Key Factors for Activated Carbon Adsorption of Pharmaceutical Compounds from Wastewaters: A Multivariate Modelling Approach

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Appendix A. Supplementary information

Text S1

The analysis of the PhCs required water sample clean up and PhC extraction/concentration by solid-phase extraction (SPE) following a method adapted from Gaffney et al. [1]. The SPE cartridges (OASIS, HLB 500 mg, 6 mL) were conditioned and equilibrated with 10 mL methanol and 10 mL of ultrapure water (2 mL/min). After sample loading (300 mL, 4 mL/min), the cartridges were washed with 4 mL methanol 5% and eluted five times with 1 mL methanol 100%. The eluate was dried under N_2 atmosphere in a water bath at 40 °C. The dried residues were afterwards resuspended in a precise volume of methanol 5% (1-3 mL, i.e. yielding a concentration factor of 100-300), centrifuged

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(10000 × g, 5 min) and analysed by HPLC with a photo-diode array detection (HPLC-PDA Summit from Dionex, Sunnyvale, CA, USA) system equipped with an auto-sampler and column compartment (UltiMate3000, from Thermo Scientific, Waltham, MA, USA). The PhCs were separated on a reverse-phase column (Purospher STAR RP-18*e* column, LichroCART 250 mm x 4 mm d.i. coupled to Purospher STAR RP-18*e*, 4 mm x 4 mm d.i. guard-column, from Merck). The mobile phase consisted of a gradient of 0.1% formic acid in ultrapure water (A) and acetonitrile (B) with the following gradient programme, according to Salgado et al. (2010) [2]: 0 min, 15% B at 0.6 mL/min; 2 min, 15% B at 0.6 mL/min; 20 min, 100% B at 0.6 mL/min; 25 min 100% B at 1.0 mL/min; 27 min 15% B at 1.0 mL/min; 37 min 15% B at 0.6 mL/min. The sample volume was 50 µL and the column temperature was 40ºC. The diode array detector was operated at 200-400 nm and the detection wavelength was 277 nm. Carbamazepine (CBZ), diclofenac (DCF) and sulfamethoxazole (SMX) were identified by retention time and UV spectrum comparison with those of standards. Eight-point calibration curves were used for each PhC with standard solutions ranging from 0.1 mg/L to 14 mg/L. Samples and standards were analysed in duplicate. Chromeleon 6.8 software was used to analyse chromatographic data.

The results of the analysis of 48 wastewater samples spiked with known concentrations of CBZ, DCF and SMX were computed as analytical concentration/theoretical concentration x100 showing the following mean recoveries, 94% (stdev 9%, *n*= 48) for carbamazepine, 80% (stdev 14%, n= 46) for diclofenac and 87% (stdev 9%, *n*= 43). The experimental reproducibility, regarding sample treatment, solid phase extraction procedure and PhCs quantification was also accesses through the analysis of replicate data. The relative standard deviation of replicate analyses (duplicate to quadruplicate)

from eight blank samples were always lower than 10% (except for one duplicate analysis of DCF which was 13%) revealing quite fair reproducible measurements.

Table S1. Summary of the combinations tested (PhC, PAC and secondary effluent).

		PhC			PAC							Wastewater					
Data #	**Fold #**	**CBZ**	**DCF**	**SMX**	**Comm1**	**Comm2**	**Comm3**	**Comm4**	**Lab1**	**Lab2**	**Lab3**	**SE1**	**SE2**	**SE3**	**SE4**	**SE5**	**SE6**
1	4			x	x												x
2	3			x			x										x
3	3			x					x								x
4	3	x			x												x
5	4	x					x										x
6	2	x							x								x
7	1	x								x							x
8	1		x		x												x
9	2		x				x										x
10	4		x						x								x
11	2		x							x							x
12	1			x				x					x				
13	3			x	x								x				
14	1			x		x							x				
15	2	x						x					x				
16	1	x					x						x				
17	4	x			x								x				
18	3	x				x							x				
19	4		x					x					x				
20	3		x				x						x				
21	2		x		x								x				
22	2		x			x							x				
23	2			x				x						x			
24	2			x			x							x			
25	1			x	x									x			
26	4			x		x								x			
27	3	x					x							x			
28	4	x			x									x			
29	3	x				x								x			
30	4		x					x						x			
31	1		x				x							x			
32	3		x		x									x			
33	1		x			x								x			
34	4			x				x				x					
35	2	x						x				x					
36	1		x					x				x					
37	1	x									x				x		
38	3		x								x				x		
39	2			x							x					x	
40	4	x									x					x	

