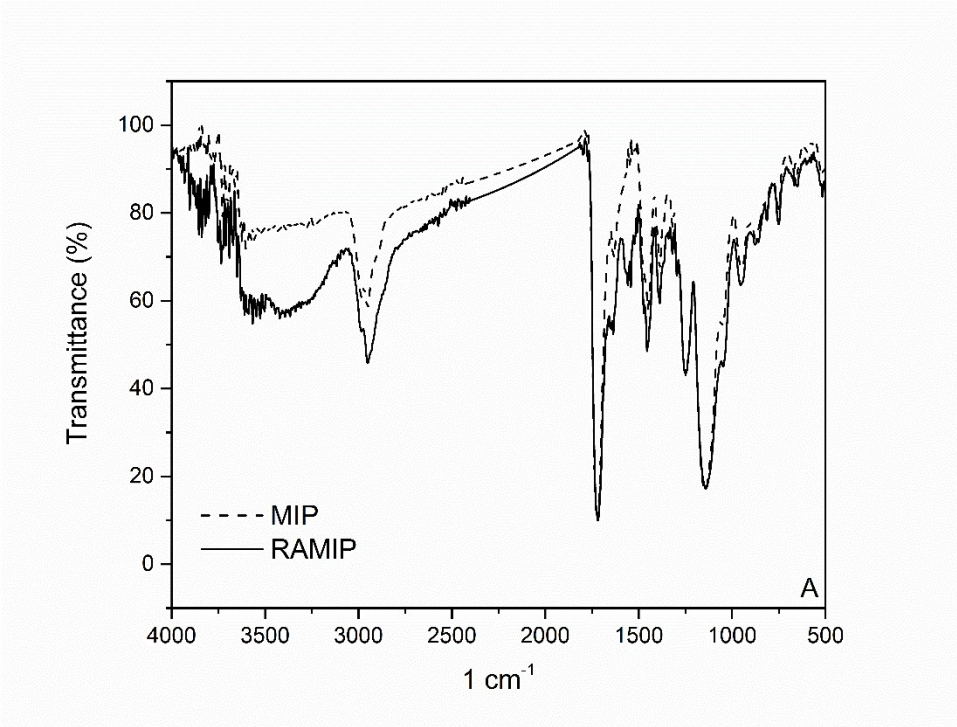
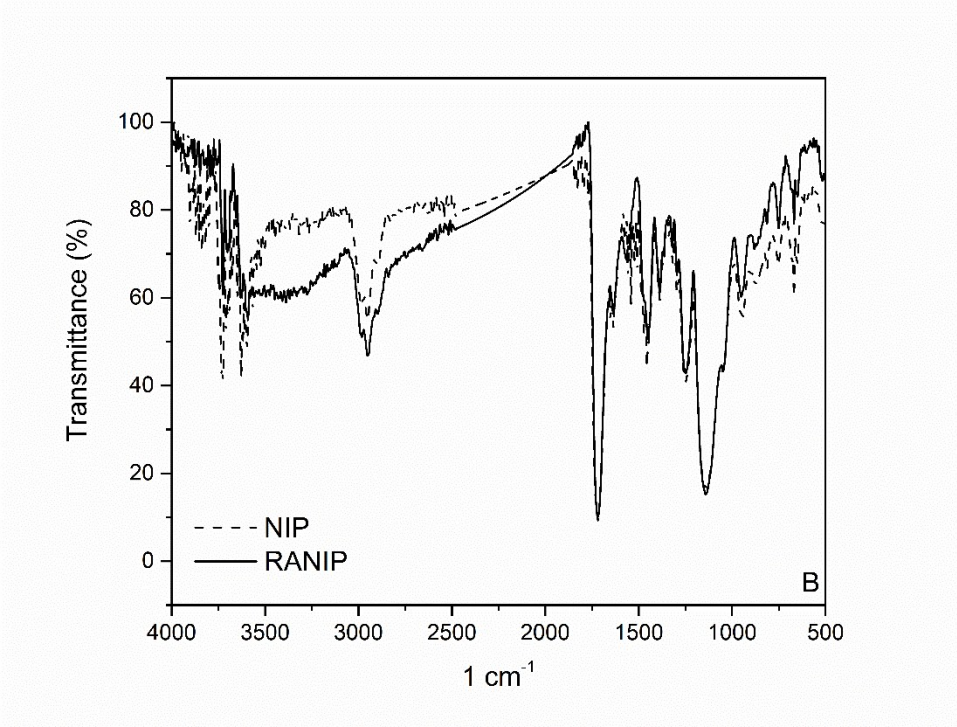
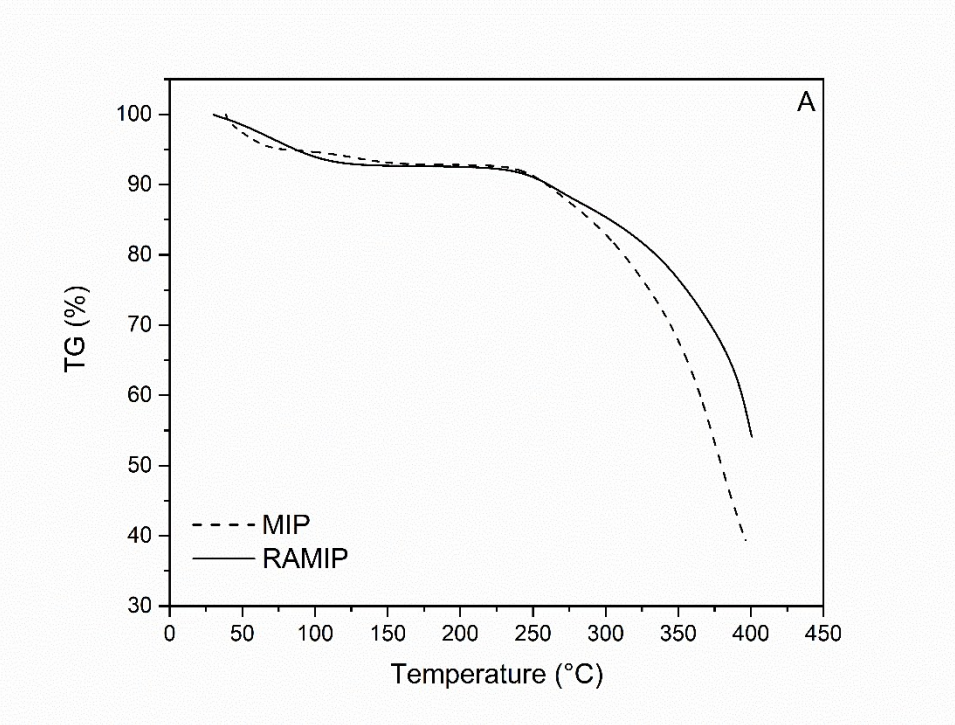
Electronic Supplementary Material (ESI) for Analyst.

