Electronic Supplementary Material (ESI) for Analytical Methods.

Supplementary Information

Efficient separation of Aristolochic acid I from *Caulis aristolochiae manshuriensis* (Guan-mu-tong) with copper mediated magnetic molecularly imprinted polymer

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1 EXPERIMENTAL SECTION

1.1 Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles are synthesized by an improved chemical co-precipitation method. In brief, 1.53 g $FeCl_3 \cdot 6H_2O$ and 0.75 g $FeCl_2 \cdot 4H_2O$ were added in a 100 mL three-mouth flask containing 50 mL water under a nitrogen atmosphere and vigorous stirring. After being heated to 80 C, 5 mL of ammonia solution was added rapidly with a syringe. After 30 min of mechanical stirring, those formed black precipitates were collected with an external magnet, followed by washing with ethanol and ultra-pure water 3 times. The product was dried in a vacuum freezer for 12 h.

1.2 Determination of Cu(II) in obtained AAI by ICP-MS

An aliquot of 2 mg AAI obtained in Section 3.5 was dissolved in 10 mL superior pure nitric acid. And then the solution was heated to 120^{o}C until almost dried. And then deionized water was added to a final volume of 25 mL, and analyzed by IPC-MS (Thermo Scientific iCAP TQs ICP-MS, US).

1.3 The stability of NPs in pH 2 solution

To further investigate the stability of NPs, an amount of 10 mg Fe_3O_4 or Cu-mMIP was immersed in 0.01 mol L^{-1} HCl solution (pH 2) under shaking. After certain intervals, the color of the solution was recorded by a camera, the particle size was measured by a zeta potential meter (UK, Malvern Nano-Zen 3600), and the magnetic respond of NPs were tested.

Figure captions

Fig. S1 Chemical structures of AAI, enalapril, norfloxacin, lappaconitine, 3,5-dinitrobenzoic acid, benzoic acid,4-nitrobenzoic acid, 4-hydroxybenzoic acid and 4-aminobenzoic acid.

Fig. S2 Optimized preparation conditions for metal ion (a); UV-Vis spectra of AAI with different functional monomers (b); ratio between AAI and TEOS (c); solvent (d); and pH (e)

Fig. S3 FT-IR spectra of Fe_3O_4, mNIP, mMIP, Cu-mMIP, Cu-mMIP-AAI and AAI.

Fig. S4 Pseudo-first-order (a) and pseudo-second-order (b) kinetic models of Cu-mMIP, mMIP and mNIP.

Fig. S5 Scatchard curves of Cu-mMIP (a); mMIP(b); mNIP(c).

Fig. S6 Fe_3O_4 or Cu-mMIP solution (a), particle size of Fe_3O_4 (b) and Cu-mMIP (c) recorded after being immersed in pH 2 solution 0 h, 12 h, and 24 h

Fig. S7 Typical chromatograms of the solutions before/after being treated with Cu-mMIP at 1^{st} (a), 2^{nd} (b), 3^{rd} (c), 4^{th} (d), 5^{th} (e), and 6^{th} (f) cycle, respectively.

Fig. S8Typical chromatograms of AAI standard (a) and Guan-mu-tong extract (b).