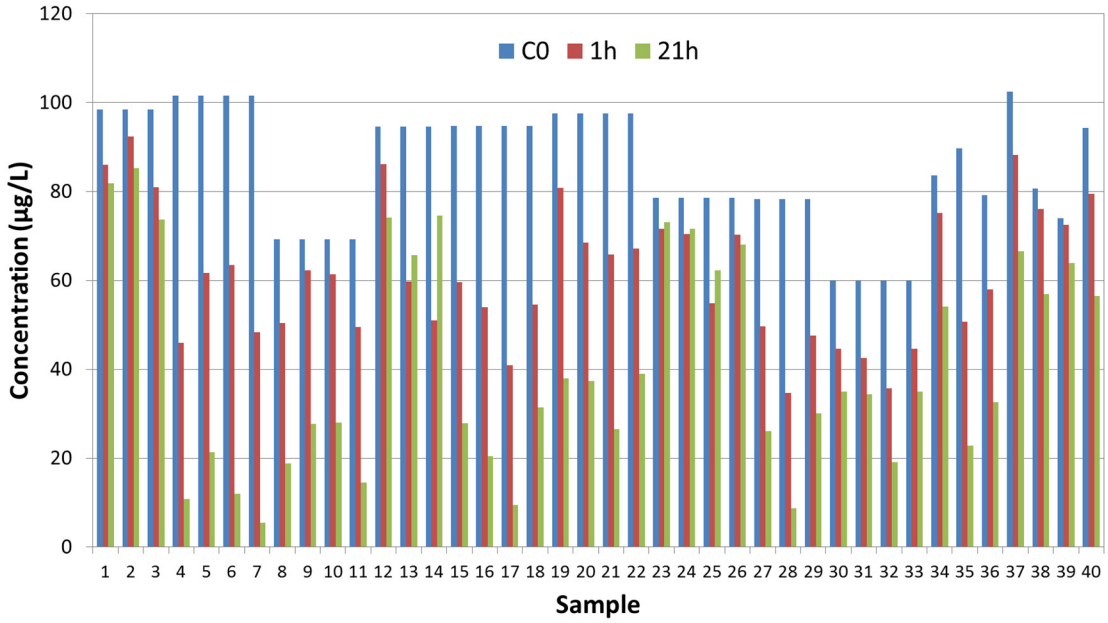


Figure S1. PhC initial concentrations (C_0) in the samples used in batch adsorption tests and respective PhC concentrations after 1h and 21h contact time.

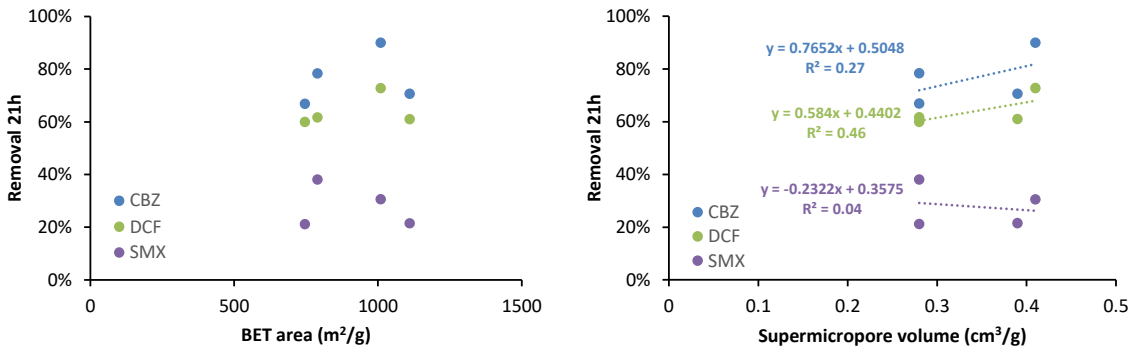


Figure S2. Univariate relation between removal efficiencies of target PhCs and PACs' textural parameters: apparent surface (BET) area (a) and supermicropore volume (b) (assays performed in SE2).

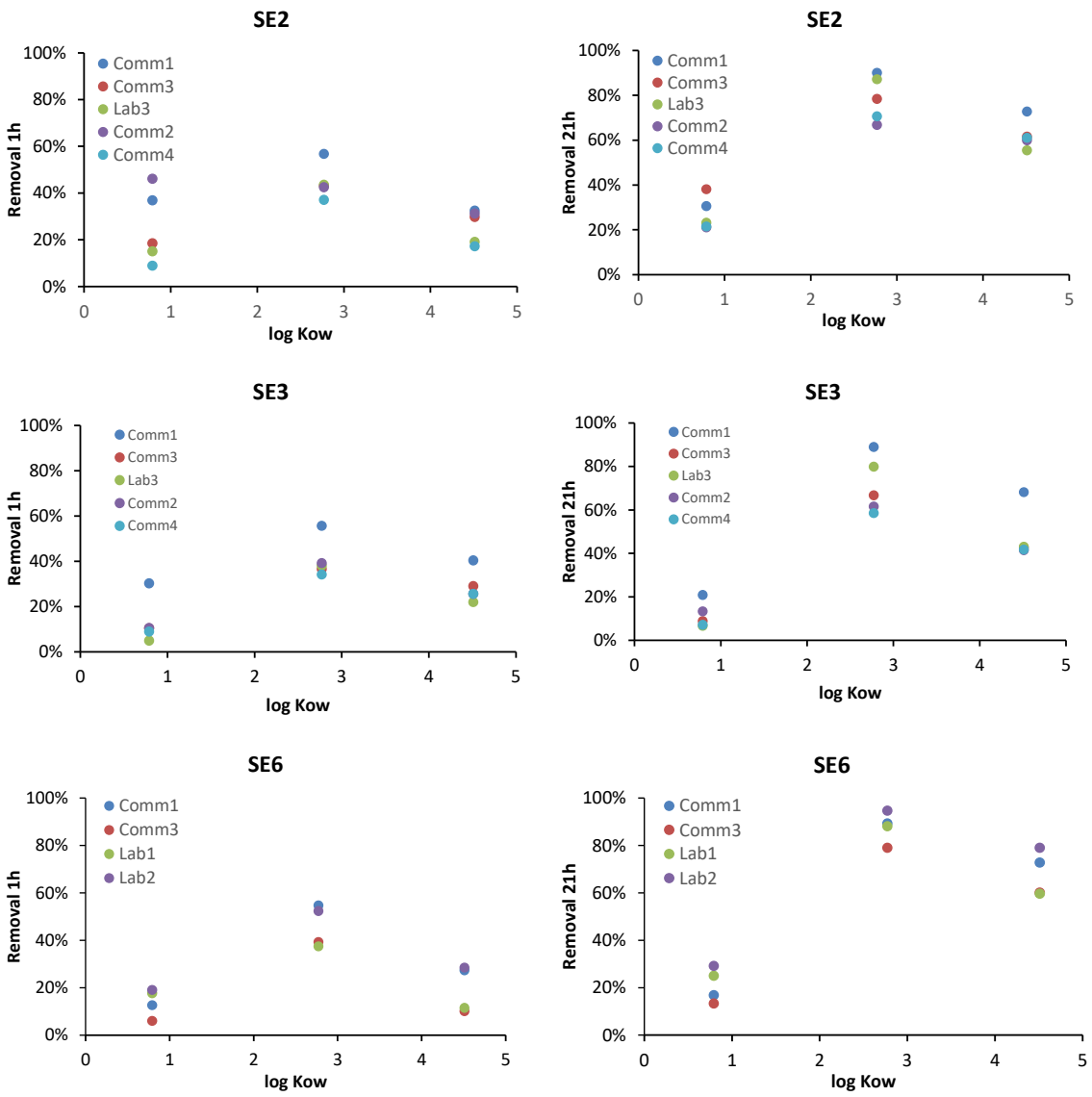


Figure S3. Univariate relation between removal efficiencies of target PhCs and PhCs' log Kow.

