Electronic Supplementary Information

Magnetic porous organic polymer for extraction of cardiovascular drugs in human urine samples followed by HPLC-UV

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Characterization of the MOPs

Fig. S1-S13

Table S1-S3

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Characterization of the MOPs

Characterizations such as TEM, SEM, EDX, magnetization curves and N_2 adsorption-desorption isotherm of the prepared MOPs were provided according to our previous work [1]. As the TEM images (Fig. S2a) shown, the MNPs are embedded in porous POPs-matrix. The lighter areas surrounding around can be ascribed to the matrix of POPs whereas the darker areas represent the MNPs. Amorphous agglomerate morphologies are proved by the SEM images (Fig. S2b). According to the EDX data (Fig. S2c), it can be confirmed that the MNPs are incorporated into POPs successfully. The magnetic property of the MOPs was measured and the result demonstrated that the superparamagnetism of initial MNPs was well retained. Excellent magnetic property assures the easy separation of the MOPs under external magnetic field (Fig. S2d). The BET surface area of the MOPs was investigated by N_2 adsorption-desorption measurements at 77 K. As shown in Fig. S2e, the special surface area of the MOPs is 327 $m^2 g^{-1}$, which is much higher than that of pure MNPs (59 $m^2 g^{-1}$) and comparable to that of pure POP (~256 $m^2 g^{-1}$) [1]. The N_2 adsorption-desorption isotherm belongs to type IV (Fig. S2e), demonstrating the existence of mesoporous in the MOPs. The pore size distribution curve evaluated from BET measurement (Fig. S2e, inset) clearly validates the meso-pore structure.

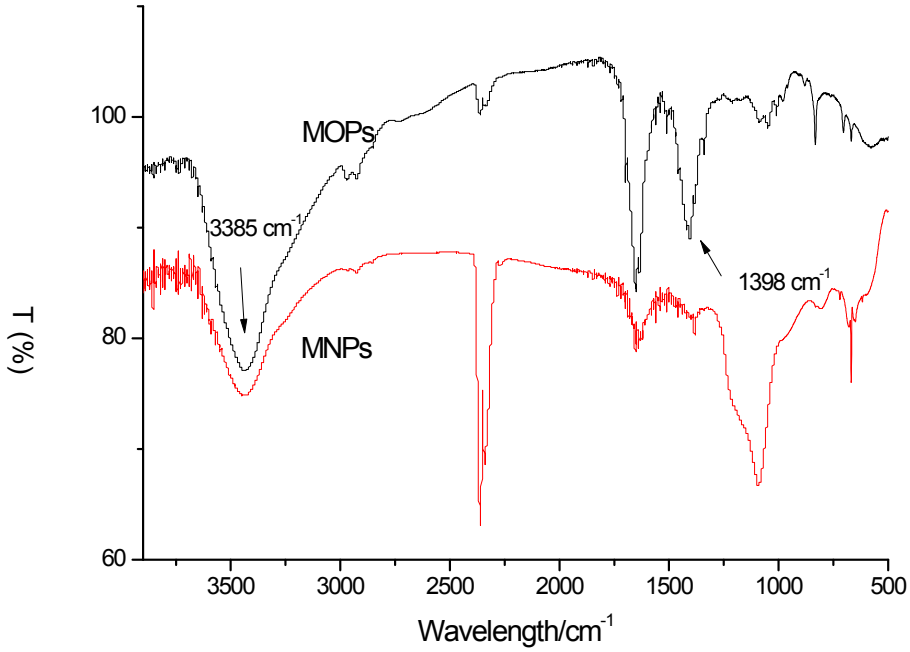
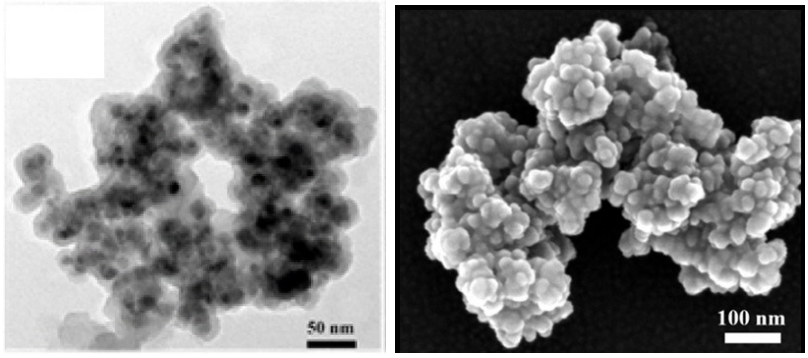
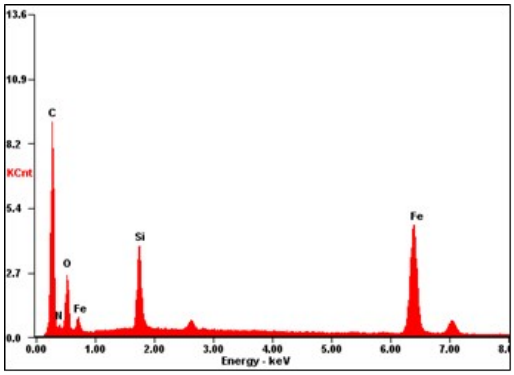


Fig. S1 FT-IR spectra of MOPs.

