Analytical methods

Electronic Supplementary Information

Simultaneous extraction of anthracyclines from urine using water-compatible magnetic nanoparticles with dummy template coupled with high performance liquid chromatography

Wenyue Zou, Pierre Dramou, Lien Ai Pham-Huy, Kai Zhang, Jia He, Chuong Pham-Huy, Deli Xiao, Hua He

Appendix S1. The procedure of synthesis of Fe_3O_4 nanoparticles.

Fe^{2+} and Fe^{3+} solutions were prepared with deionized water in two beakers, and then mixed together. When the solution was heated to 80 ℃, ammonia solution was added dropwise under nitrogen gas protection with vigorous mechanical stirring until the pH was between 10 and 11. The solution continued to be heated at 80 ℃ for 2 h, and then the precipitated powders were collected by magnetic separation. The obtained magnetic nanoparticles were washed immediately with deionized water for several times. The final product was dried into powder at 40 ℃ under vacuum oven.

Appendix S2. FT-IR spectrogram and its explanation

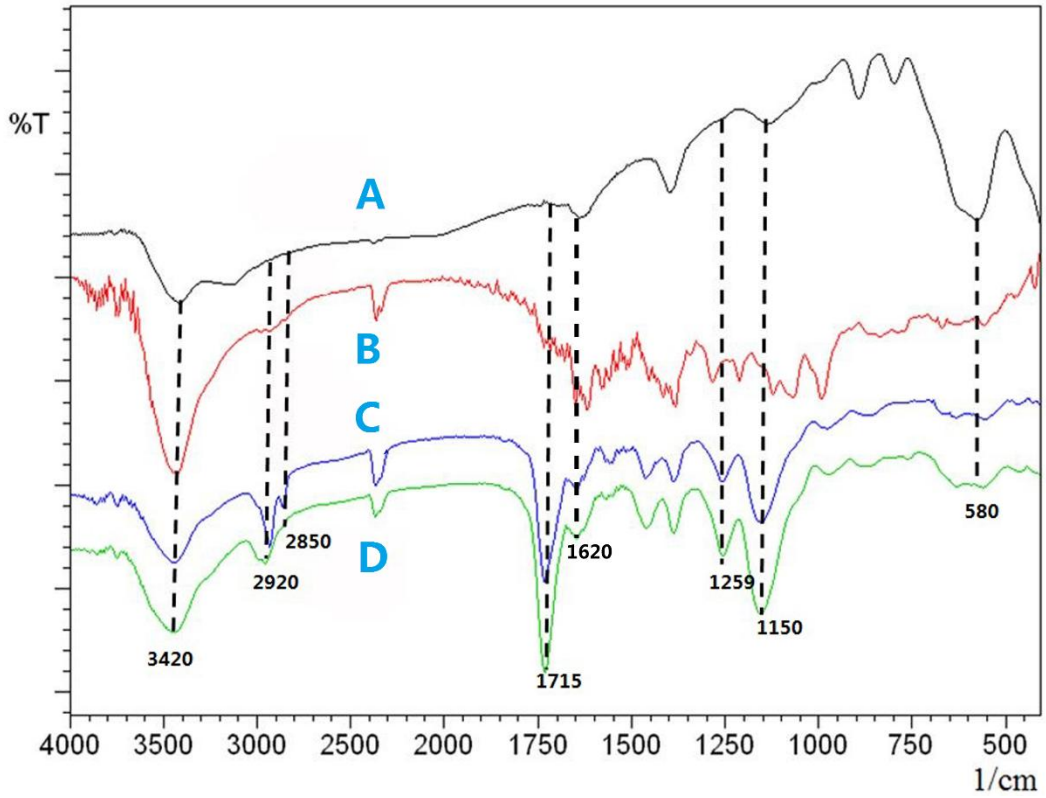

Fig. S1 FT-IR spectrogram of Fe_3O_4 (A), EPI (B), M-NIPs (C) and M-MIPs (D)

The FT-IR spectra reported in Fig. S1 shows the surface groups on Fe_3O_4 (A), EPI (B), M-NIPs (C) and M-MIPs (D) analyzed by FT-IR. The peak at 3420cm^{-1} which exists in all figures is the stretching vibration of O-H band. It is also indicative of the presence of the $Fe(OH)_3$, $Fe(OH)_2$ and FeOOH in Fe_3O_4. The Fe-O stretching peak at 580 cm^{-1} is a common peak in Fig. S1A, C and D. The variations in the peak deduce the different amounts of iron oxide. Comparing with Fig. S1B, the increased C-H typical bands located at 2920 cm^{-1} and 2850 cm^{-1} and the C=O stretching band at 1715 cm^{-1} in Fig. S1C and D are attributed to the stretching vibrations of polymer chains from the oleic acid and the existence of MAM in M-NIPs and M-MIPs. The COO- asymmetric stretching band at 1620 cm^{-1} and the C-O stretching bands at 1259 cm^{-1} and 1150 cm^{-1} in Fig. S1C and D are also the consequence of the grafting oleic acid on the polymers.