Table captions

Table S1 Kinetic constants for the Cu-mMIP, mMIP and mNIP

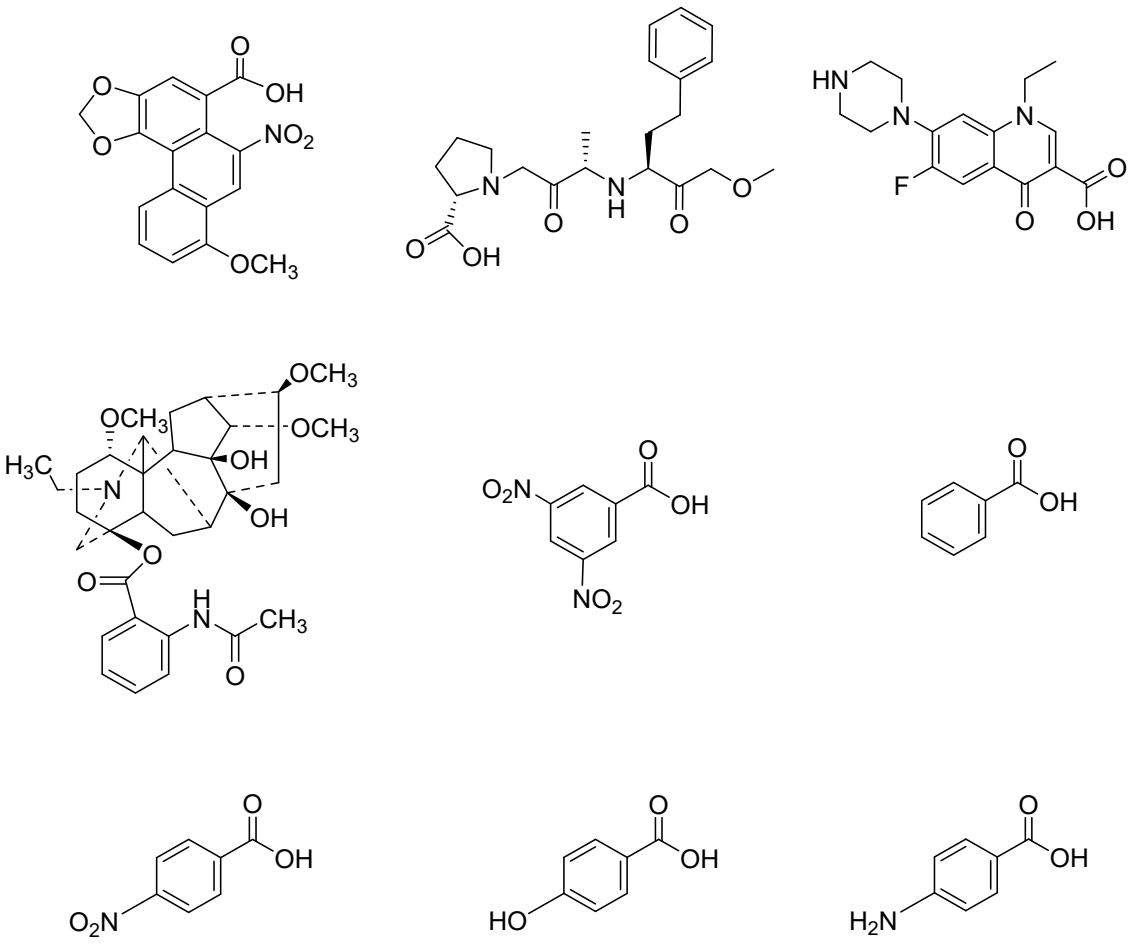


Figure S1

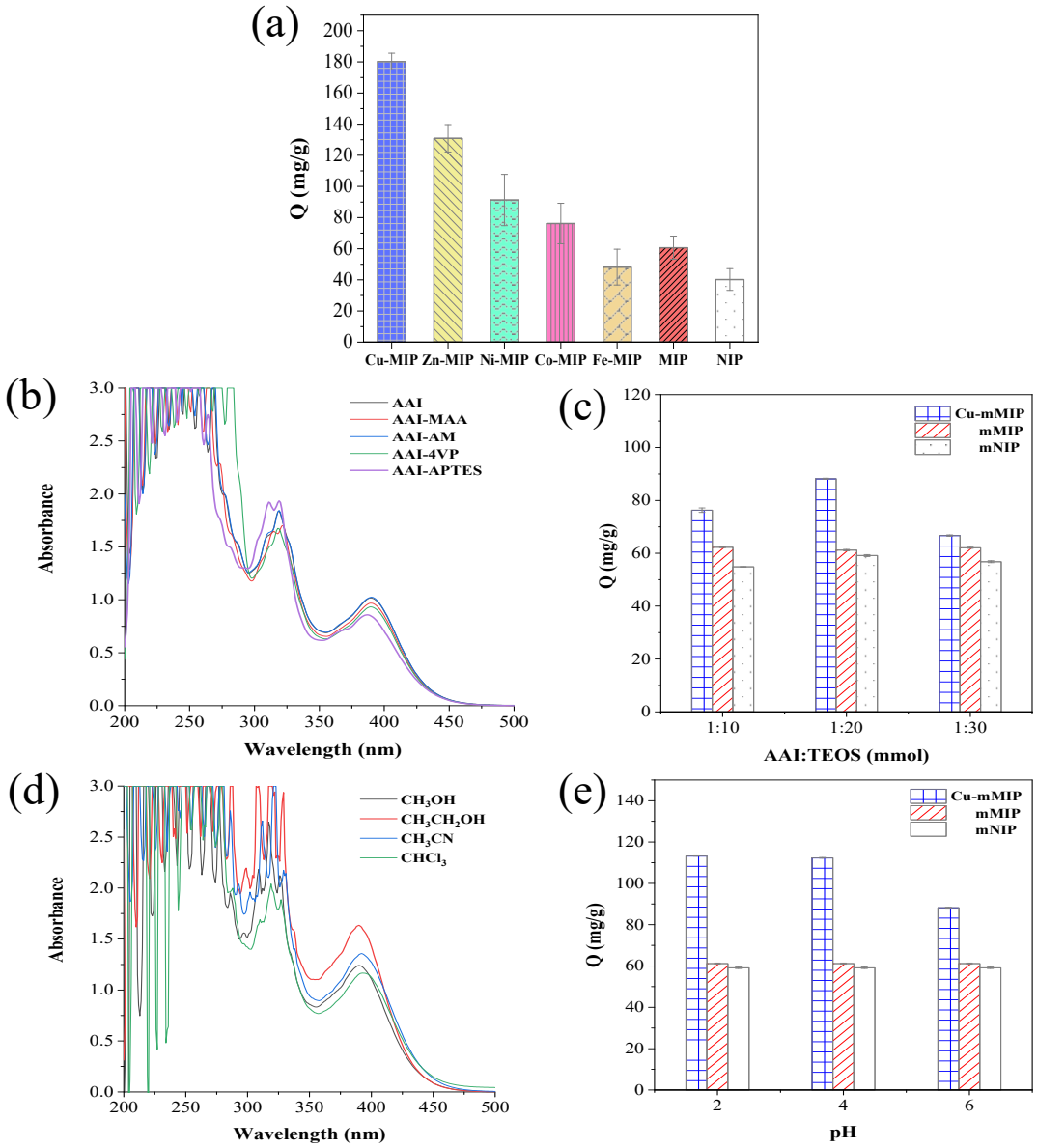

(a)
Q (mg/g)
Cu-MIP Zn-MIP Ni-MIP Co-MIP Fe-MIP MIP NIP
(b)
Absorbance
Wavelength (nm)
AAI
AAI-MAA
AAI-AM
AAI-4VP
AAI-APTES
(c)
Q (mg/g)
AAI:TEOS (mmol)
1:10
1:20
1:30
Cu-mMIP
mMIP
mNIP
(d)
Absorbance
