Electronic supplementary information (ESI)

Rapid microwave-assisted distillation-precipitation polymerization for the synthesis of magnetic molecular imprinted polymer coupled to HPTLC determination of perphenazine in human urine

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Table S1 shows details of instrumental parameters for HPTLC.

Table S1 Parameters details for HPTLC analysis of PPZ after pre-concentration by as prepared MMIPs.

Parameters	Analysis of PPZ
Stationary phase	Merck HPTLC palate silica gel 60 F_{254} (10 × 10)
Software	Win CATS-version 1.3.3
Application instrument	CAMAG automatic TLC sampler 4 (ATS 4)
Band length	3 mm
developing solvent	n-Hexane: ethyl acetate: ethanol (tetrabutylammonium bromide 10 mmol): butanol: NH_3 (5:2:0.75:1:0.1)
volume	3 mL
Development chamber	CAMAG Horizontal developing chamber
Development distance	7 cm
Tank saturation time	3 min
Development time	28 min
λ_{max}	256 nm
Scanning instrument	CAMAG TLC scanner 3 (200-400 nm scan range)
Scanning speed& resolution	5 mm/s & 25 µm/step
Documenting instrument	CAMAG TLC visualizer

Microwave program for MMIPs synthesis is brought in Fig. S1.

Table S2 indicates the nine Taguchi design and corresponding experimental value for PPZ-MMIPs prepared by microwave irradiation. The optimum values are presented in Fig. S2a and Fig. S2b.

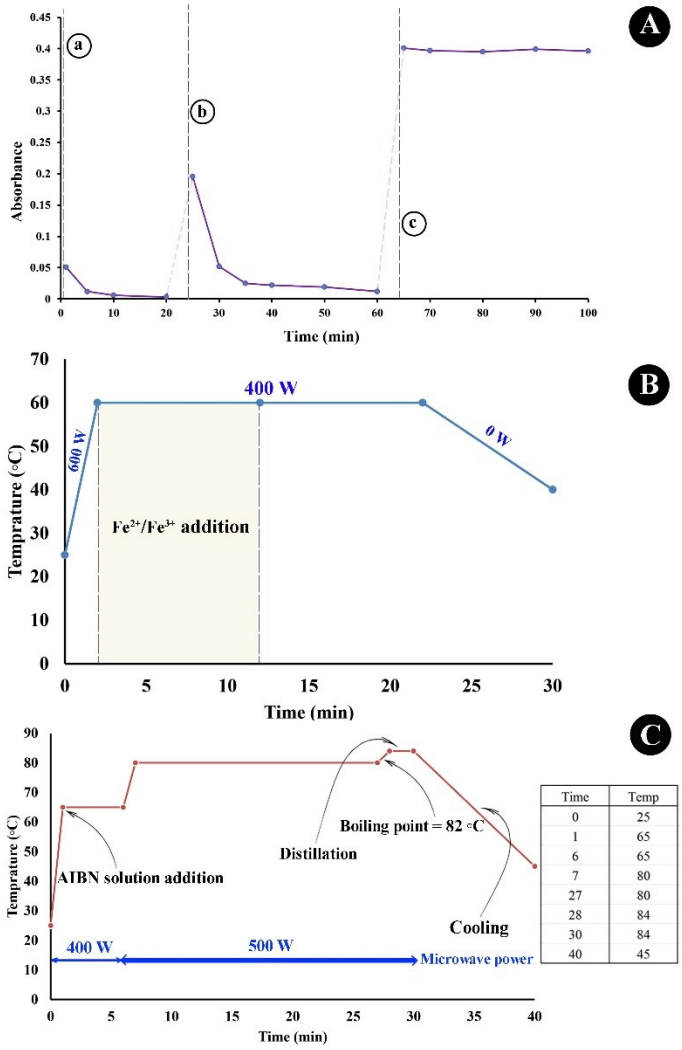
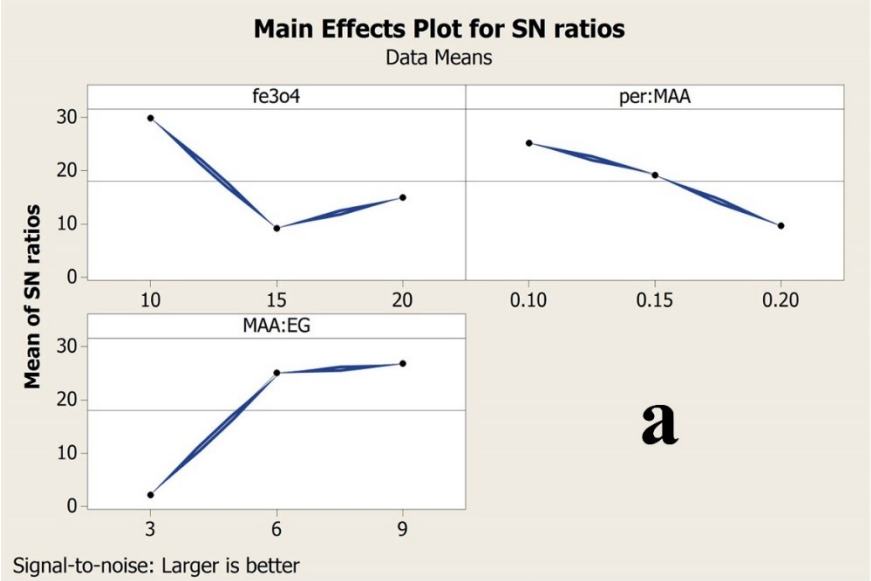