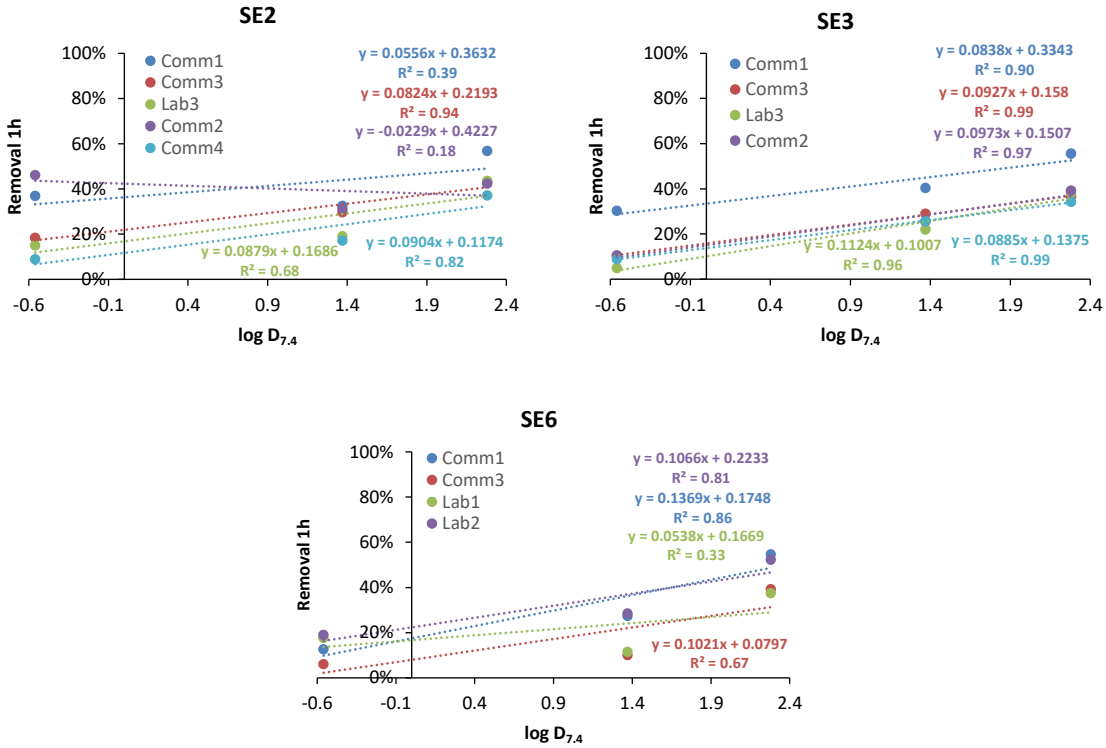


Figure S4. Univariate relation between removal efficiencies of target PhCs and PhCs' log $D_{7.4}$.