Appendix S3 XRD patterns and its explanation

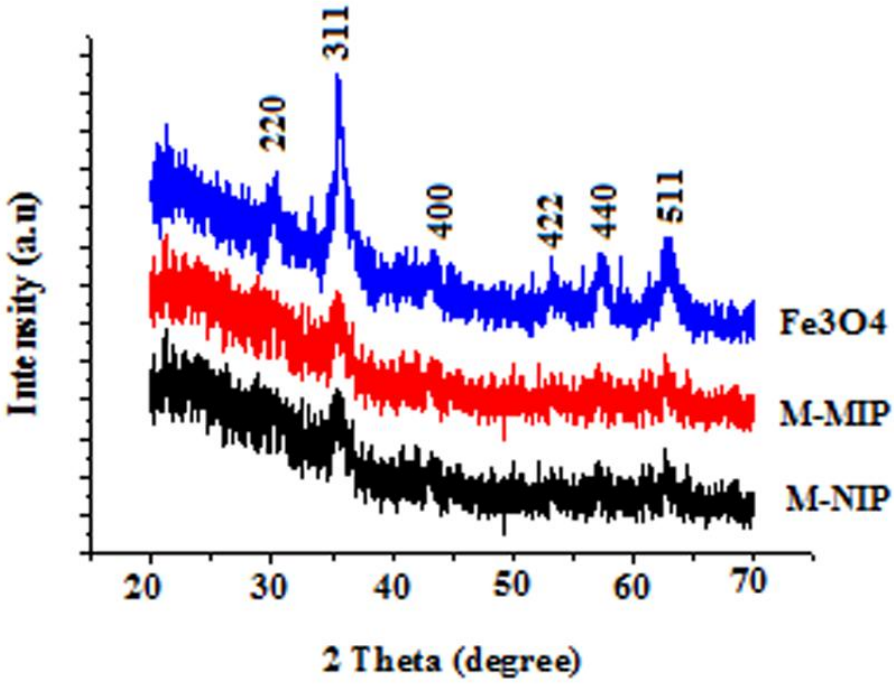

Fig. S2 XRD patterns of Fe_3O_4, M-MIPs and M-NIPs

Figure S2 shows the XRD patterns of the Fe_3O_4, M-MIPs and M-NIPs. In the 2θ region of 20~70 °, six characteristic peaks marked by their indices (220), (311), (400), (422), (511), and (440) (JCPDS card 19-0629 for Fe_3O_4) were observed for all samples. Well-resolved diffraction peaks reveal that the resulting particles are pure Fe_3O_4 with high crystallinity and also indicate that Fe_3O_4 is the dominant phase in all samples and the polymerized process does not cause any phase change of it. Because of the encapsulation by MIPs and NIPs layer on the magnetic core, the intensity of the peaks decreased slightly from Fe_3O_4 to M-MIPs and M-NIPs.