Fig. S1 A) Effect of MAA volume on simultaneous synthesis and surface modification of Fe_3O_4 determined by monitoring changes in MAA absorbance at 290 nm after addition of three 1mL portions of MAA in the same reaction vessel a) portion 1, b) portion 2, and c) portion 3; Microwave program for B) Fe_3O_4@MAA synthesis and C) synthesis of PPZ MMIPs.

Table S2 The Taguchi design and results for microwave synthesis of perphenazine MMIP. The response is adsorption capacity of as prepared sorbent in mg g^{-1}. Each experiment was repeated three times.

	Fe_3O_4@MAA*	PPZ: MAA**	MAA: EGDMA**	Trial 1	Trial 2	Trial 3	Mean
1	10	0.1	3	25.6453	28.8711	23.9007	26.139
2	10	0.15	6	34.4066	37.4174	39.186	37.0034
3	10	0.2	9	33.9284	30.6148	31.7661	32.1031
4	15	0.1	6	14.9914	15.5972	13.0813	14.5567
5	15	0.15	9	19.7231	21.6513	19.7139	20.3627
6	15	0.2	3	0.0470	1.0052	1.5148	0.8557
7	20	0.1	9	16.8955	18.1838	14.2401	16.4398
8	20	0.15	3	0.0870	1.6385	0.9624	0.8959
9	20	0.2	6	10.4172	9.6461	13.6664	11.2432