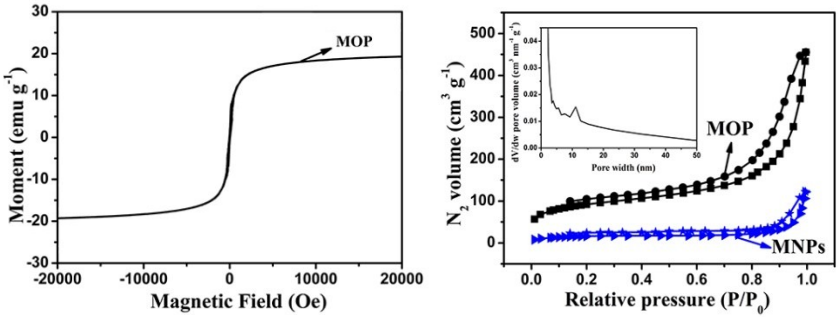


(a) (b)



Element	*Wt %*	*At %*
C K	59.84	70.53
N K	09.37	09.47
O K	18.14	16.06
SiK	02.96	01.49
FeK	09.69	02.46

(c)



(d) (e)

Fig. S2 TEM (a), SEM (b), EDX (c), magnetization curves (d) and N_2 adsorption-desorption isotherm (e) of the prepared MOPs. (Reprinted in part with permission from Ref. [1]. Copyright (2017) American Chemical Society)

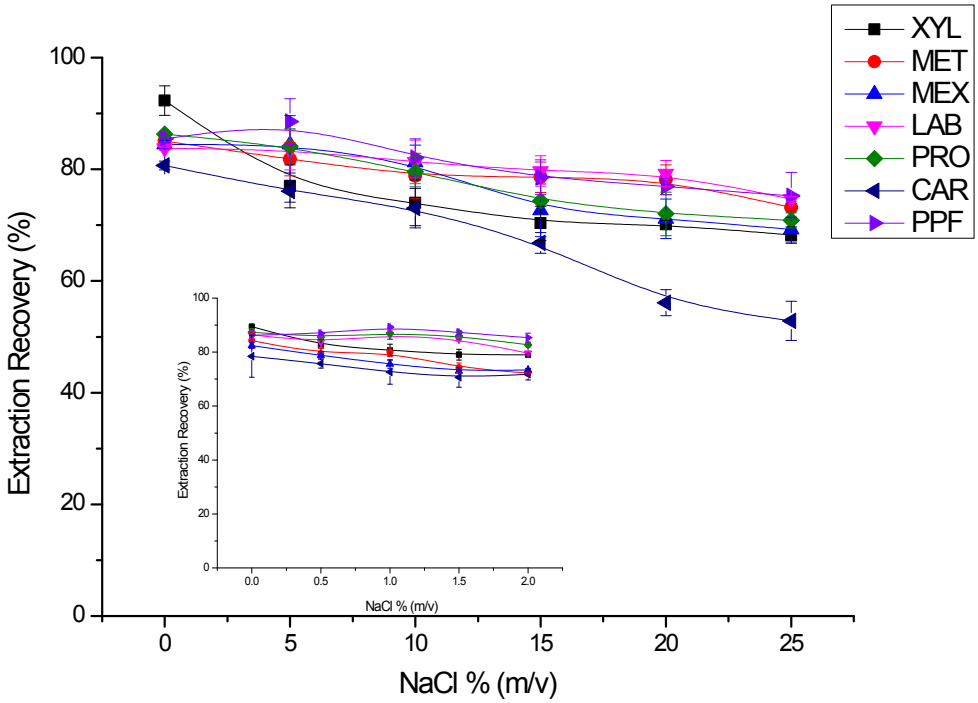


Fig. S3 Effect of ionic strength on the extraction recovery of the analytes on MOPs. Error bar corresponds to the standard deviation of triplicate analysis. Conditions: 10 mg MOPs, 40 mL sample, no pH adjustment, extraction time 10 min, desorption solvent 10 mmol/L hydrochloric acid (acetone as solvent), desorption time 3 min, desorption volume 500 μL, each analyte at 100 μg/L.