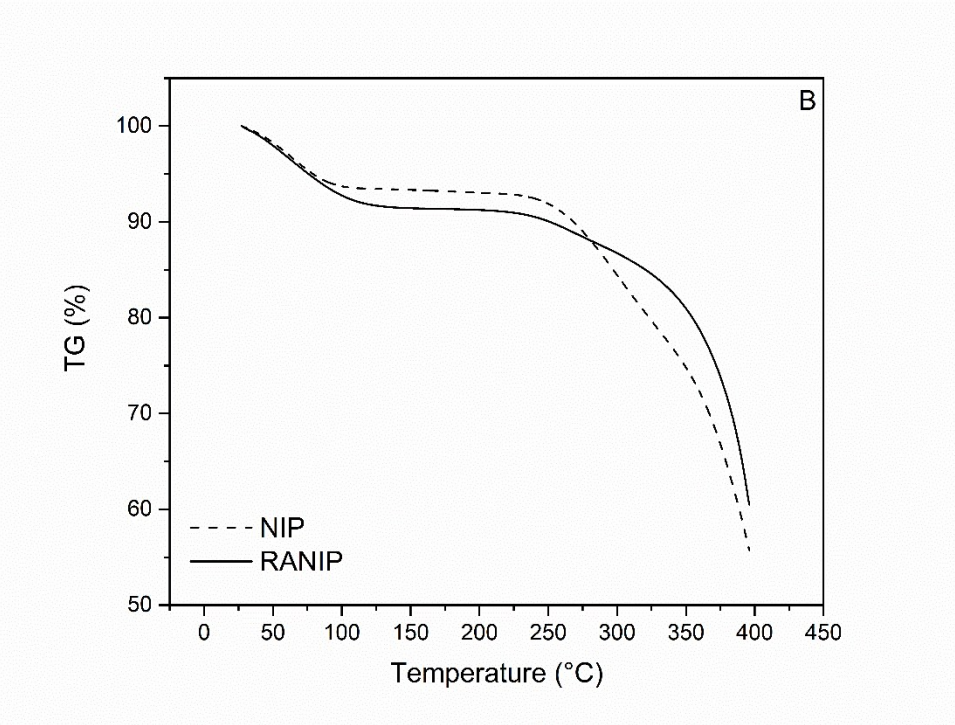
Electronic supplementary information (ESI 1). Infrared spectra of MIP and RAMIP (A), and NIP and RANIP (B) fibers.