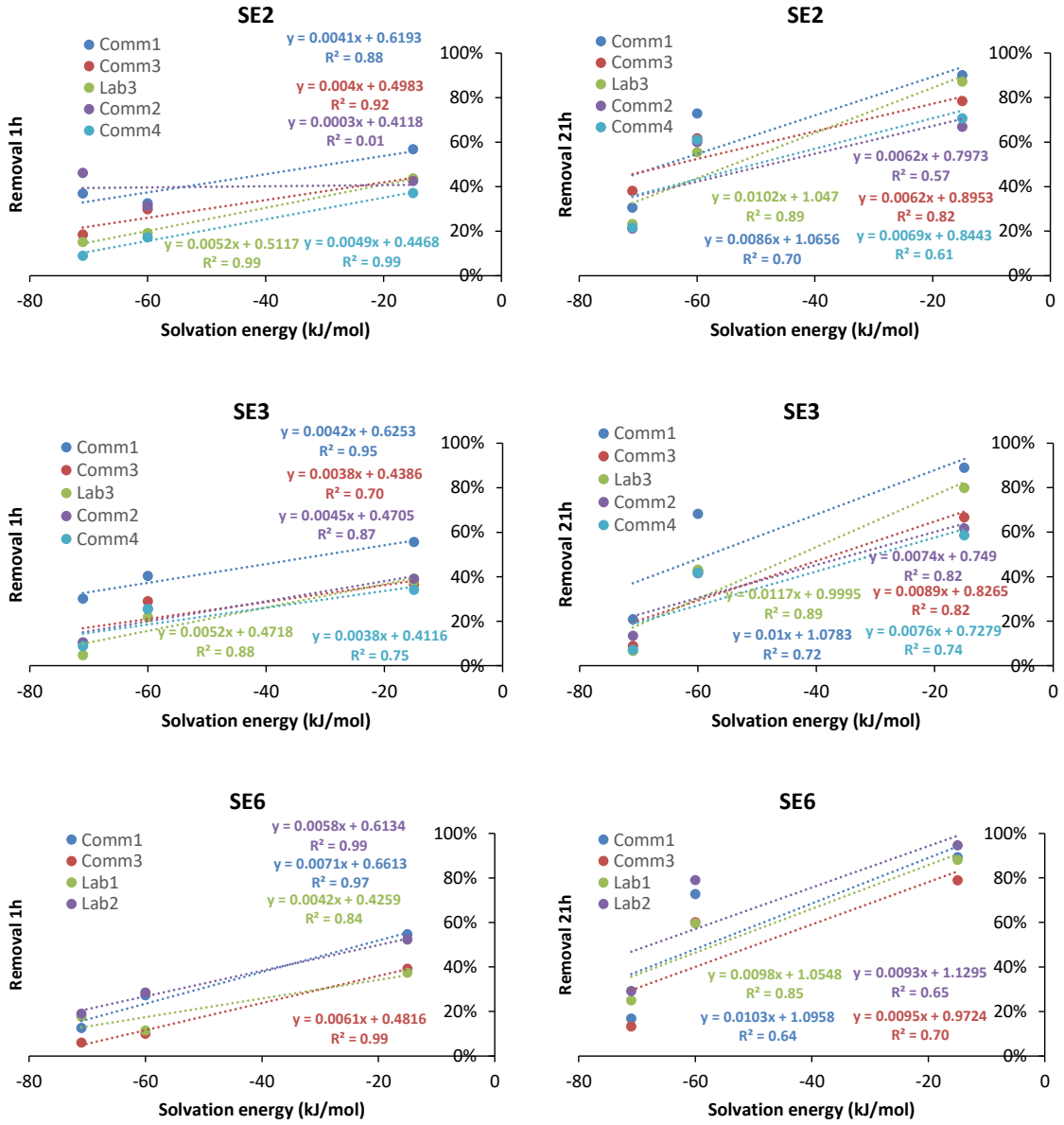
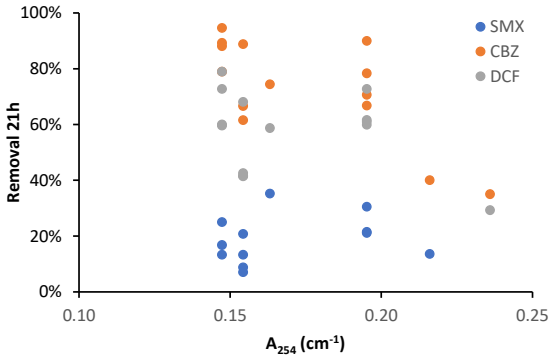
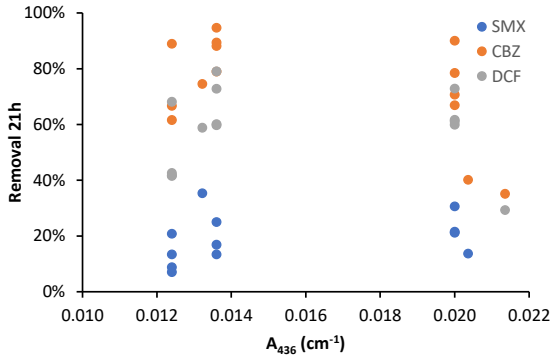
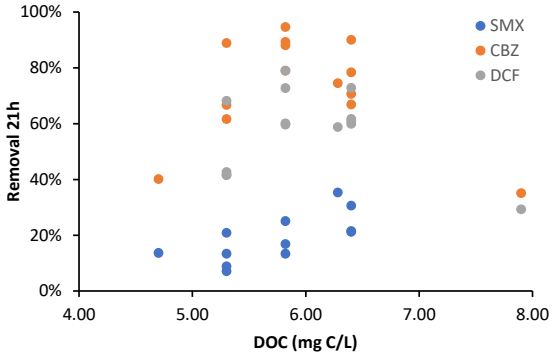
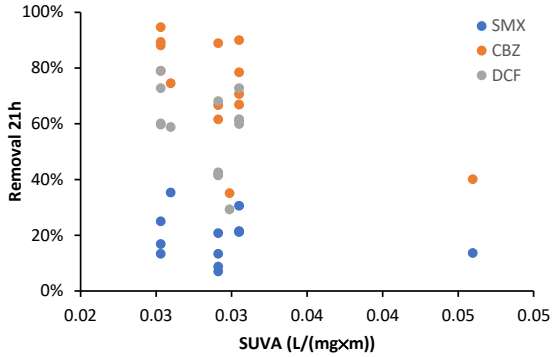


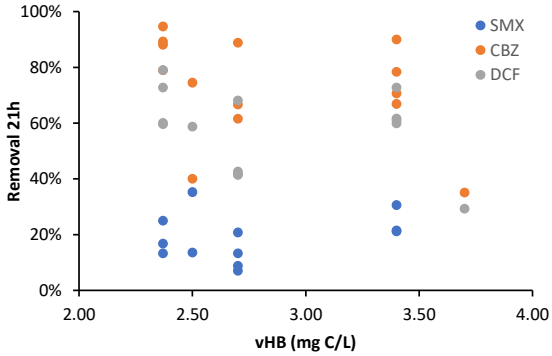
Figure S5. Univariate relation between removal efficiencies of target PhCs and PhCs' solvation energy.

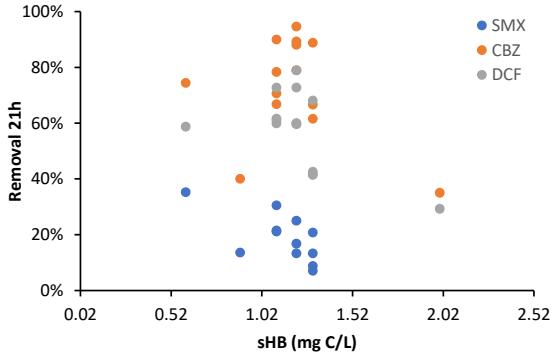

100%
80%
60%
40%
20%
0%
Removal 21h
0.10
0.15
0.20
0.25
A254 (cm-1)
SMX
CBZ
DCF

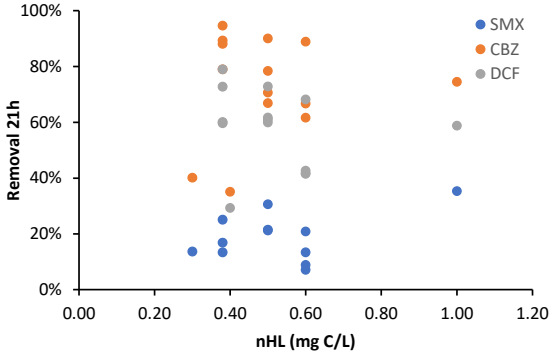

100%
80%
60%
40%
20%
0%
Removal 21h
0.010
0.012
0.014
0.016
0.018
0.020
0.022
A436 (cm-1)
SMX
CBZ
DCF