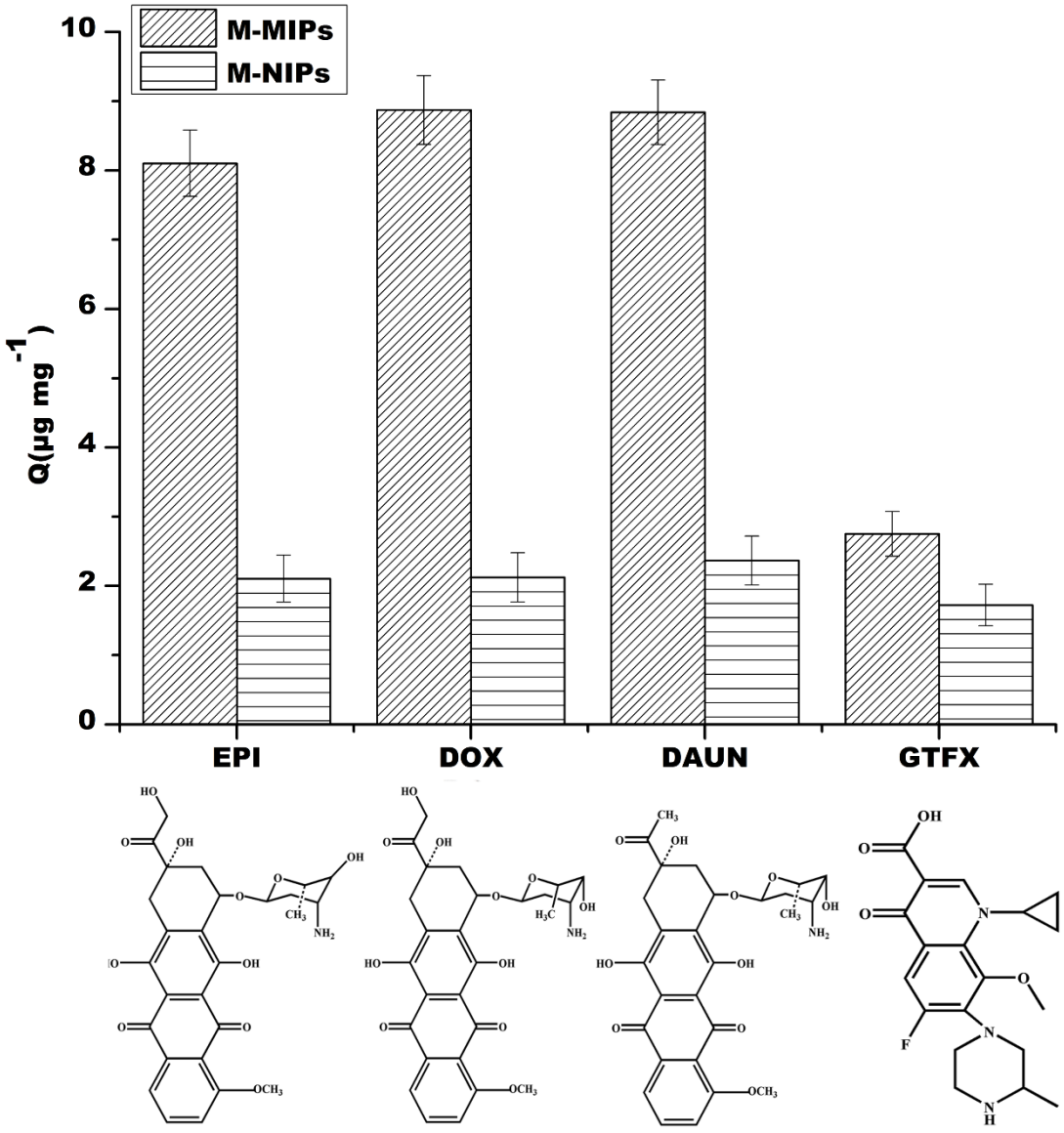

Fig. S3 Selectivity of M-MIPs and M-NIPs for EPI, DOX, DAUN and a reference compound GTFX (mixture solution: initial concentration: 20.0 μg mL^{-1}, volume: 4.0 mL; M-MIPs or M-NIPs amount: 4.0 mg)

Appendix S4 Equations of the interrelated absorbed coefficients.

To further investigate the adsorption ability of M-MIPs for different compounds under competitive condition, the interrelated absorbed coefficients were evaluated by the following equations:

The distribution coefficient:

$$K_d = \frac{Q}{C_e} \quad \text{(S1)}$$

where Q is the binding amount (μg mg^{-1}), which represents the drug concentration in the sorbent, C_e is the free drug concentration (μg mL^{-1}) in the solution at equilibrium.

In order to compare the selectivity of M-MIPs for the ANTs to reference molecule, the selectivity coefficient (K) and relative selectivity coefficient (K') were calculated according to the following equations:

The selectivity coefficient:

$$K = \frac{K_{d(ANTs)}}{K_{d(GTFX)}} \quad \text{(S2)}$$

where $K_{d(ANTs)}$ and $K_{d(GTFX)}$ are the distribution coefficient for the ANTs and GTFX, respectively.

The relative selectivity coefficient:

$$K' = \frac{K_{M-MIPs}}{K_{M-NIPs}} \quad \text{(S3)}$$

where $K_{M\text{-}MIPs}$ and $K_{M\text{-}NIPs}$ are the selectivity coefficient of M-MIPs and M-NIPs, respectively.