Electronic supplementary information (ESI 2). Thermogravimetric curves of MIP and RAMIP (A), and NIP and RANIP (B) fibers.



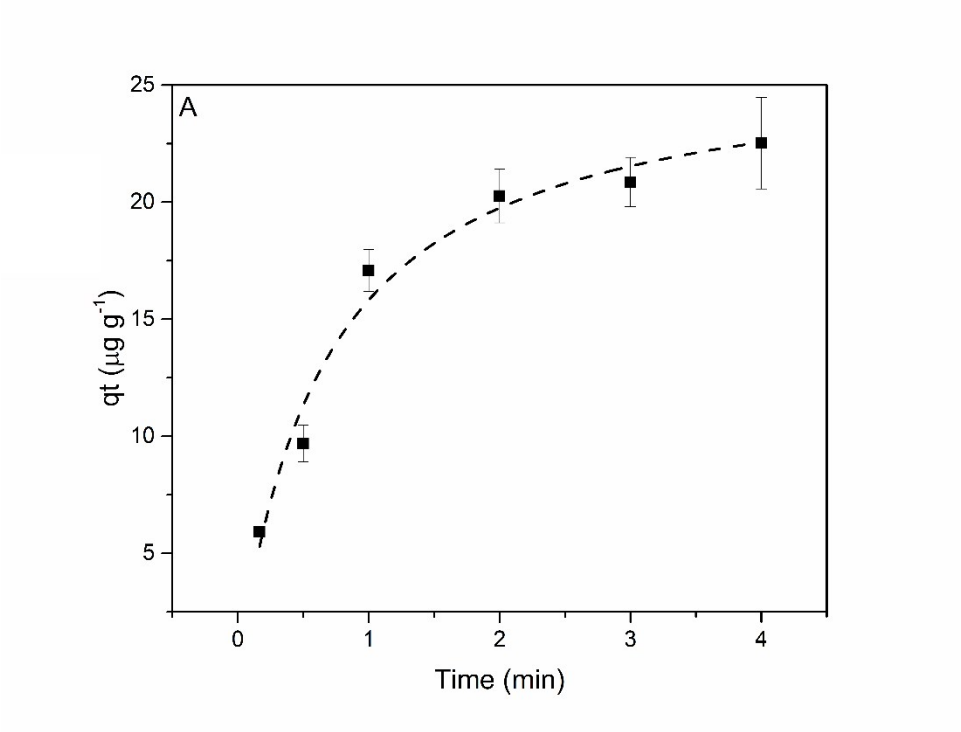


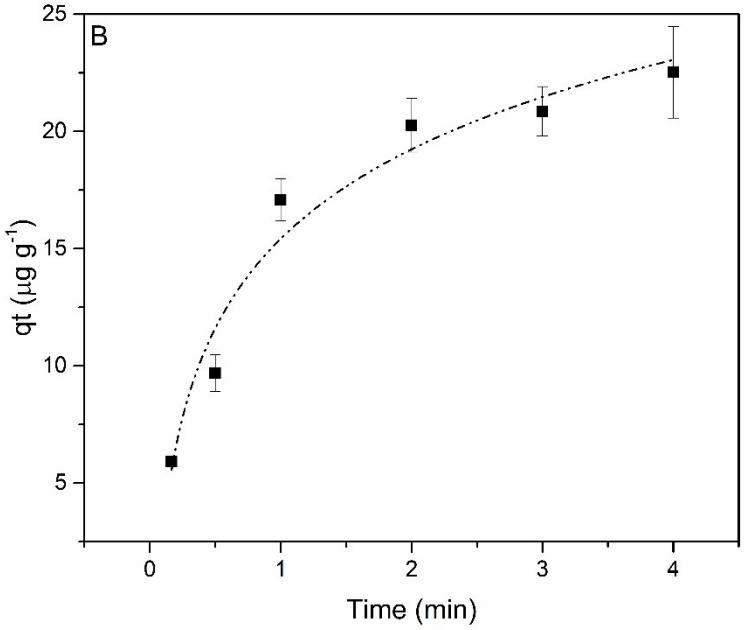
Electronic supplementary information (ESI 3). Kinetic parameters of DIA adsorption to RAMIP fibers.

