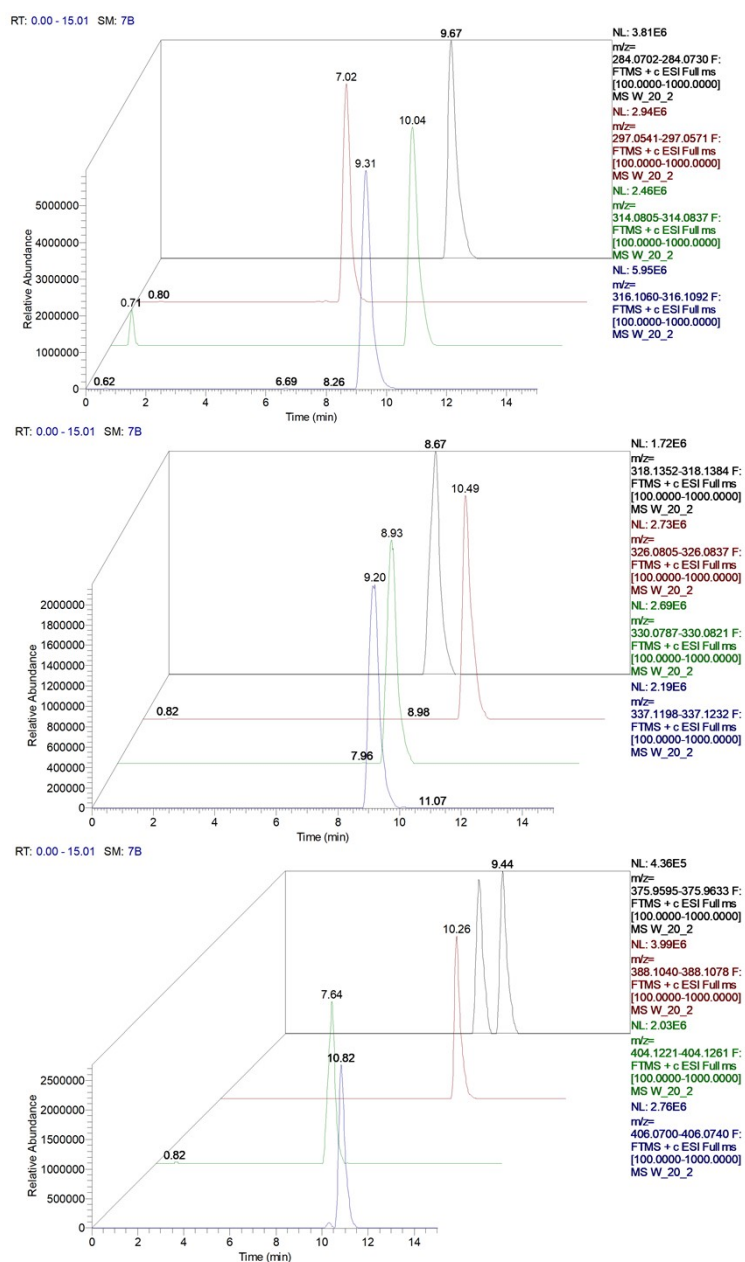


Figure S 1: Chromatograms of the 12 analytes after application of the proposed Nano-Cs-d-SPE method on wine spiked at 10 µg/kg.

