Supplementary Information

Precise evaluation of batch adsorption kinetics of plant total polyphenols based on a flow-injection online spectrophotometric method

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Captions

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1. Specification parameters of the resins tested

Table S1 Specification parameters of the resins tested.

Resins	Particle size (mm)	Surface area (m^2/g)	Average pore diameter (nm)	Polarity
D101	0.3-1.25	550-600	10-11	Non-polar
AB-8	0.3-1.25	480-520	13-14	Weak-polar
ADS-17	0.3-1.2	90-150	25-30	Moderate polar
HPD-100	0.3-1.25	650-700	8.5-9	Non-polar
HPD-300	0.3-1.2	800-870	5-5.5	Non-polar
HPD-500	0.3-1.2	500-550	55-75	Polar
HPD-600	0.3-1.2	550-600	8	Strong Polar
HPD-750	0.3-1.25	650-700	8.5-9	Moderate polar
NKA-9	0.3-1.25	250-290	15.5-16.5	Strong Polar
X-5	0.3-1.2	500-600	29-30	Weak-polar

2. Fiber-optic sensing system

The fiber-optic sensing detection system consists of a stable and continuous source of spectrum light (190-2500 nm) which was provided by a DH-2000 Deuterium-Halogen Light Source. A USB2000+ Fiber Optic spectrometer and the light source were connected by two UV-grade optical fibers (400 μm diameter, 2 m long) to a FIA-Z-SMA-Peek Lensed flow cell with 10 mm of optical path length and 60 μL of internal volume (all from Ocean Optics, Dunedin, Florida, USA). First, the light source was turned on for at least 30 min to warm-up. The spectra suite software was activated and the average number of times was adjusted to 10 ms, and the smoothing width was set to 5. Keeping the carrier stream running, the signal intensity level was adjusted to 3500 counts at the corresponding detection wavelength (765 nm), then reference and dark spectra were stored.[1,2] Afterwards, the timing diagram was opened to choose and save the acquisition data mode, detection wavelength and other parameters.

3. Determination of total polyphenol content

Table S2 Comparison of TPCs in several plants determined by the two methods (mg/g, n=6).

No.	Sample	TPCs determined by conventional method ± SD	TPCs determined by FIA method ± SD
1	Alfalfa **	9.484 ± 0.592	7.302 ± 0.0098
2	Elaeagnus angustifolia **	11.25 ± 0.564	10.53 ± 0.340
3	Apple peel **	18.36 ± 0.917	15.12 ± 0.197
4	Yellow chrysanthemum ^{ns}	49.18 ± 2.84	52.33 ± 0.381
5	Dracocephalum moldavica L ^{ns}	49.88 ± 1.935	52.96 ± 0.328
6	White chrysanthemum ^{ns}	54.07 ± 1.045	56.67 ± 0.263
7	Dried mulberry ^{ns}	60.01 ± 2.547	62.87 ± 0.275
8	Black lycium barbarum **	73.37 ± 3.525	70.28 ± 0.148
9	Snow chrysanthemum **	162.3 ± 4.112	152.6 ± 0.374
10	Pomegranate peel **	224.9 ± 15.3	222.3 ± 0.374

Note: P > 0.05 for ^{ns}, no significant difference. P ≤ 0.01 for **, extremely significant difference.

4. Resin screening

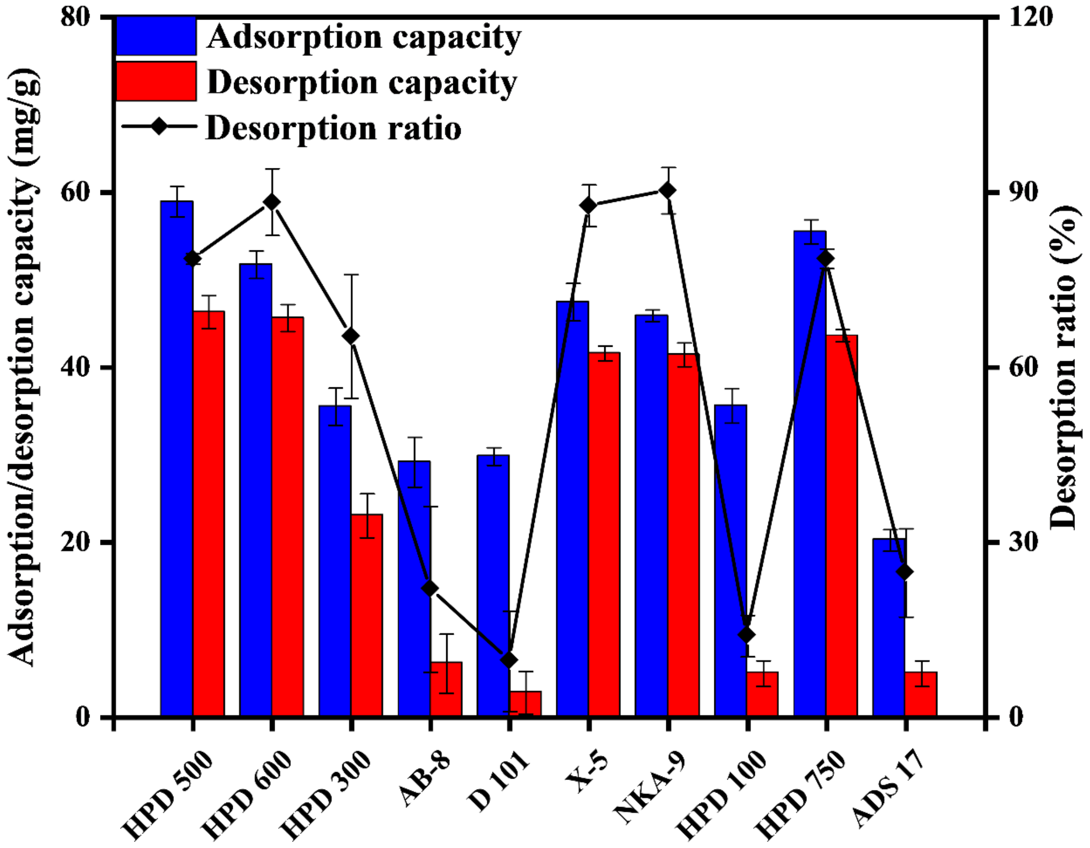

Fig. S1 Adsorption/desorption capacities and desorption ratio of PPTPs on different resins. (Initial concentration/volume of PPTP extract: 161.9 mg/L 200 mL, adsorption solvent: deionized water, desorption solvent: 60% ethanol 100 mL).