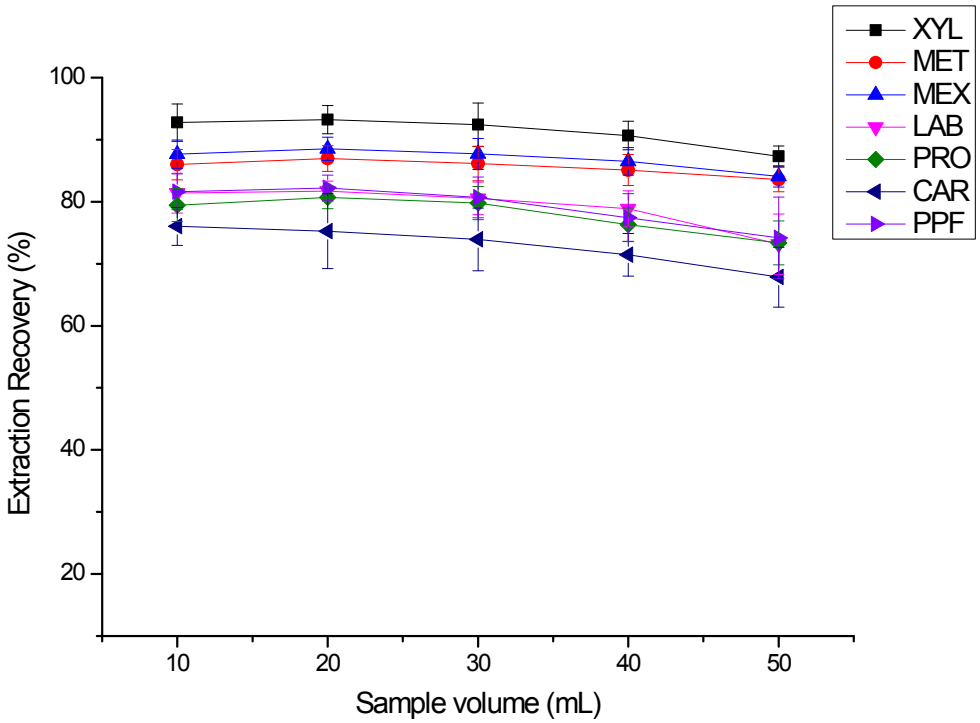


Fig. S4 Effect of sample volume on the extraction recovery of the analytes on MOPs. Error bar corresponds to the standard deviation of triplicate analysis. Conditions: 10 mg MOPs, no pH adjustment, no salt addition, extraction time 20min, desorption solvent 10 mmol/L hydrochloric acid (acetone as solvent), desorption time 10 min, desorption volume 500 μL, each analyte at 100 μg/L.

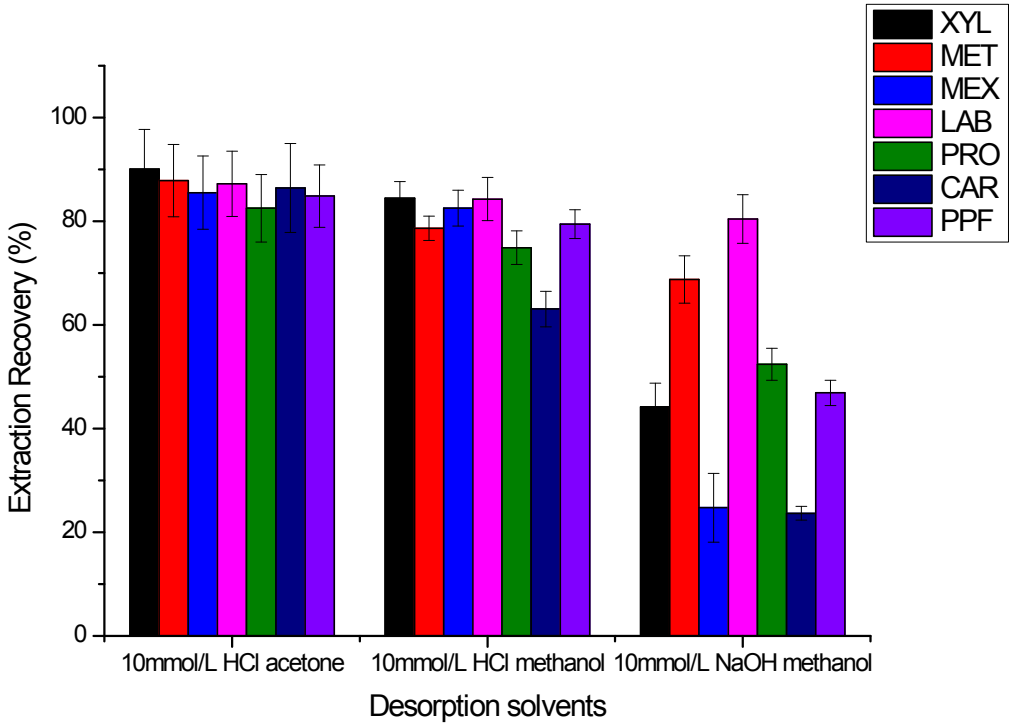


Fig. S5 Effect of desorption solvent type on the extraction recovery of the analytes on MOPs.