* mL of 20 % suspension; ** mole ratio



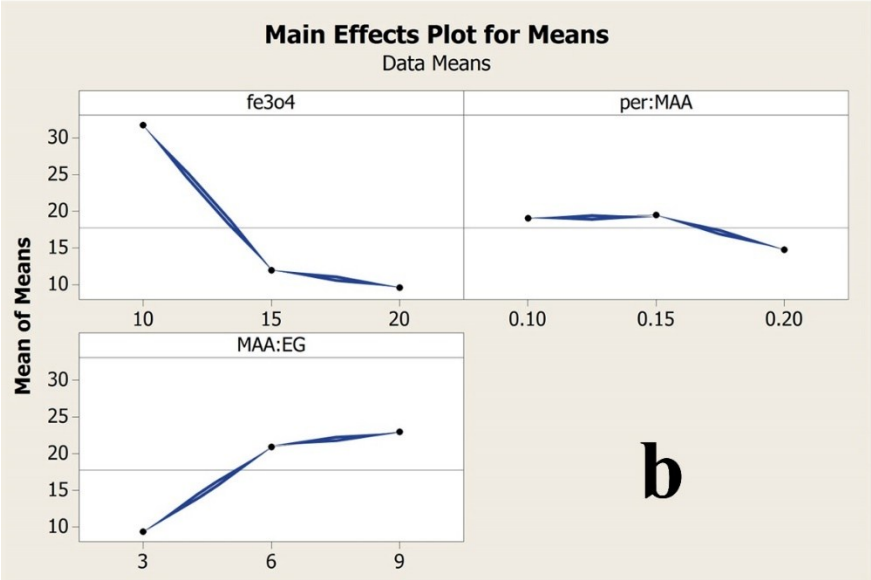


Fig. S2 Taguchi optimization graphs for microwave synthesis of MMIP.

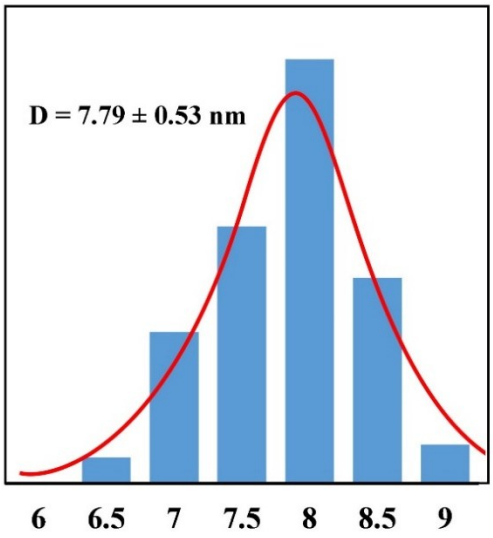


Fig. S3 Fe_3O_4@MAA size distribution determined from HRTEM image

Table S3 Parameters of system suitability for HPTLC determination of PPZ in the presence of TFP, CPZ, and AML.

Parameters	PPZ	TFP	CPZ	AML	Reference value
Capacity factor (k)	10.11	5.67	2.57	2.03	1-10
Symmetric factor	1.05	1.10	1.00	0.99	~ 1
Selectivity factor (α)	1.78		2.20	1.26	>1
Resolution (R_s)	1.33		3.50	4.80	>1.5