5. Adsorption/desorption kinetic models of SCTPs on HPD-500 resin

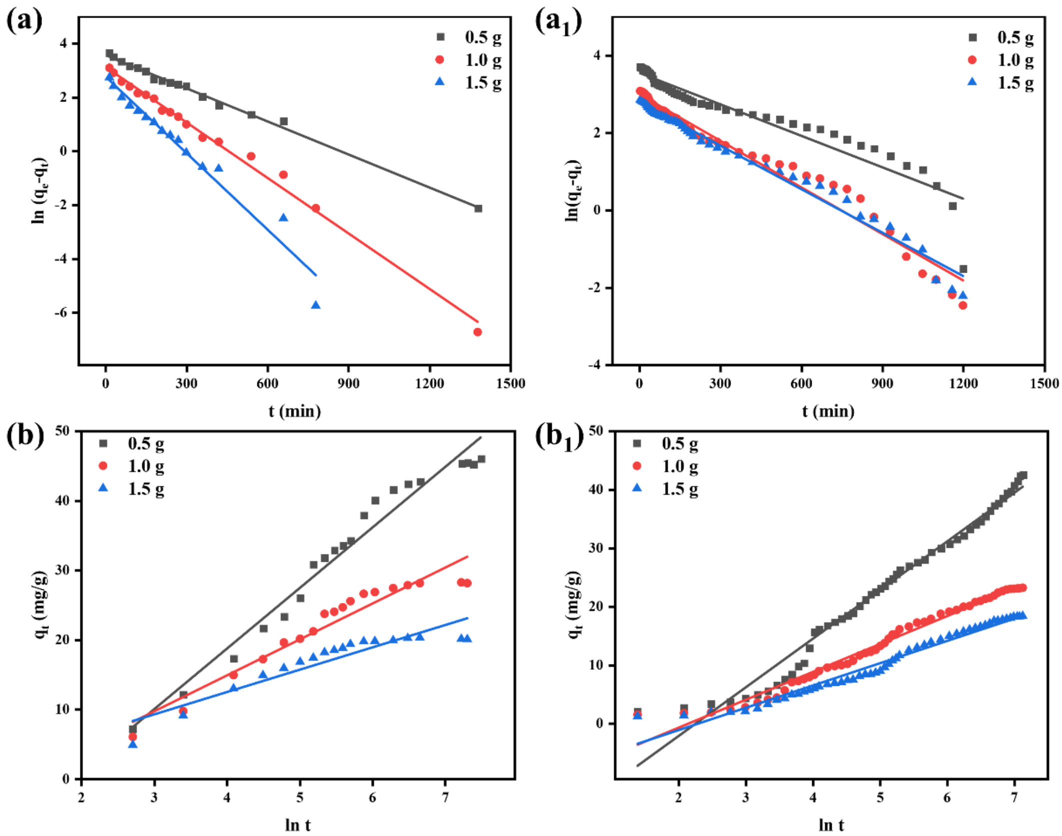

Fig. S2 Linear fitting of the adsorption kinetics of SCTPs on HPD-500 resin: (a-a$_1$). PFO model; (b-b$_1$). Elovich model.

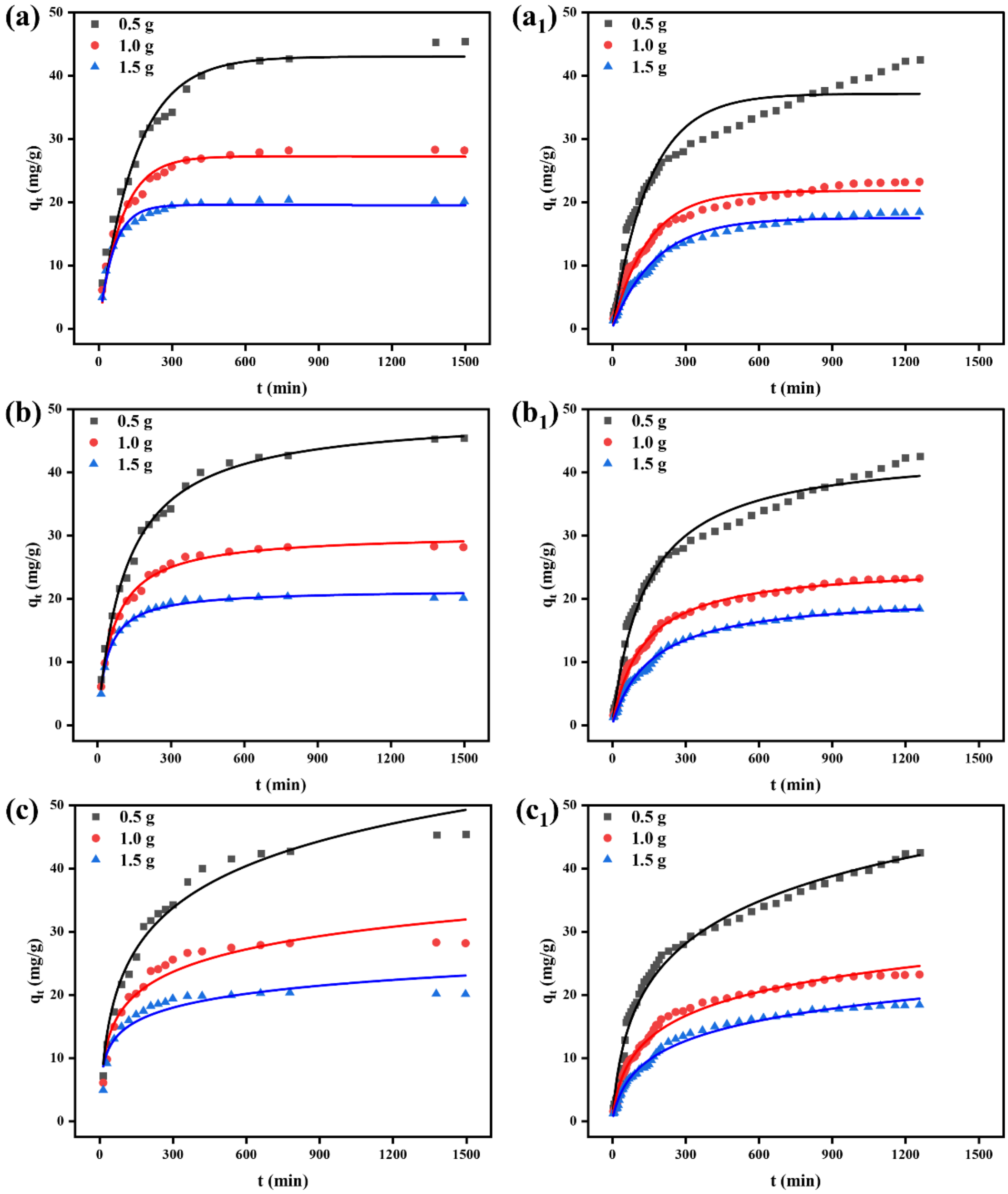

Fig. S3 Nonlinear fitting of the adsorption kinetics of SCTPs on HPD-500 resin: (a-a_1). PFO model; (b-b_1). PSO model; (c-c_1). Elovich model.