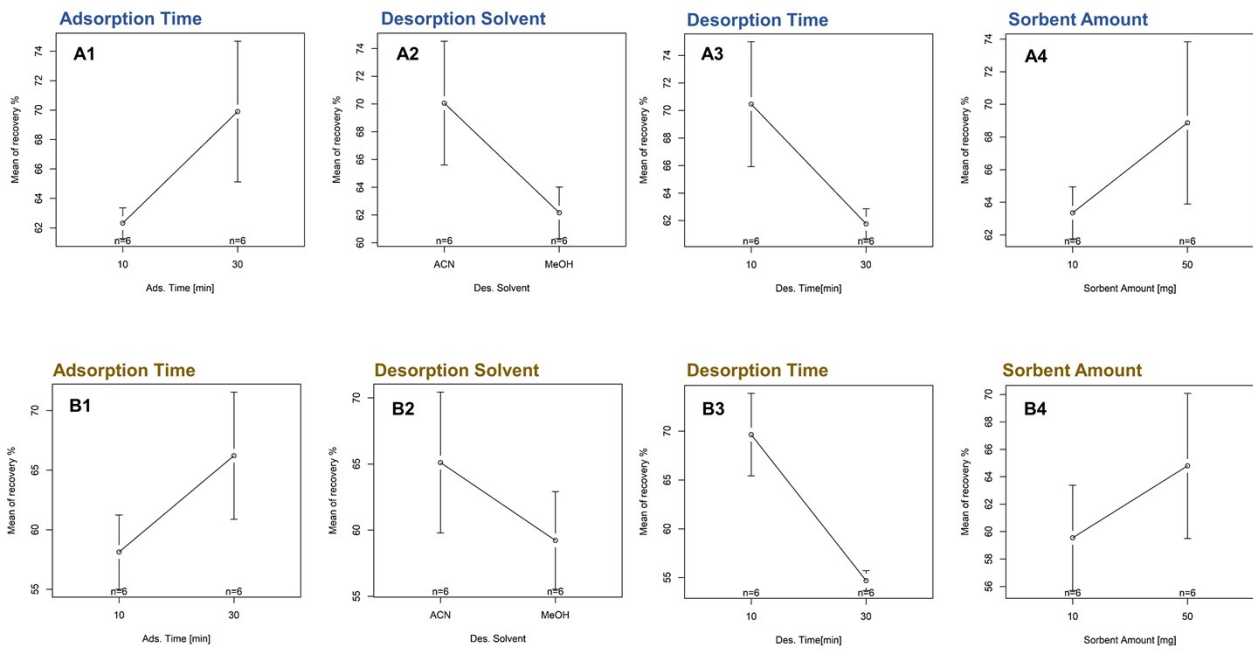


Figure S 2: Main effects plots derived from PBD, for the significant factors related to the application of Nano-Cs-NAT in water (A1, A2, A3, A4) and wine (B1, B2, B3, B4).

Table S 2: Factors and levels assessed in the Plackett-Burman design

FACTORS	LEVELS	
	-1	1
A: Desorption time	10 min	30 min
B: Sample pH	4	10
C: Sorbent amount	10 mg	50 mg
D: Adsorption time	10 min	30 min
E: Agitation speed	100 rpm	200 rpm
F: Desorption Solvent	MeOH	ACN
G: Desorption solvent volume	2 ml	5 ml

Table S 3: Plackett-Burmann design of experiments performed on wine and water with the assessed 7 factors: A) Desorption time [min], B) Sample pH, C) Sorbent amount [mg], D) Adsorption time [min], E) Agitation speed [rpm], F) Desorption solvent, G) Desorption solvent volume.

a	b	c	d	e	f	g	A	B	C	D	E	F	G
1	1	-1	1	1	1	-1	30	10	10	30	200	ACN	2
-1	1	1	-1	1	1	1	10	10	50	10	200	ACN	5
1	-1	1	1	-1	1	1	30	4	50	30	100	ACN	5
-1	1	-1	1	1	-1	1	10	10	10	30	200	MeOH	5
-1	-1	1	-1	1	1	-1	10	4	50	10	200	ACN	2
-1	-1	-1	1	-1	1	1	10	4	10	30	100	ACN	5
1	-1	-1	-1	1	-1	1	30	4	10	10	200	MeOH	5
1	1	-1	-1	-1	1	-1	30	10	10	10	100	ACN	2
1	1	1	-1	-1	-1	1	30	10	50	10	100	MeOH	5
-1	1	1	1	-1	-1	-1	10	10	50	30	100	MeOH	2
1	-1	1	1	1	-1	-1	30	4	50	30	200	MeOH	2
-1	-1	-1	-1	-1	-1	-1	10	4	10	10	100	MeOH	2

Table S 4: Statistical significance for the seven factors screened through Plackett-Burman experimental design performed on spiked river water samples.