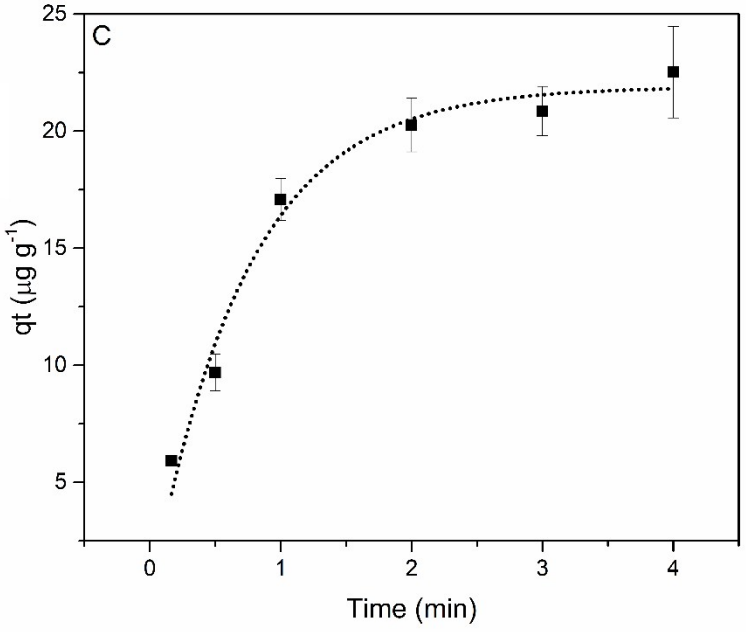
Kinetic model	Equation	Parameter	Value obtained	Standard error
Pseudo-first order	$q_t = q_e[1 - exp(-k_1 t)]$	q_e (μg g^{-1})	21.8951	0.7893
		k_1 (min^{-1})	1.3806	0.1724
		R^2	0.9723	-
		F_{error}	0.2121	-
Pseudo-second order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	q_e (μg g^{-1})	26.2909	1.4848
		k_2 (g μg^{-1} min^{-1})	0.0574	0.0141
		R^2	0.9705	-
		F_{error}	0.0032	-
Chemisorption (Elovich)	$q_t = \frac{1}{\beta} Ln(\alpha\beta) + \frac{1}{\beta} Ln(t)$	α (μg g^{-1} min^{-1})	90.4990	19.4763
		β (g μg^{-1})	0.1816	0.0177
		R^2	0.9545	-
		F_{error}	0.0000	-
Fractionary order (Avrami)	$q_t = q_e\{1 - exp[-(k_{AV} t)]^n$	q_e (μg g^{-1})	21.8951	0.7893
		k_{AV} (min^{-1})	1.3806	0.1724
		n_{AV}	1	0
		R^2	0.9723	-
		F_{error}	0.2449	-

q_t: Amount of analyte adsorbed at time t; q_e: Amount of analyte adsorbed at equilibrium *per* gram material; t: Time of contact; k_1: Pseudo-first order rate constant; k_2: Pseudo-second order rate constant; α: Inicial adsorption rate of Elovich equation; β: Elovich constant related to the extent of surface coverage and also to the activation energy involved in chemisorption; k_{AV}: Avrami kinetic constant; n_{AV}: Fractionary reaction order (Avrami) related to adsorption mechanism.

Electronic supplementary information (ESI 4). Kinetic models of DIA adsorption to RAMIP fibers. Pseudo-second order (A), chemisorption (B), and fractionary order (C).