Conditions: 10 mg MOPs, 10 mL sample, no pH adjustment, no salt addition, extraction time 20 min, desorption time 10 min, desorption volume 500 μL, each analyte at 100 μg/L.

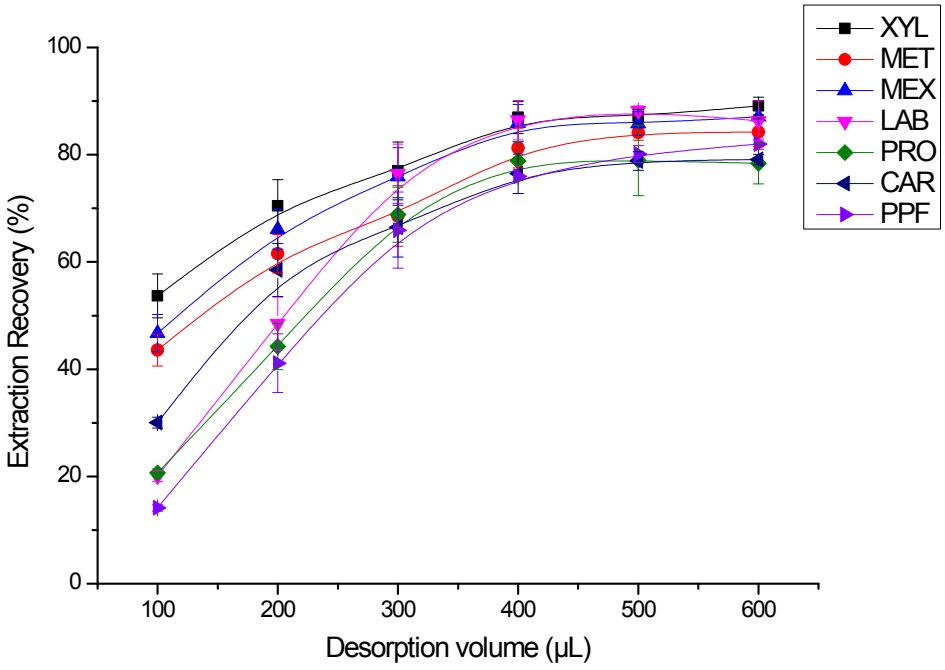


Fig. S6 Effect of desorption volume on the extraction recovery of the analytes on MOPs.

Conditions: 10 mg MOPs, 10 mL sample, no pH adjustment, no salt addition, extraction time 20 min, desorption solvent 10 mmol/L hydrochloric acid (acetone as solvent), desorption time 10 min, each analyte at 100 μg/L.

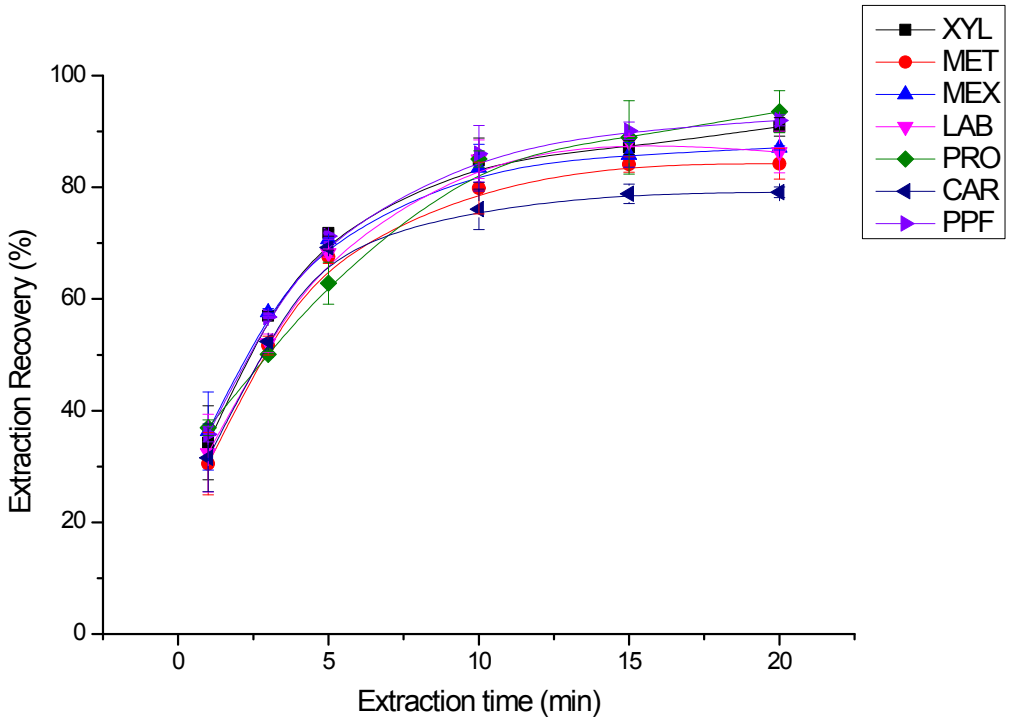


Fig. S7 Effect of extraction time on the extraction recovery of the analytes on MOPs. Error bar corresponds to the standard deviation of triplicate analysis. Conditions: 10 mg MOPs, 40 mL sample, no pH adjustment, no salt addition, desorption solvent 10 mmol/L hydrochloric acid (acetone as solvent), desorption time 10 min, desorption volume 500 μL, each analyte at 100 μg/L.