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	66.1142	0.7859	84.124	1.2e-07	***
A	-4.3475	0.7859	-5.532	0.00522	**
B	-0.7025	0.7859	-0.894	0.42192	
C	2.7558	0.7859	3.507	0.02475	*
D	-3.7892	0.7859	-4.821	0.00851	**
E	1.8375	0.7859	2.338	0.07955	.
F	3.9508	0.7859	5.027	0.00735	**
G	-0.8008	0.7859	-1.019	0.36583	

Table S 5: Statistical significance for the seven factors screened through Plackett-Burman experimental design performed on spiked wine samples.

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	62.1717	0.9172	67.781	2.84e-07	***
A	-7.4667	0.9172	-8.140	0.00124	**
B	-1.7367	0.9172	-1.893	0.13124	
C	2.6217	0.9172	2.858	0.04601	*
D	-4.0450	0.9172	-4.410	0.01160	*
E	-0.4083	0.9172	-0.445	0.67922	
F	2.9433	0.9172	3.209	0.03262	*
G	-0.6800	0.9172	-0.741	0.49964	

Table S 6: Box-Behnken design of experiments performed on wine and water to optimize the 3 factors A) Desorption time [min], B) Adsorption time [min] and C) Sorbent amount [mg].

a	b	c	A	B	C
1	0	1	10	30	60
1	0	-1	10	30	20
-1	-1	0	2	20	40
1	1	0	10	40	40
0	-1	-1	6	20	20
0	0	0	6	30	40
-1	0	-1	2	30	20
0	0	0	6	30	40
-1	1	0	2	40	40
0	1	-1	6	40	20
0	-1	1	6	20	60
0	0	0	6	30	40
1	-1	0	10	20	40
0	0	0	6	30	40
-1	0	1	2	30	60
0	1	1	6	40	60

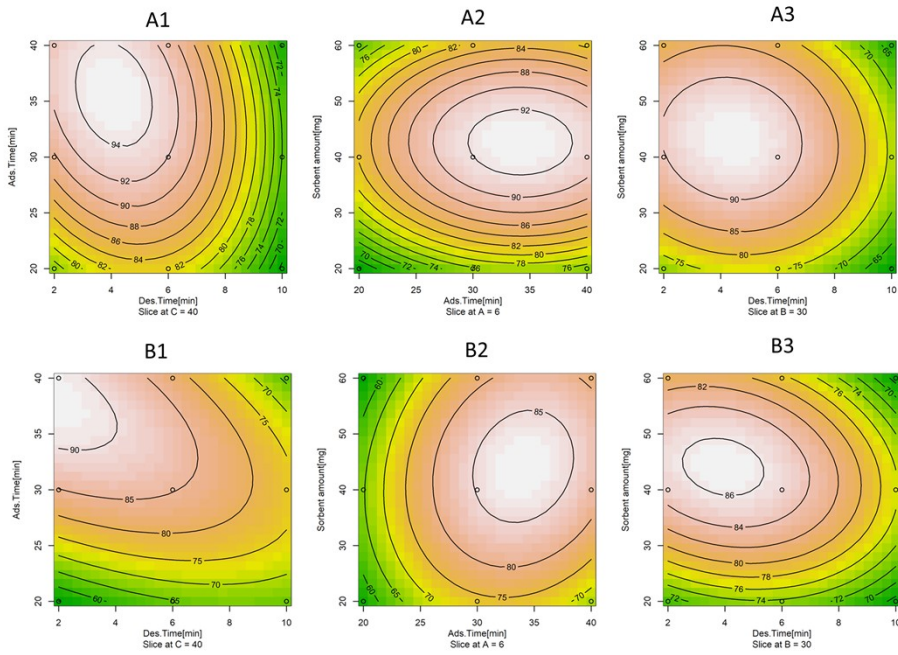


Figure S 3: Contour plots derived from the Box-Behnken design of experiments.

Table S 7: Effect on the response (fungicide average recovery from spiked river water samples) for the factors A) Desorption time, B) Adsorption time and C) Sorbent amount, their two-way interactions and their pure-quadratic interactions.