B
qt (μg g-1)
Time (min)
25
20
15
10
5
0
1
2
3
4


C
qt (μg g-1)
Time (min)
25
20
15
10
5
0
1
2
3
4

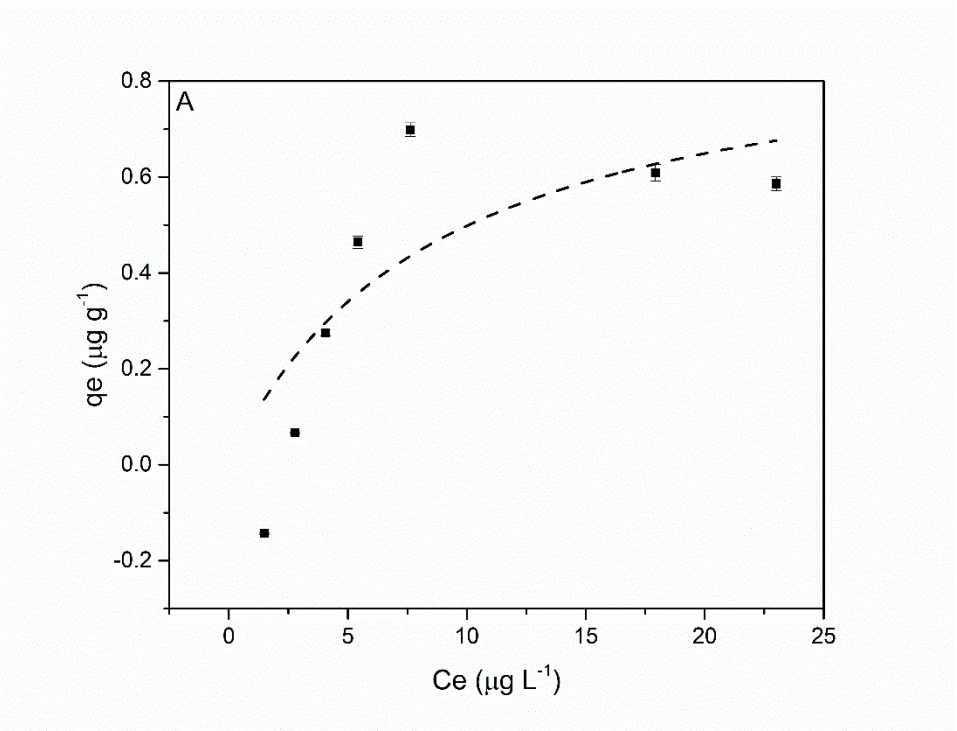
Electronic supplementary information (ESI 5). Isotherm parameters of DIA adsorption to RAMIP and RANIP fibers.

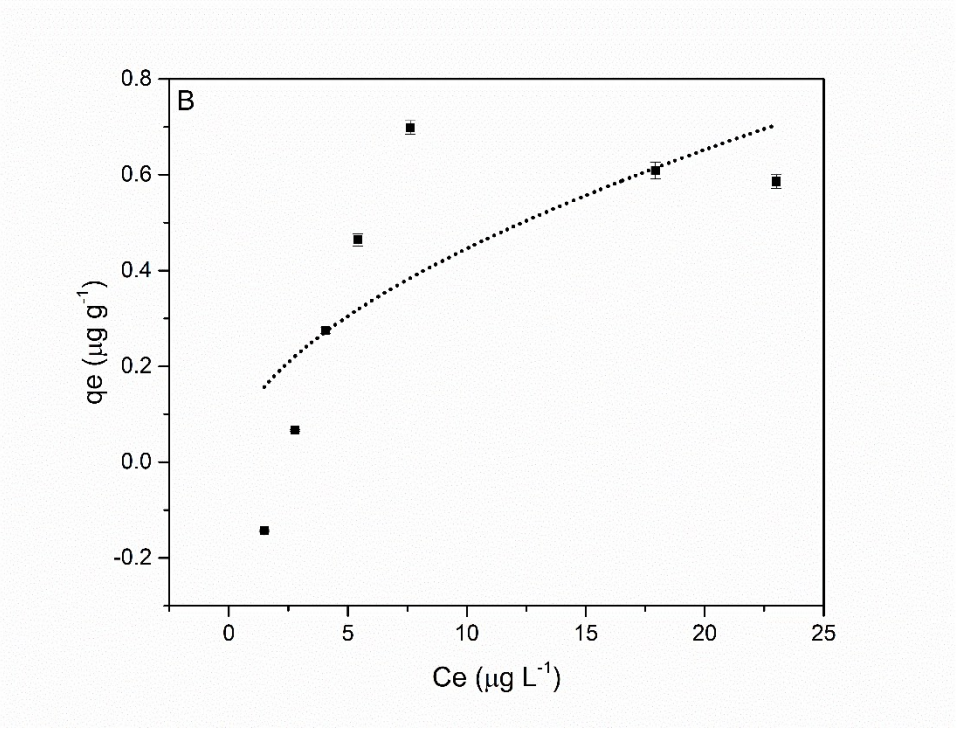
Isotherm model	Equation	Parameter	Value obtained	Standard error
Langmuir	$q_e = \frac{q_s K_L C_e}{1 + K_L C_e}$	q_s (µg g^{-1})	0.9316	0.4300
		K_L (µg L^{-1})	0.1150	0.1196
		R^2	0.6042	-
		F_{error}	0.0177	-
Freundlich	$q_e = K_F C_e^{1/n_F}$	K_F (µg g^{-1}) (µg L^{-1})^n	0.1260	0.0934
		n_F	1.8220	0.9258
		R^2	0.4917	-
		F_{error}	0.0060	-
	$q_s K_s C_e^{1/n_s}$	q_s (µg g^{-1})	0.6294	0.0578
		K_s (µg L^{-1})	0.0002	0.0010