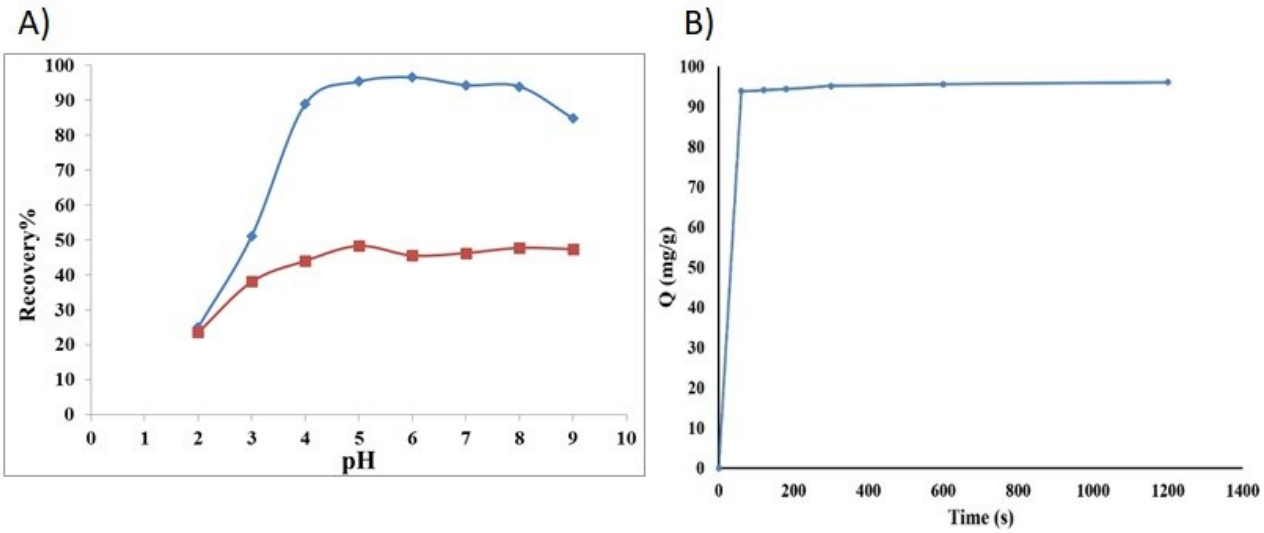


Fig. S4 A) pH optimization for PPZ by as prepared MMIP particles. Red line is data obtained for MNIPs, and B) Effect of contact time on PPZ adsorption on MMIPS synthesized by microwave assisted distillation precipitation polymerization.

Fig. S5 is HPLC chromatogram of urine and urine spiked with three different concentration of PPZ after pre-concentration and desorption from as prepared MMIPs using the procedure mentioned in the main manuscript.

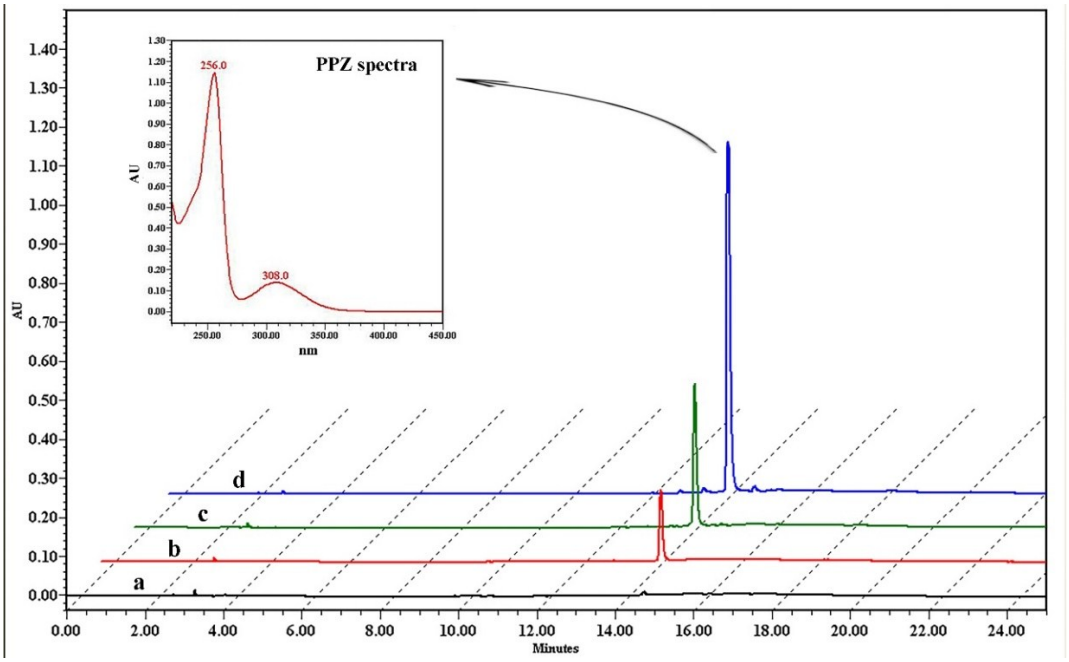


Fig. S5 HPLC chromatogram of urine sample (a) and urine spiked with 0.5 µg mL^{-1} (b) 1 µg mL^{-1} (c) and 3 µg mL^{-1} (d) of PPZ after pre-concentration and desorption from as synthesized MMIP. Inset shows PPZ spectra at its corresponding retention time.