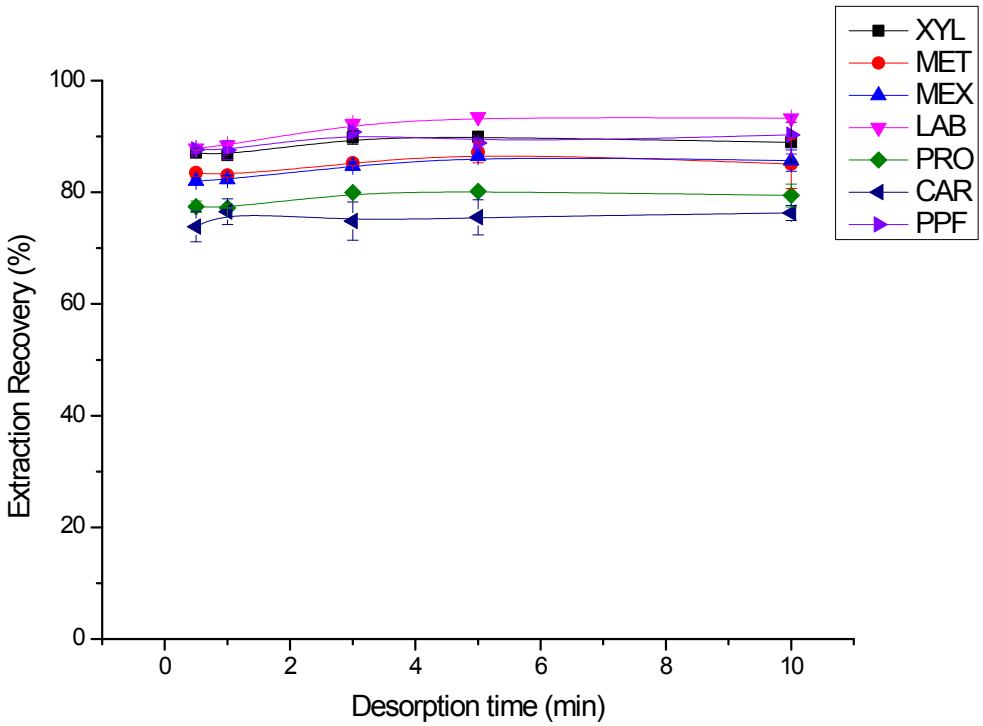


Fig. S8 Effect of desorption time on the extraction recovery of the analytes on MOPs. Error bar corresponds to the standard deviation of triplicate analysis. Conditions: 10 mg MOPs, 40 mL sample, no pH adjustment, no salt addition, extraction time 10 min, desorption solvent 10 mmol/L hydrochloric acid (acetone as solvent), desorption volume 500 μL, each analyte at 100 μg/L.

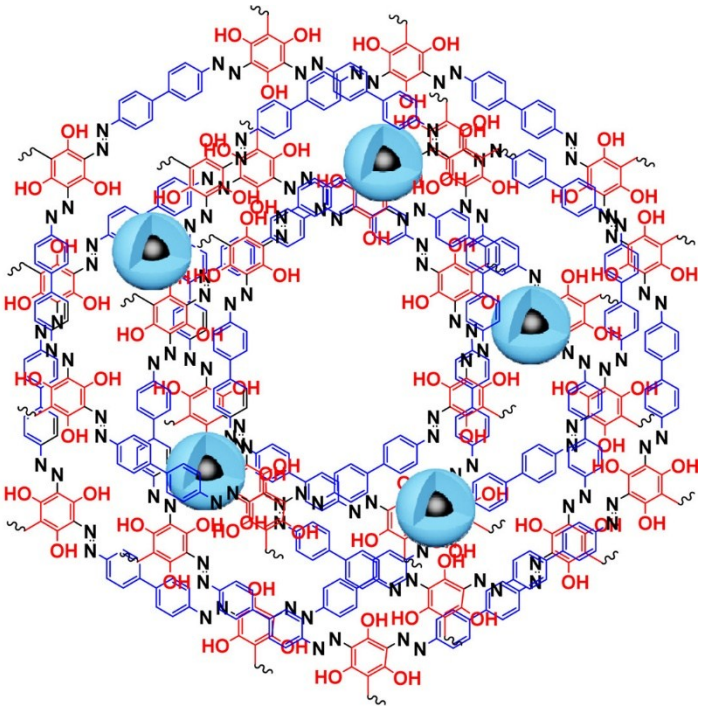


Fig. S9 The schematic illustration of conjugated network structure of the prepared MOPs.