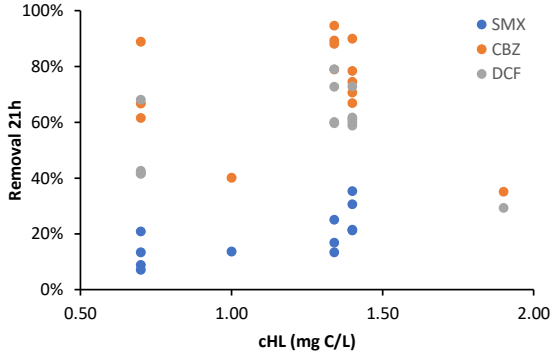

100%
80%
60%
40%
20%
0%
Removal 21h
4.00
5.00
6.00
7.00
8.00
DOC (mg C/L)
SMX
CBZ
DCF


100%
80%
60%
40%
20%
0%
Removal 21h
0.02
0.03
0.03
0.04
0.04
0.05
0.05
SUVA (L/(mg×m))
SMX
CBZ
DCF


100%
80%
60%
40%
20%
0%
Removal 21h
2.00
2.50
3.00
3.50
4.00
vHB (mg C/L)
SMX
CBZ
DCF


100%
80%
60%
40%
20%
0%
Removal 21h
0.02
0.52
1.02
1.52
2.02
2.52
sHB (mg C/L)
SMX
CBZ
DCF


100%
80%
60%
40%
20%
0%
Removal 21h
0.00
0.20
0.40
0.60
0.80
1.00
1.20
nHL (mg C/L)
SMX
CBZ
DCF


100%
80%
60%
40%
20%
0%
Removal 21h
0.50
1.00
1.50
2.00
cHL (mg C/L)
SMX
CBZ
DCF

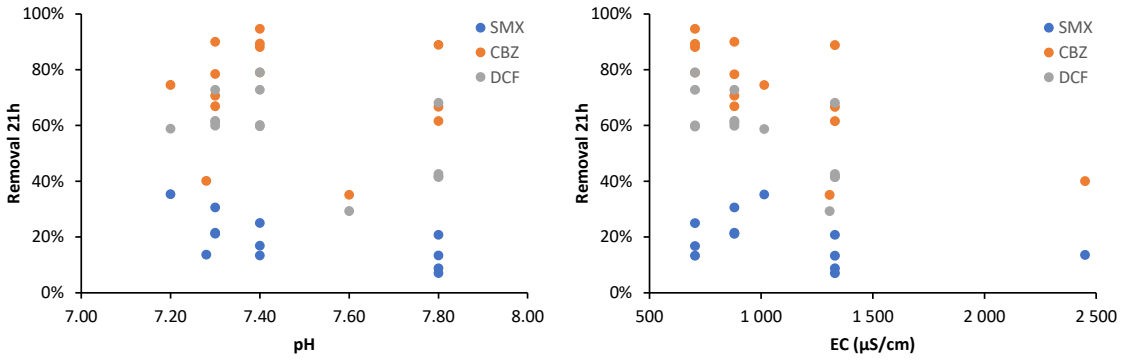


Figure S6. Univariate relation between removal efficiencies of target PhCs and waters' properties.

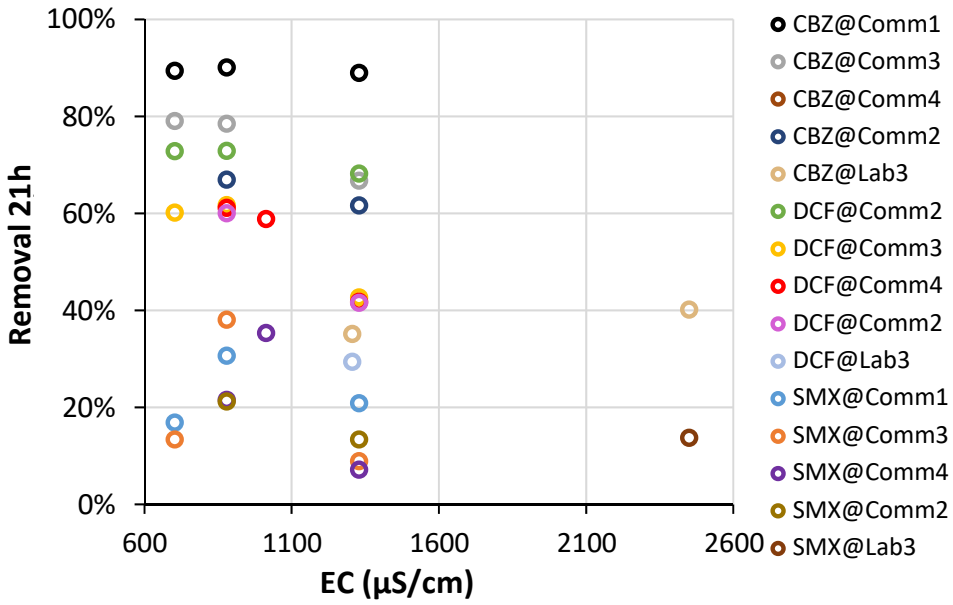


Figure S7. Univariate relation between removal efficiencies of target PhCs and waters' electrical conductivity (identifying the PAC used in each assay).