	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	91.978218	1.493912	61.5687	1.234e-09	***
A	-7.907824	1.056355	-7.4860	0.0002936	***
B	4.428306	1.056355	4.1921	0.0057361	**
C	3.459714	1.056355	3.2751	0.0169250	*
A:B	-3.193871	1.493912	-2.1379	0.0763689	
A:C	-1.969921	1.493912	-1.3186	0.2353869	
B:C	-0.095923	1.493912	-0.0642	0.9508893	
A^2	-10.140816	1.493912	-6.7881	0.0005001	***
B^2	-5.318234	1.493912	-3.5599	0.0119280	*
C^2	-12.860478	1.493912	-8.6086	0.0001352	***

Table S 8: Effect on the response (fungicide average recovery from spiked wine samples) for the factors A) Desorption time, B) Adsorption time and C) Sorbent amount, their two-way interactions and their pure-quadratic interactions.

	Estimate	Std. Error	tA value	Pr(> t)	
(Intercept)	85.2282	2.0774	41.0258	1.402e-08	***
A	-4.2828	1.4690	-2.9155	0.0267863	*
B	8.8033	1.4690	5.9929	0.0009706	***
C	2.4597	1.4690	1.6745	0.1450634	
A:B	-9.4439	2.0774	-4.5459	0.0039086	**
A:C	-2.4699	2.0774	-1.1889	0.2793825	
B:C	3.4041	2.0774	1.6386	0.1524089	
A^2	-4.6408	2.0774	-2.2339	0.0669038	
B^2	-11.8182	2.0774	-5.6889	0.0012730	**
C^2	-9.1105	2.0774	-4.3855	0.0046407	**

Table S 9: Extensive results for intra-day and inter-day recovery experiments and relative standard deviations (n=3).

	Spike $\mu\text{g/L}$	Penconazole		Imazalil		Hexaconazole		Flusilazole		Triticonazole		Diniconazole		Epoconazole		Fenbuconazole		Bromuconazole		Pyraclostrobin		Azoxytrob n		Difenoconazole		
		RE%	RSD	RE%	RSD	RE%	RSD	RE%	RSD	RE%	RSD	RE%	RSD	RE%	RSD	RE%	RSD	RE%	RSD	RE%	RSD	RE%	RSD	RE%	RSD	
River water	Intra-day	0	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-
		0.2	73	4	74	8	77	6	78	6	72	7	82	6	85	5	81	4	76	5	80	5	80	5	85	5
		0.6	87	4	80	7	84	5	93	6	82	6	87	6	92	5	95	5	88	3	89	5	77	2	86	4
		2	92	2	90	1	97	2	94	5	94	3	97	3	96	4	93	3	87	1	94	3	92	3	96	4
	Inter-day	0	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-
		0.2	75	7	75	11	78	9	79	8	73	9	83	8	86	7	82	6	77	6	81	7	77	4	86	7
		0.6	88	5	81	8	85	6	93	5	82	8	87	7	92	5	96	5	88	4	89	5	78	3	87	5
		2	92	5	90	2	97	1	95	7	94	5	97	5	96	6	93	6	87	2	95	5	93	5	97	2
Wine	Intra-day	0	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-
		5	88	2	87	2	93	1	93	2	85	1	97	1	102	3	100	3	98	2	95	2	97	1	102	3
		10	98	2	97	3	93	2	104	3	90	1	98	1	102	5	102	1	93	2	101	3	96	2	100	2
		20	96	3	93	7	91	3	99	0	88	4	94	5	100	2	100	3	90	2	97	1	95	2	95	5
	Inter-day	0	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-	N.D.	-
		5	89	5	88	4	93	4	93	2	86	4	97	2	102	2	101	7	98	2	95	2	97	4	102	2
		10	97	6	96	5	92	2	103	7	89	6	97	3	101	8	101	4	93	3	100	7	95	5	100	6
		20	96	6	93	11	92	6	99	4	88	6	94	8	101	2	100	3	90	3	98	3	96	6	95	8