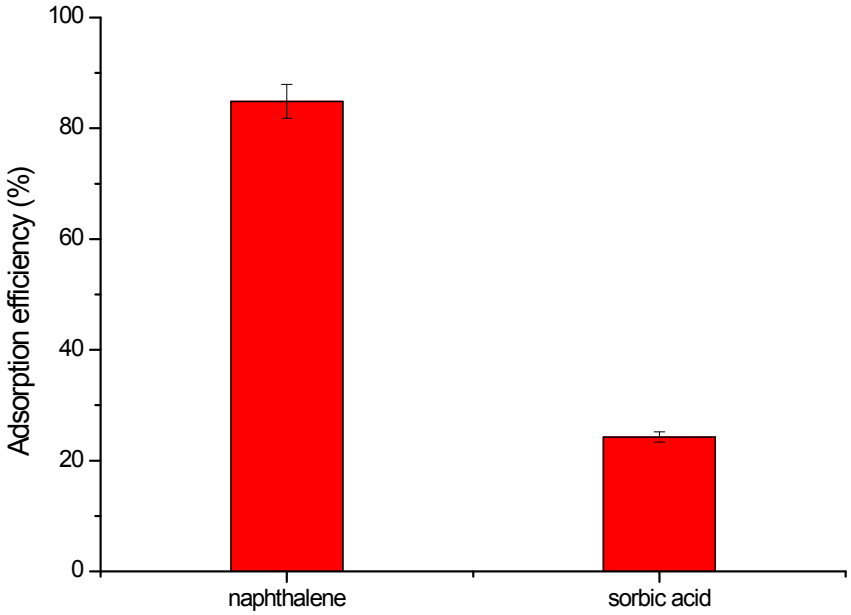


Fig. S10 Adsorption efficiency of naphthalene and sorbic acid on MOPs. Conditions: 10 mg MOPs, 10 mL sample, no pH adjustment, no salt addition, extraction time 20 min, each analyte at 3 mg/L.