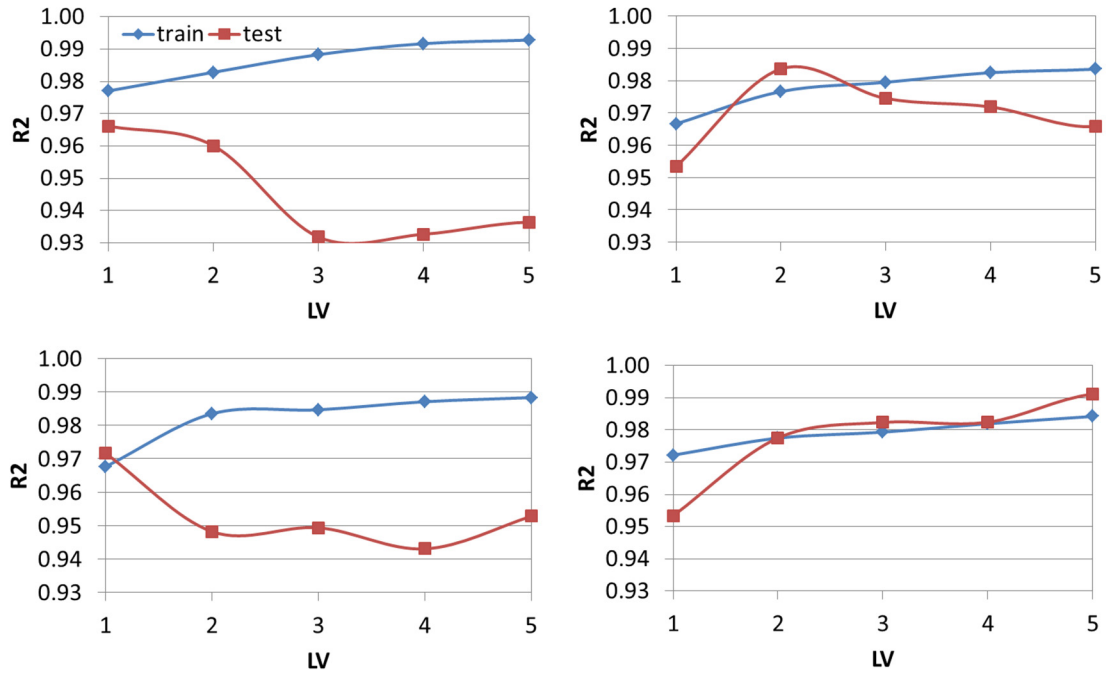


Figure S8. R^2 for the 4 training sets and the 4 test sets as a function of the number of latent variables (21 h batch adsorption).

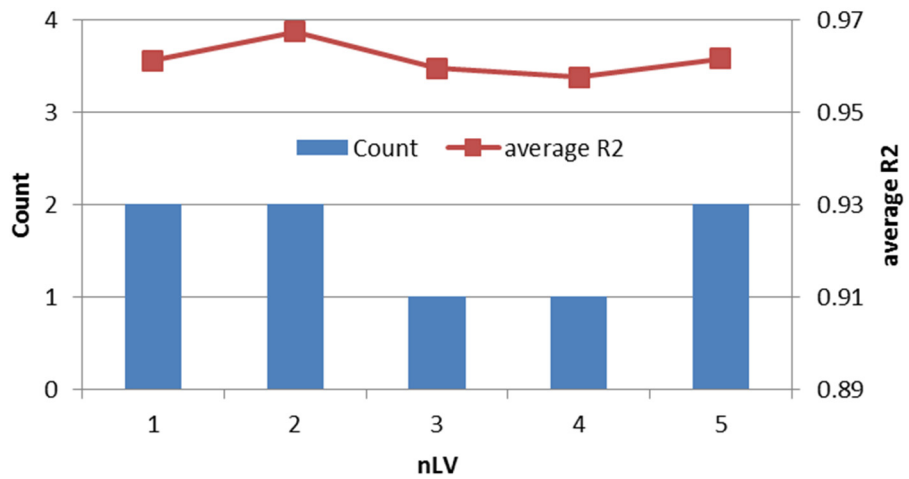


Figure S9. Frequency plot of the number of latent variables selected for the 4 test sets (best two) and the average R2 for the 4 test sets as a function of the number of latent variables (21 h batch adsorption).

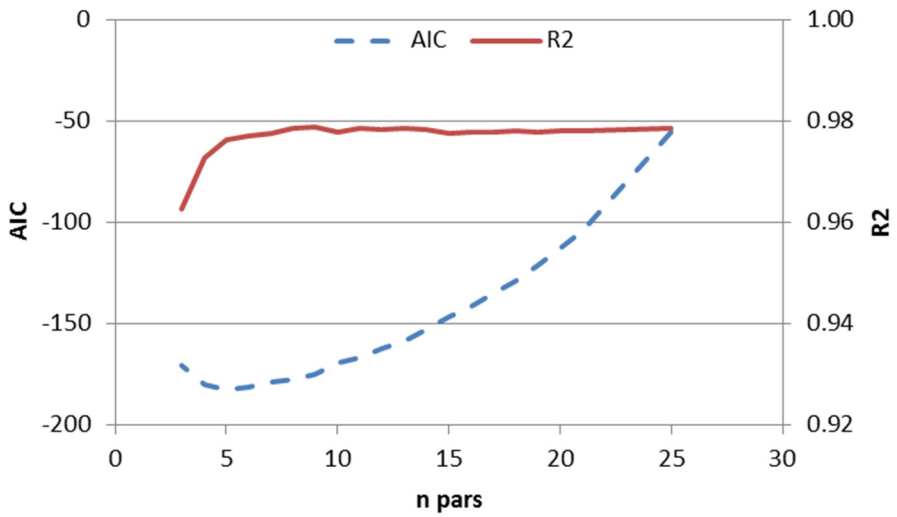


Figure S10. AIC and R2 values as a function of the number of the model parameters (21 h batch adsorption).

Text S2

The number of latent variables was selected following the same procedure as described in section 2.7. The frequency plot of the number of latent variables selected for the 4 test sets (best two) and the average R^2 for the fittings of the 4 test sets as a function of the number of latent variables are depicted in Figure S11.