Table S3 Nonlinear fitting parameters of adsorption kinetic models for SCTPs on HPD-500 resin.

Detection methods	Adsorbent (g)	q_{exp} (mg/g)	PFO q_{cal} (mg/g)	PFO $k_1\times10^2$ (1/min)	PFO R^2	PSO q_{cal} (mg/g)	PSO $k_2\times10^{-3}$ [g/(mg·min)]	PSO R^2
conventional	0.5	46.01	43.01	0.662	0.9641	49.04	1.776	0.9916
	1.0	28.12	27.20	1.0063	0.9623	30.28	5.119	0.9911
	1.5	20.04	19.50	1.639	0.9676	21.38	11.5	0.9905
FIA	0.5	42.53	37.13	0.648	0.9607	43.76	1.64	0.9844
	1.0	23.17	21.72	0.679	0.9804	25.31	3.08	0.9957
	1.5	18.34	17.39	0.558	0.9821	20.66	2.98	0.9946

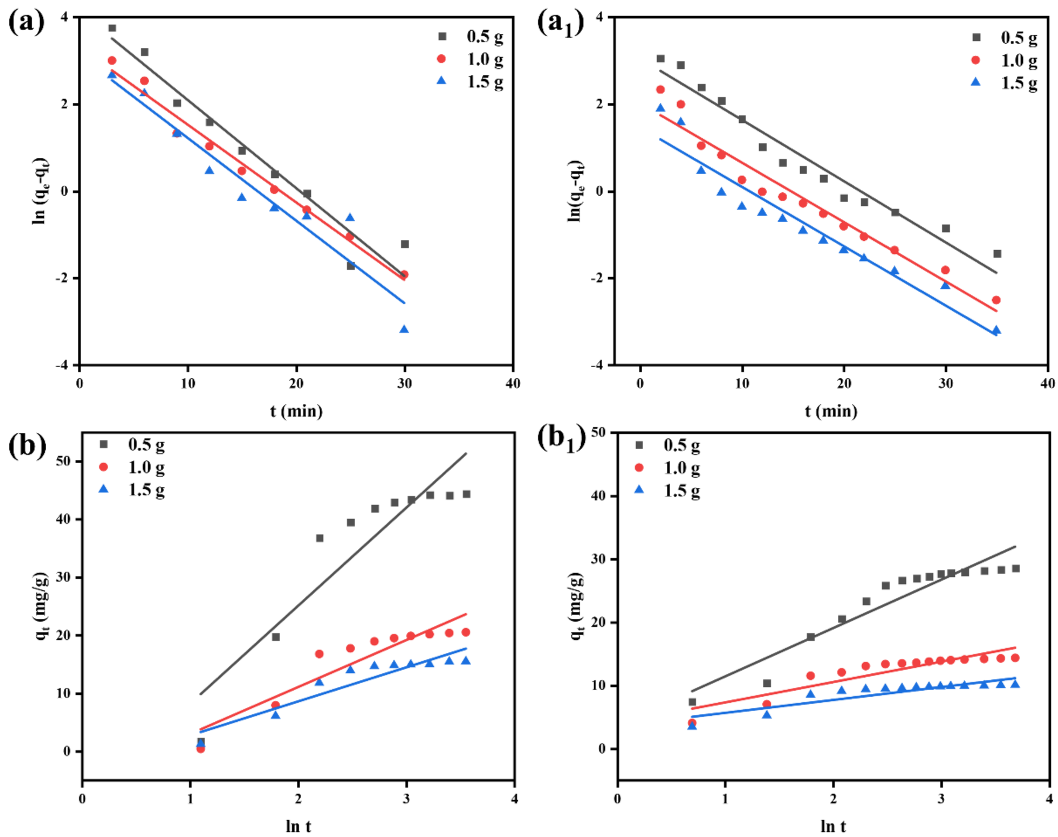

Fig. S4 Linear fitting of the desorption kinetics of SCTPs on HPD-500 resin: (a-a_1). PFO model; (b-b_1). Elovich model.

Table S4 Linear fitting parameters of desorption kinetic models for SCTPs on HPD-500 resin.

Detection methods	Adsorbent (g)	q_{exp} (mg/g)	PFO q_{cal} (mg/g)	PFO $k_1 \times 10$ (1/min)	PFO R^2	PSO q_{cal} (mg/g)	PSO $k_2 \times 10^{-3}$ [g/(mg·min)]	PSO R^2
conventional	0.5	44.38	61.44	2.026	0.9413	40.50	0.3556	0.9817
	1.0	20.51	27.41	1.787	0.9801	18.94	8.405	0.9843
	1.5	15.46	22.61	1.901	0.9127	14.32	10.97	0.9804
FIA	0.5	28.56	21.01	1.410	0.9484	33.44	5.74	0.9813
	1.0	14.33	7.514	1.367	0.9474	15.81	19.8	0.9900
	1.5	10.04	4.297	1.366	0.9233	10.83	37.8	0.9932

Table S5 IPD desorption kinetic model parameters of SCTPs on HPD-500 resin.

Detection methods	Adsorbent (g)	K_{id1} [mg/(mL·min$^{1/2}$)]	R^2	K_{id2} [mg/(mL·min$^{1/2}$)]	R^2	K_{id3} [mg/(mL·min$^{1/2}$)]	R^2
conventional	0.5	27.57	0.9930	3.498	0.8929	0.1863	0.8034
	1.0	12.80	0.9712	1.897	0.9256	0.3859	0.9897
	1.5	8.258	0.9704	0.8824	0.9932	0.5844	0.8480
FIA	0.5	9.677	0.8059	6.833	0.9533	0.6312	0.8957
	1.0	7.118	0.9247	1.514	0.7919	0.2997	0.9125
	1.5	4.797	0.8873	0.4664	0.8909	0.1603	0.9507