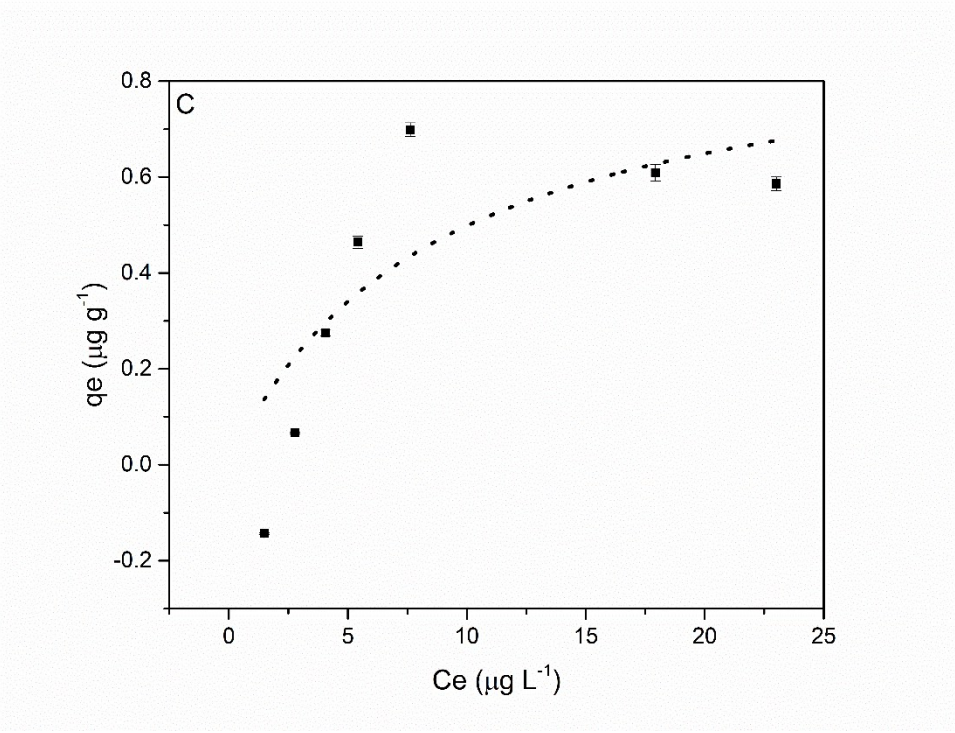
		n_s	5.7814	3.1568
		R^2	0.9146	-
		F_{error}	0.0080	-
Khan	$q_e = \frac{q_s b_K C_e}{(1 + b_K C_e)^{a_K}}$	q_s (μg g^{-1})	1.3775	0.2212
		a_K	3.1530	2.8428
		b_K	0.0572	0.0162
		R^2	0.6889	-
		F_{error}	0.0417	-
Redlich-Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e^g}$ where $0 \leq g \leq 1$	K_R (g L^{-1})	0.1071	0.2441
		a_R (μg L^{-1})	0.1150	1.1245
		g	1	2.1995
		R^2	0.5053	-
		F_{error}	0.0198	-
Toth	$q_e = \frac{K_T C_e}{(a_T + C_e)^{1/t}}$	K_T (μg g^{-1})	607.21	4833.57
		a_T (L μg^{-1})	7693.31	62868.5
		t	0.320	0.264
		R^2	0.689	-
		F_{error}	0.042	-