Table S4 Delibrate changes in some method parameters in HPTLC analysis of PPZ

Parameters	% Mean recovery ± SD	% Bias	% RSD	R_f
Developing solvent composition[a]				
(5.1:2:0.75:1:0.1)	97.29 ± 1.60	2.71	1.09	0.09
(5:2.1:0.75:1:0.1)	97.46 ± 1.07	2.54	1.09	0.09
(5:2:0.75:1.1:0.1)	97.83 ± 1.81	2.17	1.85	0.09
(5:2:0.75:1:0.110)	96.82 ± 2.10	3.18	2.17	0.1
(5:2:0.85:1:0.1)	97.54 ± 1.05	2.46	1.07	0.08
Developing solvent volume[b]				
3.1	97.44± 1.66	2.56	1.70	0.09
2.9	97.86 ± 1.85	2.14	1.89	0.09
Chamber saturation time[c]				
3.5	97.85 ± 1.65	2.15	1.69	0.09
2.5	97.90 ± 1.51	2.10	1.54	0.09
developing distance[d]				
7.5	97.84 ± 2.06	2.16	2.11	0.1
6.5	97.48 ± 1.86	2.52	1.91	0.08
λ_{max} (nm)				
257	96.29 ± 1.22	3.71	1.26	0.09
255	97.08 ± 1.45	2.92	1.49	0.09
Stability up to 30 h	96.22 ± 2.01	3.78	2.09	0.09

[a] n-Hex:Et-Ac:10mmol TBABr in EtOH:But-OH:NH_3; [b] mL; [c] min; [d] Cm;

Table S5 Imprinting factor for the compounds tested for selectivity of the MMIPs prepared by microwave irradiation.

Heating methods	Drugs	Q_{MMIP}	Q_{MNIP}	IF
Conventional*	**PPZ**	**52.71**	**21.90**	**2.41**
Microwave	PPZ	86.48	16.34	5.39
Microwave	TFP	67.98	18.42	3.69
Microwave	TRZ	25.96	14.12	1.84
Microwave	HXZ	36.49	17.01	2.15
Microwave	AML	4.47	3.62	1.24
Microwave	CPZ	10.19	6.73	1.51
Microwave	PRM	72.58	21.12	3.44

*is extracted from our previous study [1].

Analyte	Num. of steps in synthesis	Time of polymerization (min)	Time of extraction (min)	Average size (nm)	Heating method	Ref.
4-nitrophenol	4	1440	150	175	Conventional	[2]
rhodamine B	3	1440	20	50	Conventional	[3]
Triazines	3	120	30	12×10^4-15×10^4	Microwave	[4]
ractopamine	3	60	120	80×10^3	Microwave	[5]
Atrazine	3	125	240	12×10^4-15×10^4	Microwave	[6]
β-sitosterol	3	66	40	11×10^4	Microwave	[7]
GA3	3	66	50	50×10^3-18×10^4	Microwave	[8]
Letrozole	3	1440	--	100	Conventional	[9]
PPZ	2	90	1	140	Conventional	[1]
PPZ	2	30	1	13	Microwave	This study

Table S6 Comparison of present synthetics protocol with some previously reported synthesis of MMIPs.

Table S7 Comparisons of the present HPTLC method with those reported in the literature for PPZ.

Method	Detection technique	matrix	Dilution (times)	LOD (ng mL^{-1})	LDR (ng mL^{-1})	R%	RSD%	Extraction time (min)	Ref
LLE	HPLC/UV	Serum	0	4.0	2-500	95.6	3.6	8	[10]
-	CE-ECL	Urine	20	2	40-2×10^6	-	1.6	-	[11]
IL-SE-UA-ME	HPLC/UV	Urine	NR	1	5-1000	89	3.5	25	[12]
DLLME-FASS	CE/UV	Urine, Plasma	3	1	4-4000	85.7	5.2	6	[13]
-	Amperometric	Urine, Serum, Breast Milk	3	18800	323×10^3-323×10^4	-	3.18	-	[14]
Chemical oxidation	Spectrophotometry	Tablet, Serum	-	49	50-25×10^3	98.86	0.86	30	[15]
MMIP	HPTLC/PDA	Urine	0	10	25-5000	97.79	1.74	1	This Work

NR stands for not reported.

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