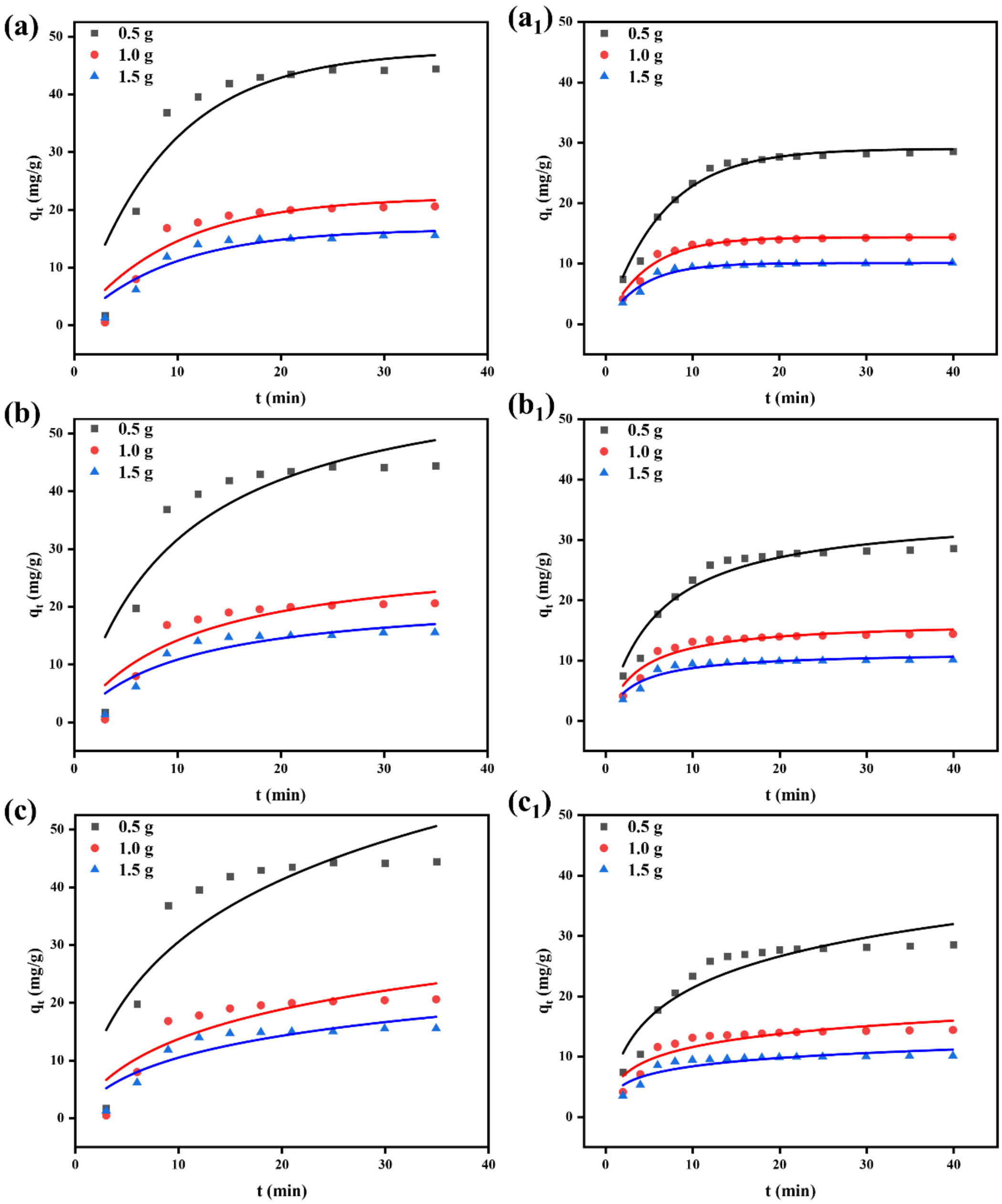

Fig. S5 Nonlinear fitting of the desorption kinetics of SCTPs on HPD-500 resin: (a-a_1). PFO model; (b-b_1). PSO model; (c-c_1). Elovich model.

Table S6 Nonlinear fitting parameters of desorption kinetic models for SCTPs on HPD-500 resin.

Detection methods	Adsorbent (g)	q_{exp} (mg/g)	PFO			PSO		
			q_{cal} (mg/g)	$k_1 \times 10$ (1/min)	R^2	q_{cal} (mg/g)	$k_2 \times 10^2$ [g/(mg·min)]	R^2
conventional	0.5	44.38	47.60	1.147	0.8517	62.51	0.163	0.8058
	1.0	20.51	22.12	1.060	0.8456	29.60	0.306	0.8062
	1.5	15.46	16.58	1.091	0.8733	21.96	0.434	0.8309
FIA	0.5	28.56	28.96	1.536	0.9778	34.83	0.497	0.9353
	1.0	14.33	14.26	2.116	0.9623	16.48	1.621	0.9039
	1.5	10.04	9.985	2.398	0.9538	11.35	2.827	0.8848