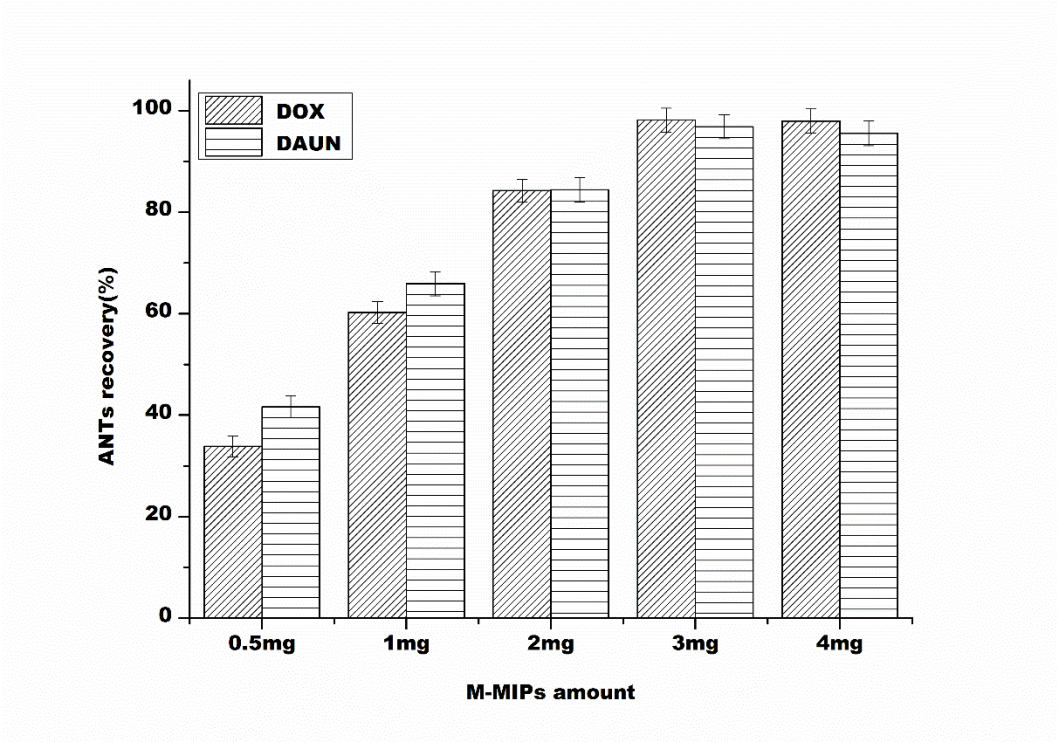

Fig. S4 The effect of the amount of M-MIPs on the recovery of ANTs (urine samples: 10.0 μg mL^{-1}, volume: 4.0 mL) (The experiments were repeated 3 times.)