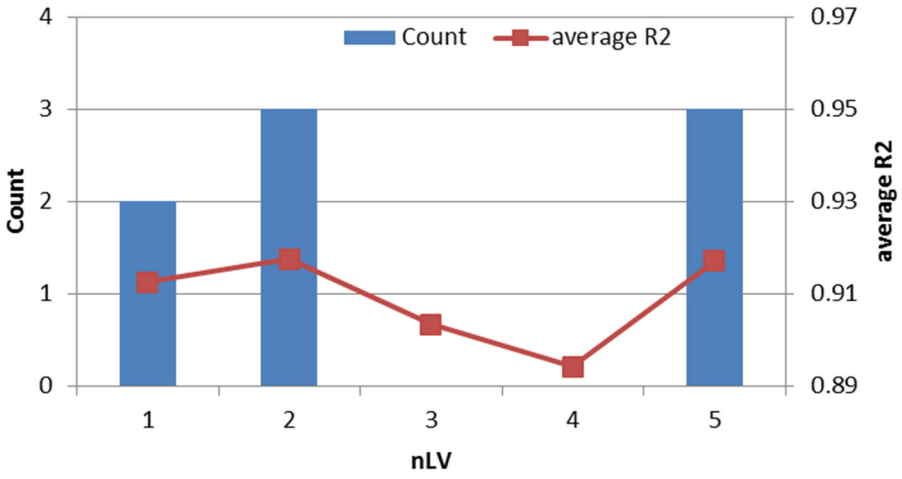


Figure S11. Frequency plot of the number of latent variables selected for the 4 test sets (best two) and the average R2 for the 4 test sets as a function of the number of latent variables (1 h batch adsorption).

Regarding the frequency of LVs, it was observed that both 2 and 5 LVs were the most frequent. Concerning the average R^2 values of the 4 test sets, the highest value was obtained for 2 LVs, which were then selected for performing the PLS.

The model parameters were selected following the same procedure as described in section 2.7. Figure S12 depicts the AIC and R^2 values as a function of the number of the model parameters.

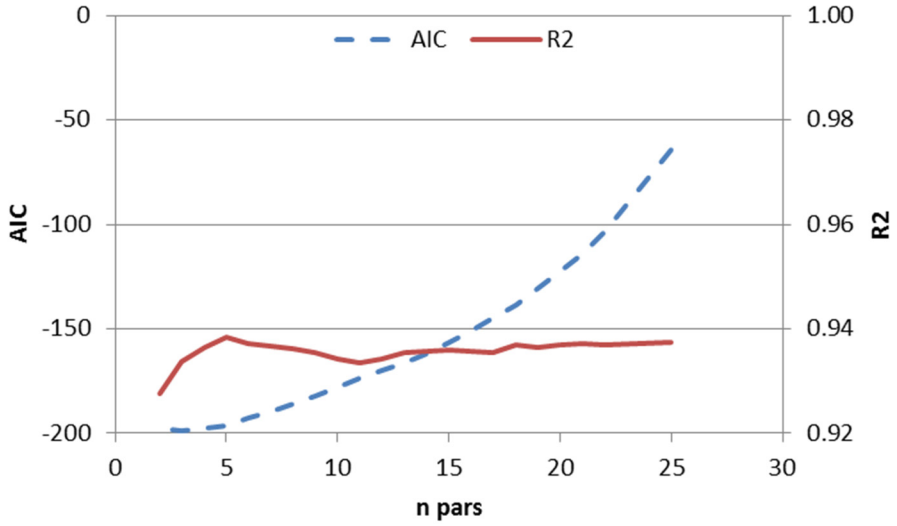


Figure S12. AIC and R2 values as a function of the number of the model parameters (1 h batch adsorption).

The 9 parameters model fitting (observed removals plotted versus model-fitted removals) and the standardised coefficients of the model are depicted in Figure S13 and Figure S14, respectively.

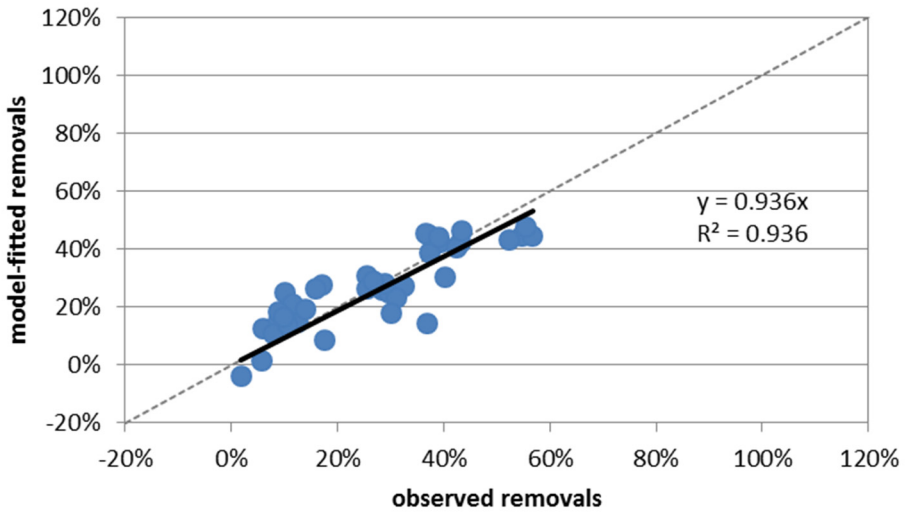


Figure S13. Observed removals versus model-fitted removals (9 parameters model, 1 h batch adsorption).