6. Adsorption and desorption kinetic curves of PPTPs on HPD-500 resin

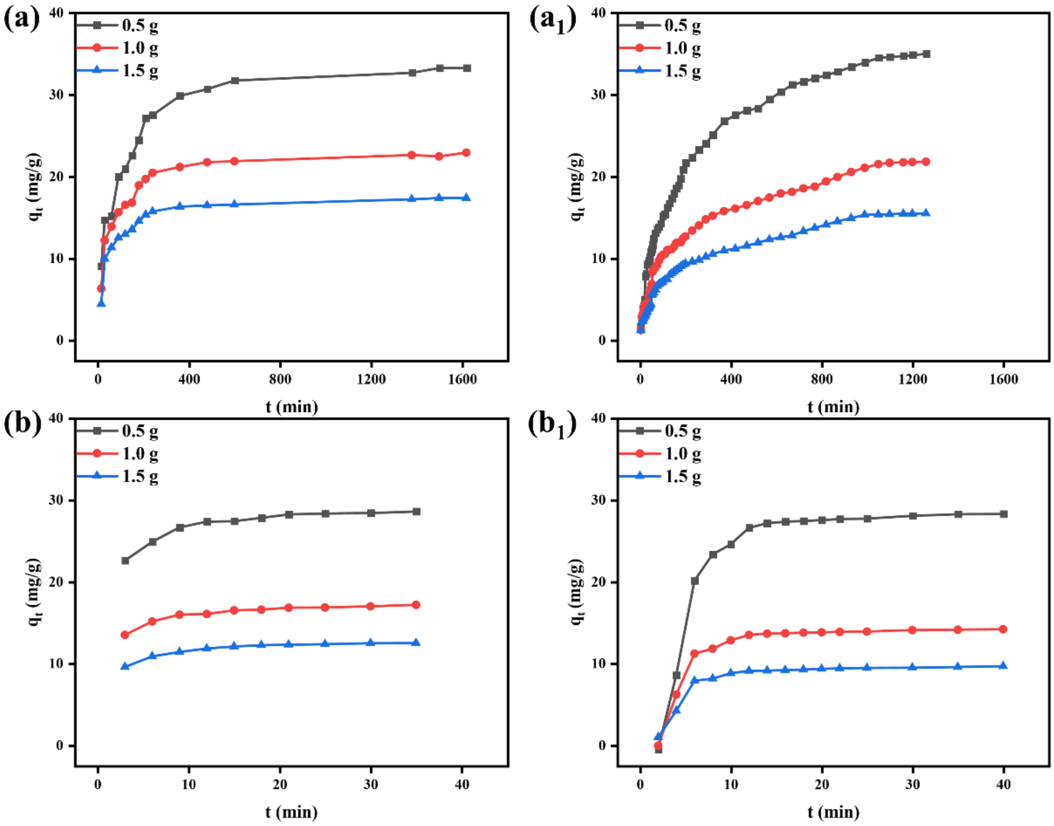

Fig. S6 Adsorption and desorption kinetic curves of PPTPs on HPD-500 resin: (a-b). obtained by conventional spectrophotometric method; (a_1-b_1). obtained by FIA spectrophotometric method.

7. Adsorption/desorption kinetic models of PPTPs on HPD-500 resin

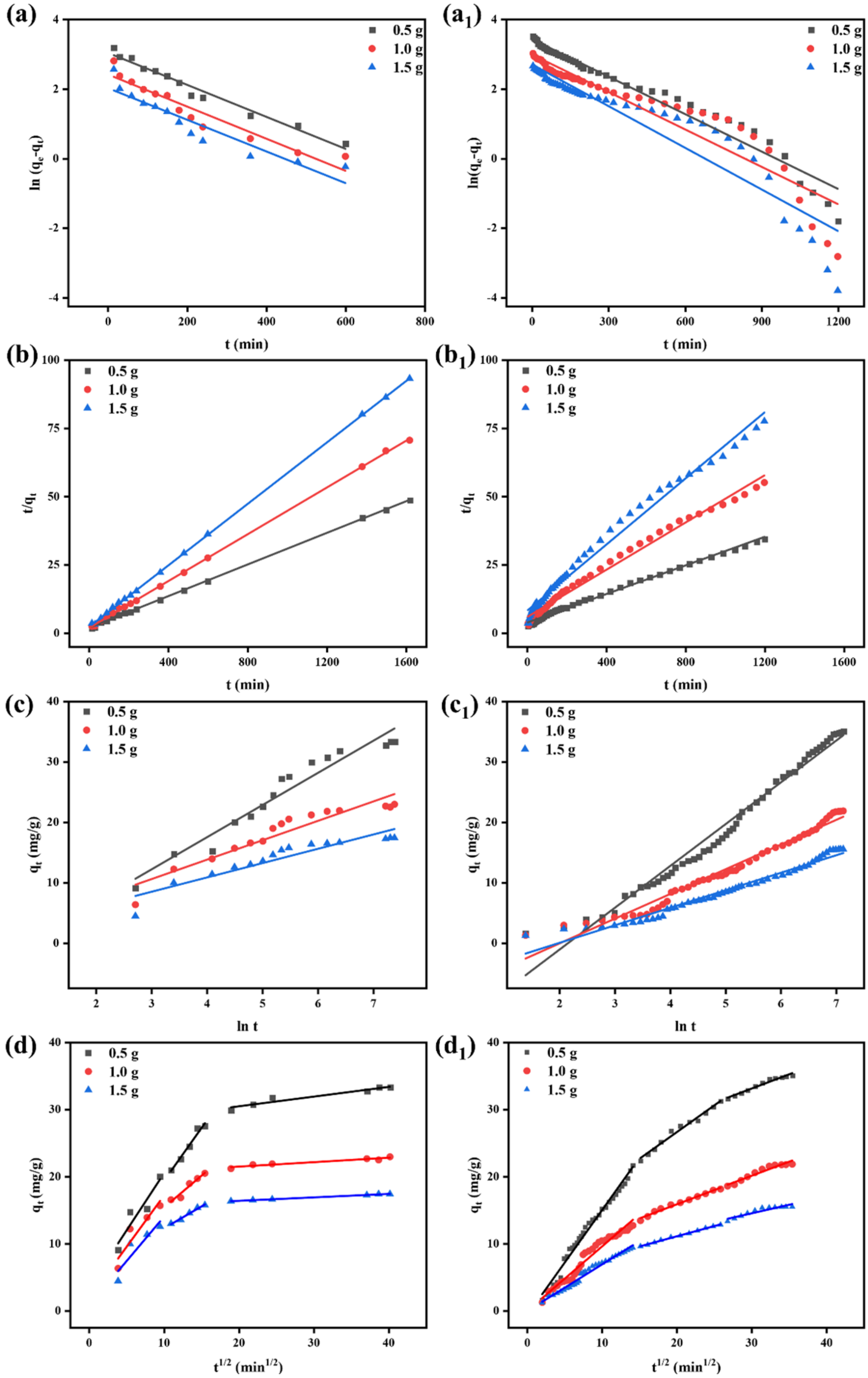

Fig. S7 Linear fitting of the adsorption kinetics of PPTPs on HPD-500 resin: (a-a_1). PFO model; (b-b_1). PSO model; (c-c_1). Elovich model; (d-d_1). IPD model.

Table S7 Linear fitting parameters of adsorption kinetic models for PPTPs on HPD-500 resin.

Detection methods	Adsorbent (g)	q_{exp} (mg/g)	PFO q_{cal} (mg/g)	PFO $k_1 \times 10^2$ (1/min)	PFO R^2	PSO q_{cal} (mg/g)	PSO $k_2 \times 10^{-4}$ [g/(mg·min)]	PSO R^2
conventional	0.5	33.30	20.96	0.4612	0.9684	34.52	4.675	0.9995
	1.0	22.94	11.25	0.4634	0.9080	23.33	10.54	0.9997
	1.5	17.37	7.591	0.4562	0.8670	17.76	15.09	0.9999
FIA	0.5	35.04	31.04	0.3592	0.9630	38.17	1.865	0.9952
	1.0	21.83	19.94	0.3598	0.8889	23.10	3.272	0.9893
	1.5	15.49	14.98	0.4002	0.8878	16.50	4.573	0.9875

Table S8 IPD adsorption kinetic model parameters of PPTPs on HPD-500 resin.