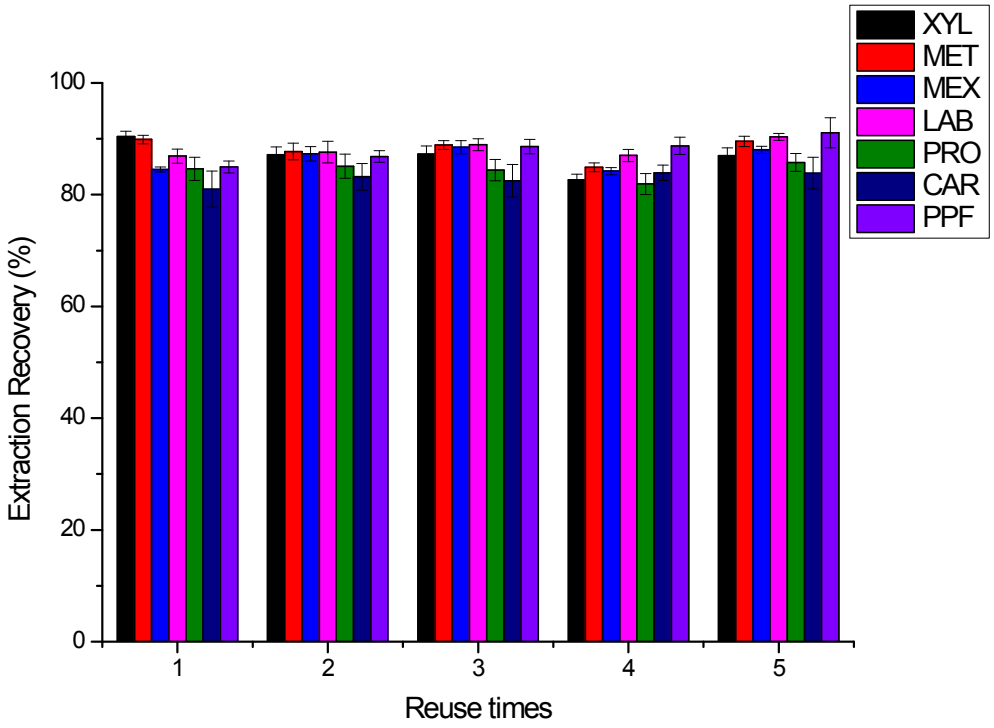
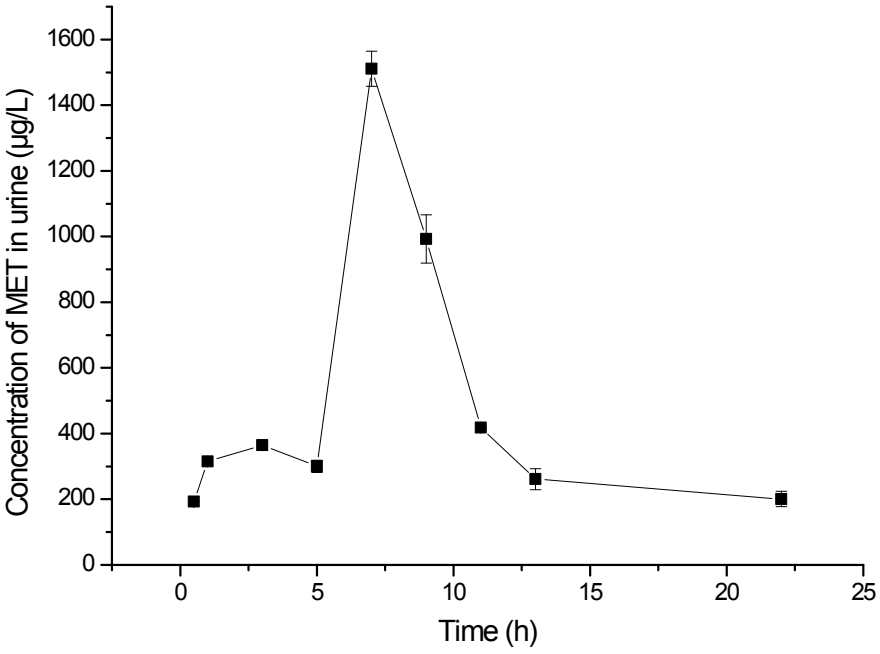
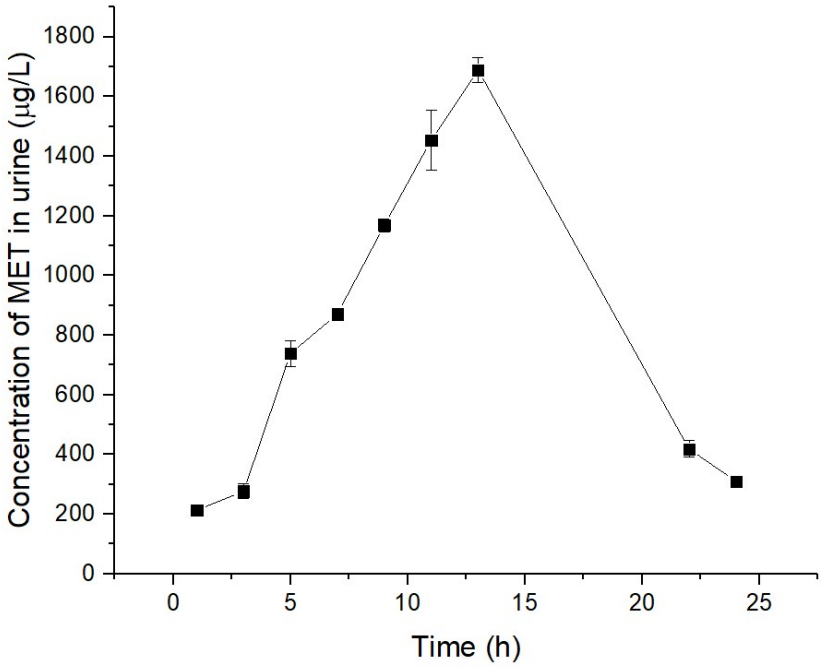


Fig. S11 Effect of reuse times on the extraction recovery of the analytes on MOPs. Error bar corresponds to the standard deviation of triplicate analysis. Conditions: 10 mg MOPs, 40 mL sample, no pH adjustment, no salt addition, extraction time 10 min, desorption solvent 10 mmol/L hydrochloric acid (acetone as solvent), desorption time 3 min, desorption volume 500 μL, each analyte at 100 μg/L.