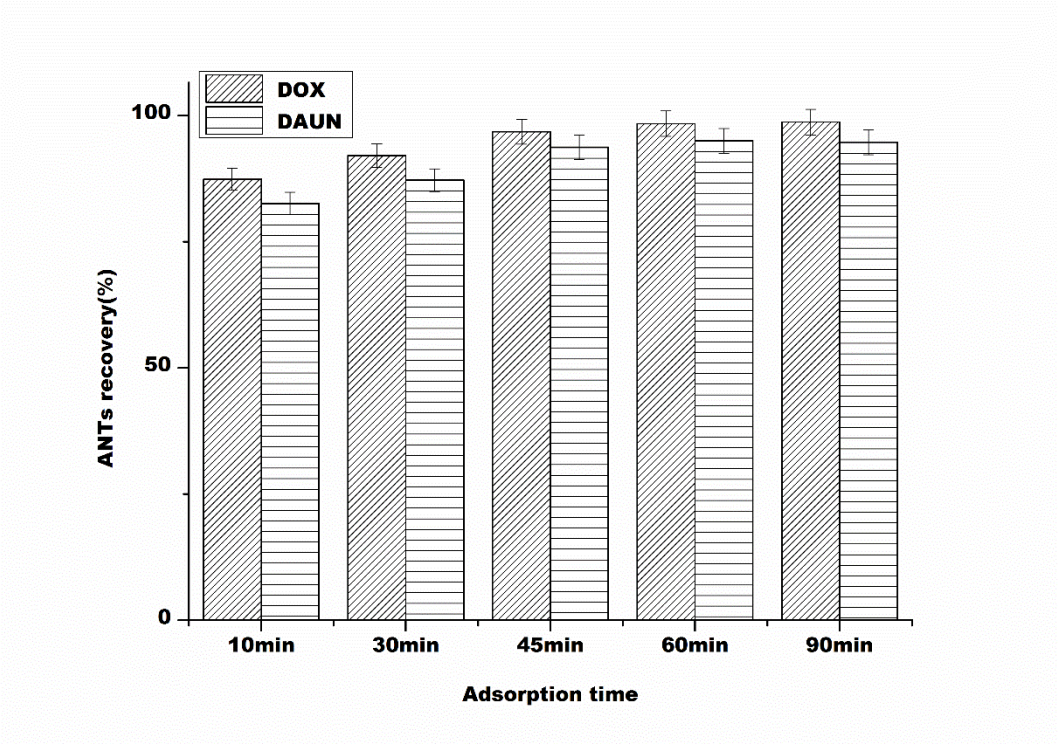

Fig. S5 The effect of the adsorption time on the recovery of ANTs (urine samples: 10.0 μg mL^{-1}, volume: 4.0 mL; M-MIPs amount: 3.0 mg) (The experiments were repeated 3 times.)

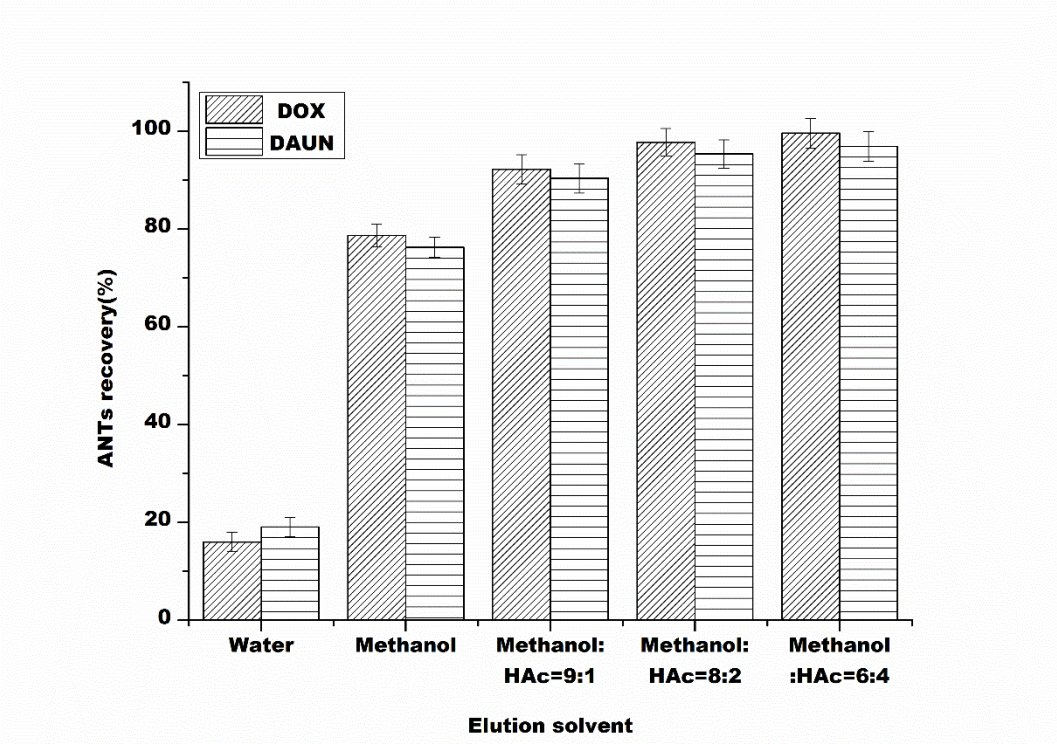

Fig. S6 The effect of the elution solvent on the recovery of ANTs (urine samples: 10.0 μg mL^{-1}, volume: 4.0 mL; M-MIPs amount: 3.0 mg) (The experiments were repeated 3 times.)

Table S1 Recovery of DOX and DAUN from spiked urine samples (The experiments were repeated 5 times.)

Analyte	0.1 μg mL^{-1}		1.0 μg mL^{-1}		10.0 μg mL^{-1}	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
DOX	93.9	5.2	96.4	3.9	98.9	2.3
DAUN	94.4	6.7	97.2	3.8	100.0	3.4