Detection methods	Adsorbent (g)	K_{id1} [mg/(mL·min$^{1/2}$)]	R^2	K_{id2} [mg/(mL·min$^{1/2}$)]	R^2	K_{id3} [mg/(mL·min$^{1/2}$)]	R^2
conventional	0.5	1.702	0.8257	1.571	0.9614	0.1442	0.9137
	1.0	1.530	0.8019	0.9494	0.9293	0.06630	0.9018
	1.5	1.322	0.7425	0.6517	0.9809	0.05100	0.9957
FIA	0.5	1.564	0.9827	0.7947	0.9799	0.4223	0.9606
	1.0	0.961	0.9576	0.4225	0.9821	0.4176	0.9252
	1.5	0.6940	0.9785	0.3038	0.9963	0.2539	0.8582

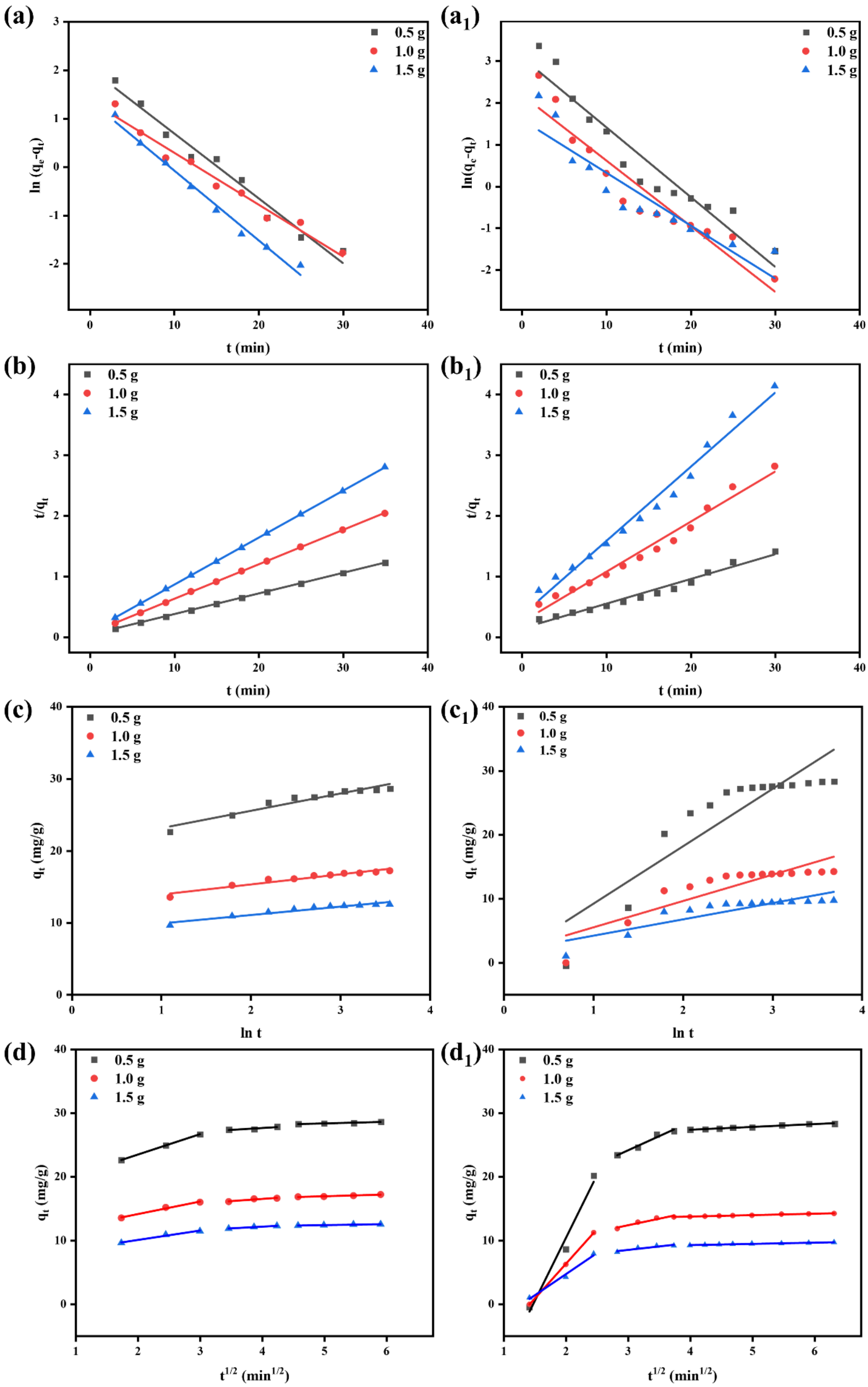

Fig. S8 Linear fitting of the desorption kinetics of PPTPs on HPD-500 resin: (a-a$_1$). PFO model; (b-b$_1$). PSO model; (c-c$_1$). Elovich model; (d-d$_1$). IPD model.

Table S9 Linear fitting parameters of desorption kinetic models for PPTPs on HPD-500 resin.

Detection methods	Adsorbent (g)	q_{exp} (mg/g)	PFO			PSO		
			q_{cal} (mg/g)	k_1×10 (1/min)	R^2	q_{cal} (mg/g)	k_2×10 [g/(mg·min)]	R^2
conventional	0.5	28.61	7.592	1.340	0.9723	29.32	0.3556	0.9999
	1.0	17.19	3.898	1.072	0.9692	17.60	0.5721	0.9991
	1.5	12.49	3.901	1.442	0.9862	12.91	0.7188	0.9999
FIA	0.5	28.31	21.92	1.672	0.9110	24.55	0.1217	0.9723
	1.0	14.21	8.923	1.571	0.8913	12.11	0.2790	0.9765
	1.5	9.669	4.912	1.267	0.8406	8.179	0.4201	0.9787

Table S10 IPD desorption kinetic model parameters of PPTPs on HPD-500 resin.