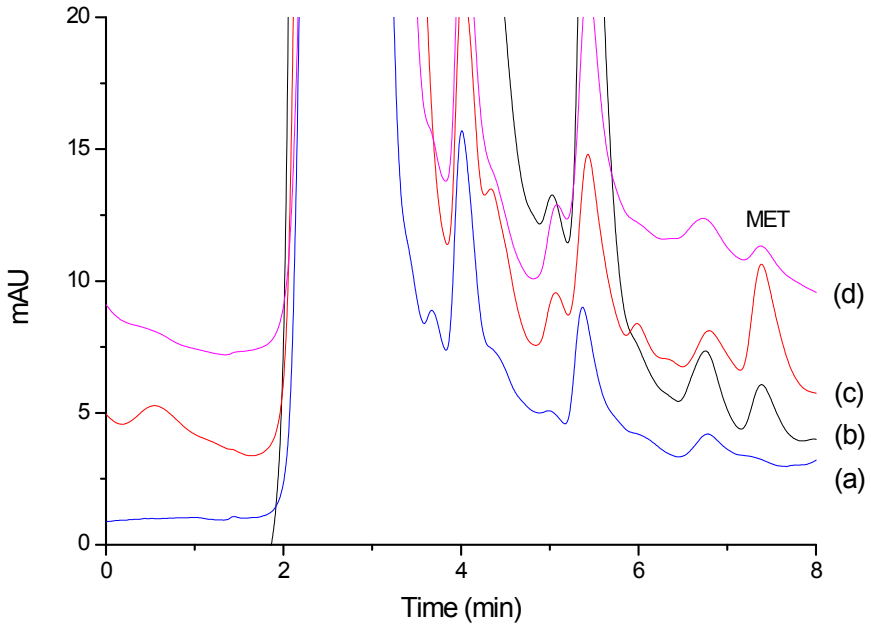


(a)

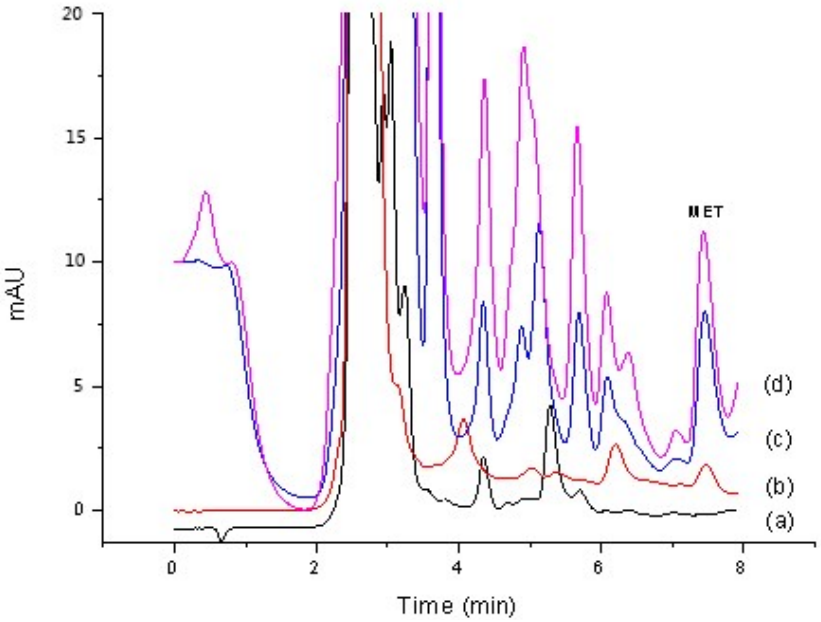


(b)

Fig. S12 The concentration of metoprolol in female (a) and male (b) urine samples *vs* time after drugs administration.



(A)



(B)

Fig. S13 Chromatograms of metoprolol obtained by MSPE-HPLC-UV for female urine samples (A) collected before (a), and 3 h (b), 7 h (c), 13 h (d) after taking metoprolol tablets, and for male urine samples (B) collected before (a), and 1 h (b), 9 h (c), 13 h (d) after taking metoprolol tablets.

Table S1 Comparison of adsorption kinetics (K_2) of the proposed method with others for the adsorption of cardiovascular drugs

Adsorption materials	K_2 (g mg^{-1} min^{-1})	Cardiovascular drugs	Adsorption time (min)	Desorption time (min)	Ref
granular activated carbon	0.02	atenolol	90	—	[2]
acid-activated attapulgite	0.04	propranolol	25	—	[3]
graphene oxides	0.16	atenolol	180	—	[4]
montmorillonite	0.08	atenolol	120	—	[5]
MOPs	0.07	xylocaine	10	3	This work

Table S2 Preparation reproducibility of the MOPs in one batch and batch to batch

Analytes	RSD[a] (%) (n=5) In one batch	RSD[a] (%) (n=5) Batch to batch
XYL	2.0	7.5
MET	2.1	6.3
MEX	2.1	4.2
LAB	1.6	3.9
PRO	2.5	5.1
CAR	4.5	7.5
PPF	1.8	4.3

a: XYL, MET, MEX, LAB, PRO, CAR, PPF, 100 μg/L.

Table S3 The concentration and amount of metoprolol in urine sample collected after administration of metoprolol tablets

Urine sample		Concentration (μg/L)	Volume (mL)	Amount (μg)
Time after taking metoprolol tablets (h)	1	214±14	300	64±4
	3	277±24	245	68±6
	5	739±44	320	236±14
	7	871±10	365	318±4
	9	1169±21	290	339±6
	11	1454±102	148	215±15
	13	1689±41	110	186±5
	22	419±27	380	159±10
	24	310±9	210	65±2

Reference

[1] L. J. Huang, M. He, B. B. Chen, Q. Cheng and B. Hu, Facile Green Synthesis of Magnetic Porous Organic Polymers for Rapid Removal and Separation of Methylene Blue, ACS Sustain. Chem. Eng. 5 (2017) 4050-4055.

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