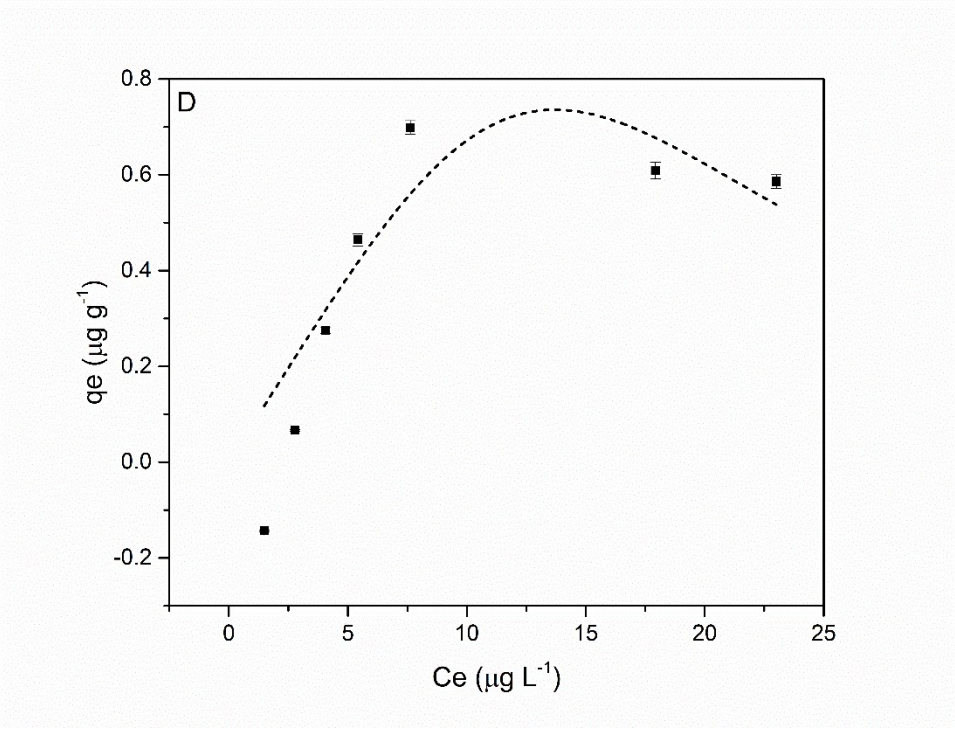
q_e: Amount of adsorbed analyte at equilibrium *per* gram of material; q_s: Theoretical saturation capacity; K_L: Langmuir affinity constant; C_e: Analyte concentration at equilibrium; K_F and n_F: Constant and exponent of Freundlich model, respectively; K_s and n_s: Constant and exponent of Sips model, respectively; a_K and b_K: Constant and exponent of Khan model, respectively; K_R and a_R: Constant and g is exponent of Redlich-Peterson model, respectively; K_T and a_T: Constants isotherm of Toth model; t: Exponent of Toth model.

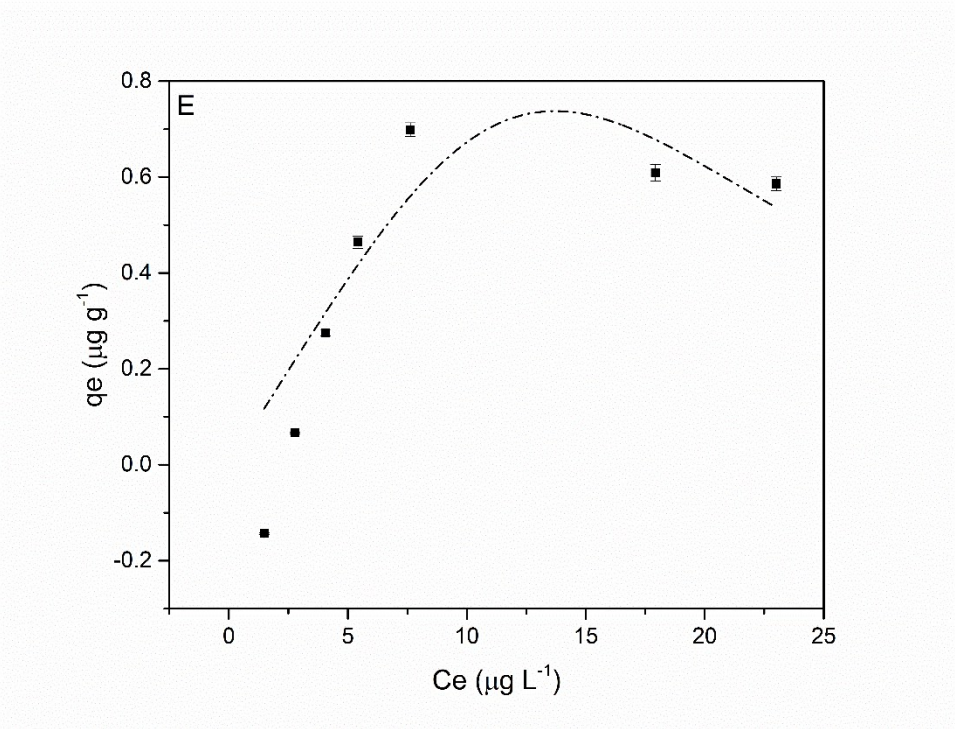
Electronic supplementary information (ESI 6). Adsorption isotherm models of DIA to RAMIP fibers. Langmuir (A), Freundlich (B), Redlich-Peterson (C), Toth (D), and Khan (E).