Detection methods	Adsorbent (g)	K_{id1} [mg/(mL·min$^{1/2}$)]	R^2	K_{id2} [mg/(mL·min$^{1/2}$)]	R^2	K_{id3} [mg/(mL·min$^{1/2}$)]	R^2
conventional	0.5	3.201	0.9999	0.5963	0.6407	0.2489	0.9368
	1.0	1.966	0.9740	0.6870	0.7797	0.2704	0.9010
	1.5	1.471	0.9533	0.5306	0.9770	0.1581	0.9179
FIA	0.5	19.73	0.9586	4.432	0.9508	0.4424	0.9723
	1.0	10.88	0.9997	2.052	0.8946	0.2229	0.8078
	1.5	6.624	0.9752	1.086	0.8078	0.1908	0.9586

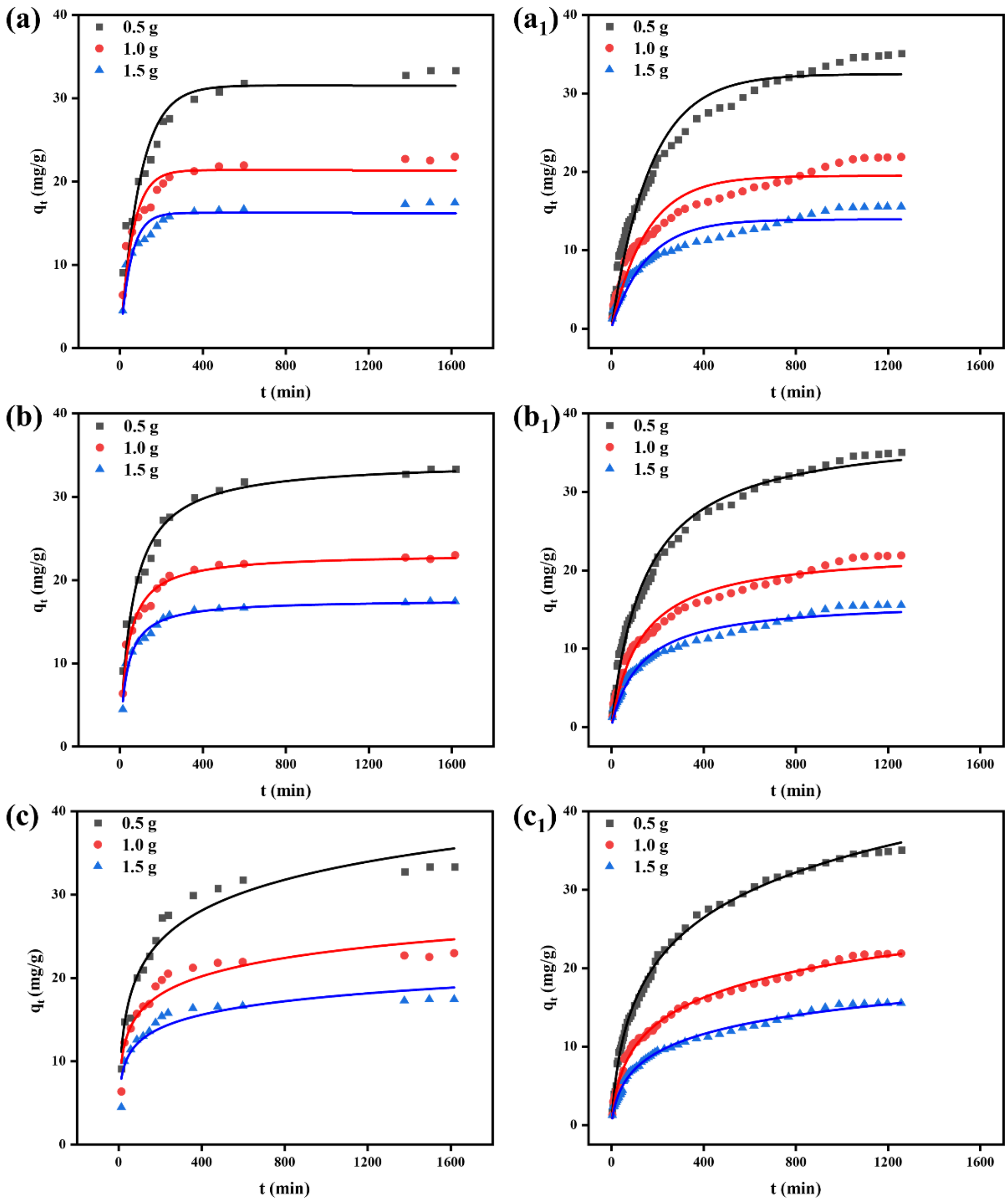

Fig. S9 Nonlinear fitting of the adsorption kinetics of PPTPs on HPD-500 resin: (a-a_1). PFO model; (b-b_1). PSO model; (c-c_1). Elovich model.

Table S11 Nonlinear fitting parameters of adsorption kinetic models for PPTPs on HPD-500 resin.

Detection methods	Adsorbent (g)	q_{exp} (mg/g)	PFO			PSO		
			q_{cal} (mg/g)	$k_1 \times 10^2$ (1/min)	R^2	q_{cal} (mg/g)	$k_2 \times 10^{-3}$ [g/(mg·min)]	R^2
conventional	0.5	33.30	31.50	1.043	0.8881	34.27	4.750	0.9611
	1.0	22.94	21.32	1.644	0.8682	23.12	11.2	0.9698
	1.5	17.37	16.19	1.924	0.8751	17.59	16.7	0.9667
FIA	0.5	35.04	32.41	0.591	0.9616	38.03	1.78	0.9882
	1.0	21.83	19.42	0.652	0.9346	22.61	3.78	0.9752
	1.5	15.49	13.84	0.650	0.9297	16.13	4.71	0.9729