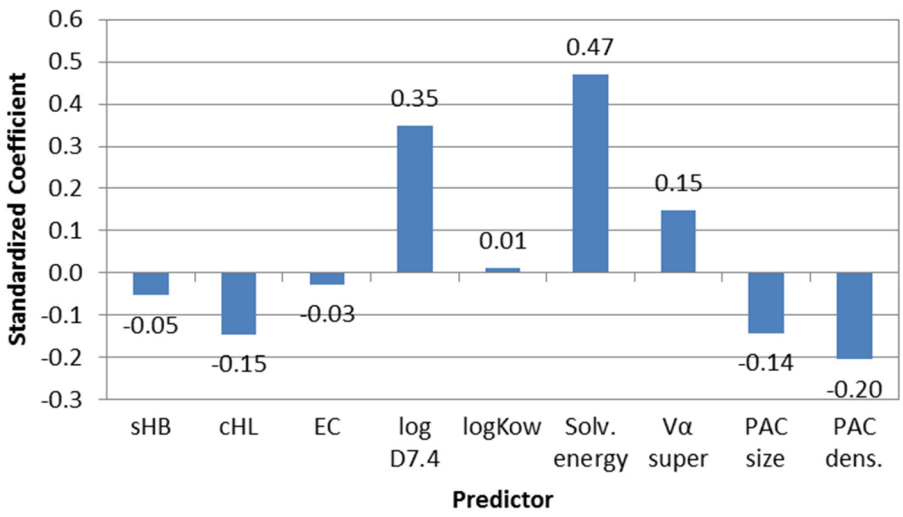


Figure S14. Standardised coefficients of the nine parameters' model fitting (1 h batch adsorption).

As observed in S13, a good fitting was obtained, with an R^2 value of 0.936 and with a slope of the predicted versus the observed removals close to 1 (0.936).

Further elimination of model variables was then carried out with no restrictions, and as observed in Figure S12 the models with 3, 4 and 5 parameters presented similar and the lowest AIC values. By having a higher R^2 value, the model with 5 parameters was selected as the optimised model. The model fitting and the standardised coefficients of the model are depicted in Figure S15 and Figure S16, respectively.
Figure S15 shows the solution corresponds to a reasonably good fitting, with an R^2 value of 0.938, an RMSE of 8 % and a slope of the model-fitted versus the observed removals of 0.938.

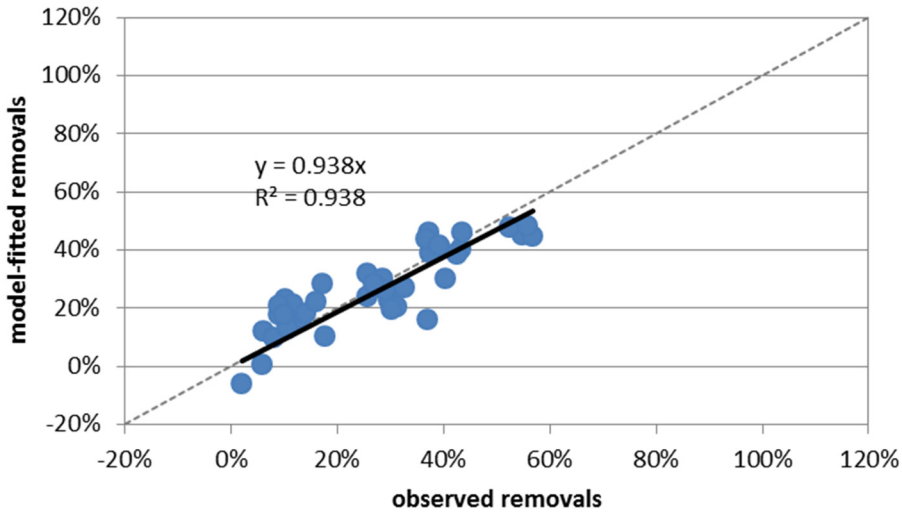


Figure S15. Observed removals versus model-fitted removals (5 parameters model, 1 h batch adsorption).

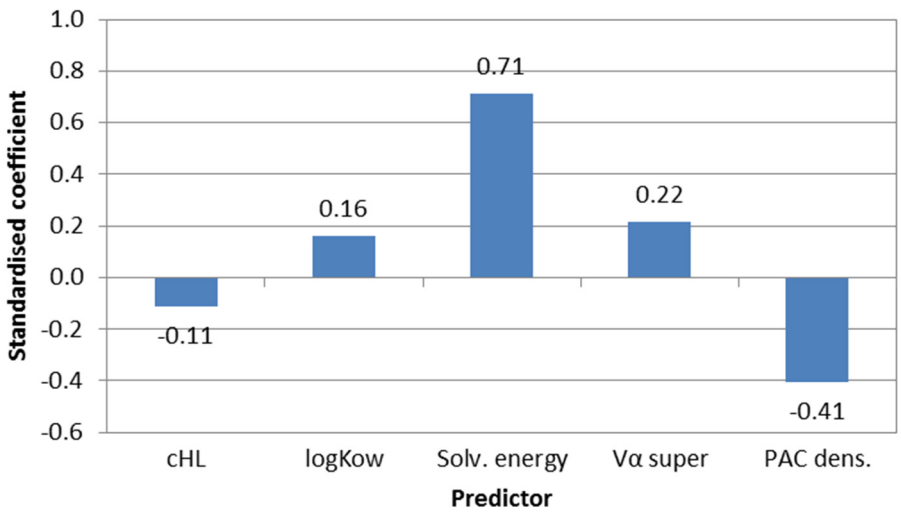


Figure S16. Standardised coefficients of the 5 parameters' model fitting (1 h batch adsorption).

[1] V.D. Gaffney, V.V. Cardoso, A. Rodrigues, E. Ferreira, M.J. Benoliel, C.M.M. Almeida, Analysis of pharmaceutical compounds in water by SPE-UPLC-ESI-MS/MS, Quimica Nova 37 (2014) 138-U191.
[2] R. Salgado, J.P. Noronha, A. Oehmen, G. Carvalho, M.A.M. Reis, Analysis of 65 pharmaceuticals and personal care products in 5 wastewater treatment plants in Portugal using a simplified analytical methodology, Water Sci. Technol. 62 (2010) 2862-2871.