A
0.8
0.6
0.4
0.2
0.0
-0.2
qe (μg g-1)
0
5
10
15
20
25
Ce (μg L-1)


B
0.8
0.6
0.4
0.2
0.0
-0.2
qe (μg g-1)
0
5
10
15
20
25
Ce (μg L-1)


C
0.8
0.6
0.4
0.2
0.0
-0.2
qe (μg g-1)
0
5
10
15
20
25
Ce (μg L-1)


D
0.8
0.6
0.4
0.2
0.0
-0.2
qe (μg g-1)
0
5
10
15
20
25
Ce (μg L-1)


E
0.8
0.6
0.4
0.2
0.0
-0.2
qe (μg g-1)
0
5
10
15
20
25
Ce (μg L-1)

Electronic supplementary information (ESI 7). Optimization of the solid phase microextraction.

Regarding pH, no differences in the adsorption capacities were observed for none of the analytes. As a possible explanation, the tested pHs were higher than the main pka values of BRO, CLO, ALP, NOR, and DIA (2.65, 1.89, 5.01, 2.85, and 2.92, respectively).[32] Thus, all the analytes were in the same non-ionized form, presenting the same adsorption behavior. Given that the pH of plasma samples is about 7.2, the condition with no sample pH adjustment was selected for the next experiments. pH values lower than 6.0 were not evaluated because the efficient protein exclusion is obtained for pHs higher than the isoelectric point of the BSA (4.7 to 5.6)[21], once most of the proteins are negatively charged, resulting in electrostatic repulsion.[21,23] Besides, at the plasma pH, the carboxylic group of the MAA (pka = 4,6)[33] is ionized, while BRO, CLO, ALP, NOR, and DIA are on their non-ionized form (main pkas lower than 7.2), thus favoring the adsorption of the analytes to the fiber by ion-dipole interactions.

The sample dilution was also studied in five different proportions: 1:0.5, 1:1, 1:1.5, 1:2, and 1:2.5 (v:v, sample:water). The best results were obtained in the proportion of 1:0.5 (v:v), probably due to the lower viscosity of the sample and the dilution of the potential interferents, improving the adsorption of the main analytes. Additionally, both 200 and 1000 µL were evaluated as sample volumes, and the best adsorption was obtained for 1000 µL, being this value selected for further experiments.

The extraction times of 1, 5, 10, 15, 20, 25, and 30 min were studied to determine the equilibrium time of the distribution of the analytes from the sample matrix to the sorbent coating (RAMIP). The adsorption of the analytes increased in about 100% when the time was increased from 1 to 20 min. From this point, no enhance in the adsorption was observed (25 and 30 min). Thus, 20 min was entitled as the extraction time for these analyses.

Regarding the elution step, the following solvents were evaluated: acetonitrile, methanol, and a mobile phase consisted of water:acetonitrile:methanol

(60:30:10, v:v:v). The mobile phase elution capacity was about 20% lower than methanol and acetonitrile (both presented the same performance as eluent). Thus, acetonitrile was selected, and its volume was studied from 200 and 350 µL. The best result was obtained with 200 µL (about 60% higher in comparison with 350 µL). Lower volumes were not evaluated due to the sampling difficult during the HPLC analyses of the eluates. The elution time was also studied from 5 to 25 min, and no significant differences were observed in the analytical responses. Thus, the time of 5 min was selected as work condition.