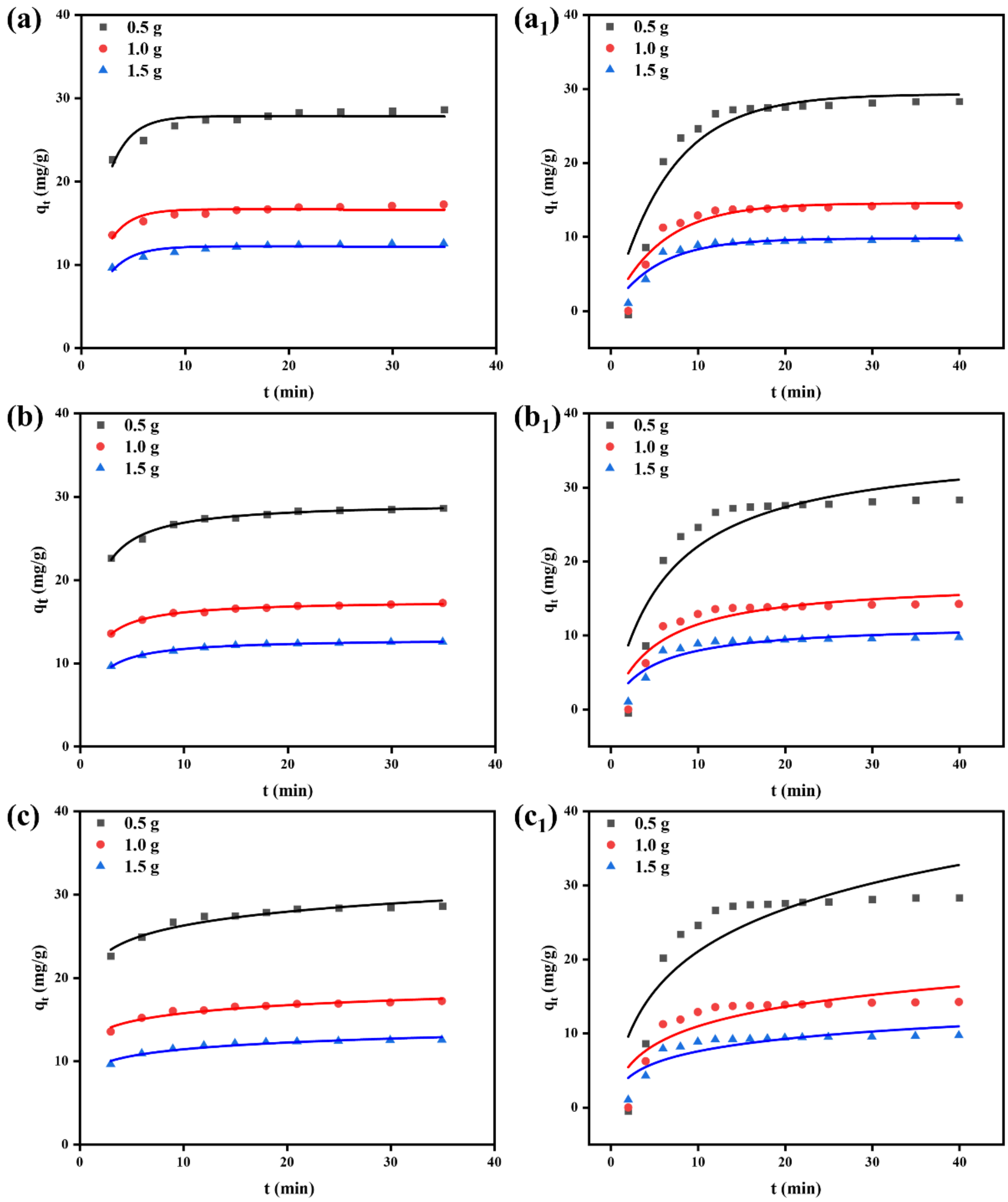

Fig. S10 Nonlinear fitting of the desorption kinetics of PPTPs on HPD-500 resin: (a-a_1). PFO model; (b-b_1). PSO model; (c-c_1). Elovich model.

Table S12 Nonlinear fitting parameters of desorption kinetic models for PPTPs on HPD-500 resin.

Detection methods	Adsorbent (g)	q_{exp} (mg/g)	PFO q_{cal} (mg/g)	PFO $k_1 \times 10$ (1/min)	PFO R^2	PSO q_{cal} (mg/g)	PSO $k_2 \times 10$ [g/(mg·min)]	PSO R^2
conventional	0.5	28.61	27.81	5.092	0.8017	29.34	0.3650	0.985
	1.0	17.19	16.61	5.208	0.8207	17.50	0.6333	0.9920
	1.5	12.49	12.15	4.7009	0.8322	12.90	0.7230	0.9955
FIA	0.5	28.31	29.26	1.522	0.8721	35.96	0.437	0.8133
	1.0	14.21	14.49	1.748	0.8690	17.41	0.1100	0.8031
	1.5	9.669	9.727	1.884	0.8969	11.52	0.1877	0.8290

8. Reliability analysis

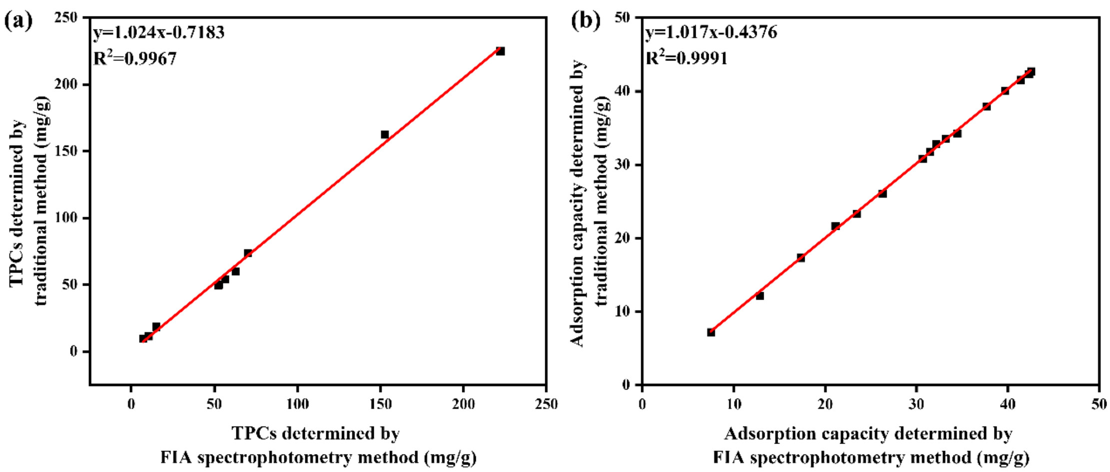

Fig. S11 (a). Comparison of conventional and FIA spectrophotometric methods for the determination of plant TPCs (b) Linear fitting of conventional and FIA spectrophotometric methods for the adsorption capacities of SCTPs on HPD-500 resin.

Table S13 Intraday (n = 10) and interday (n = 5) assays.

	Absorbance											
Day	1	2	3	4	5	6	7	8	9	10	Average	RSD/%
1	0.522	0.520	0.523	0.524	0.527	0.520	0.517	0.520	0.527	0.525	0.523	0.6
2	0.523	0.523	0.523	0.519	0.519	0.518	0.524	0.518	0.519	0.522	0.521	0.5
3	0.521	0.535	0.532	0.534	0.526	0.528	0.526	0.530	0.535	0.523	0.529	0.9
4	0.538	0.535	0.539	0.541	0.532	0.523	0.530	0.526	0.521	0.524	0.531	1.4
5	0.525	0.517	0.520	0.521	0.526	0.529	0.518	0.522	0.520	0.531	0.523	0.9

References

1 F. Gao, T. Muhammad, M. Bakri, P. Pataer and L. Chen, *ACS Omega*, 2018, **3**, 10891–10897.

2 T. Muhammad, O. Yimit, Y. Turahun, K. Muhammad, Y. Uludağ and Z. Zhao, *J. Sep. Sci.*, 2014, **37**, 1873–1879.