Wavelength (nm)
CH3OH
CH3CH2OH
CH3CN
CHCl3
(e)
Q (mg/g)
pH
Cu-mMIP
mMIP
mNIP

Figure S2

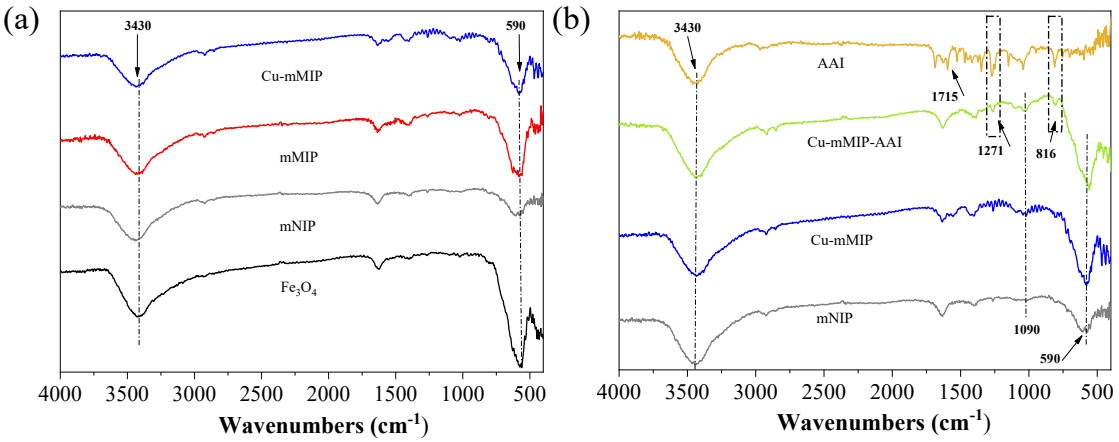

(a)
3430
590
Cu-mMIP
mMIP
mNIP
Fe_3O_4
4000 3500 3000 2500 2000 1500 1000 500
Wavenumbers (cm^{-1})
(b)
3430
AAI
1715
1271
816
Cu-mMIP-AAI
Cu-mMIP
mNIP
1090
590
4000 3500 3000 2500 2000 1500 1000 500
Wavenumbers (cm^{-1})

Figure S3

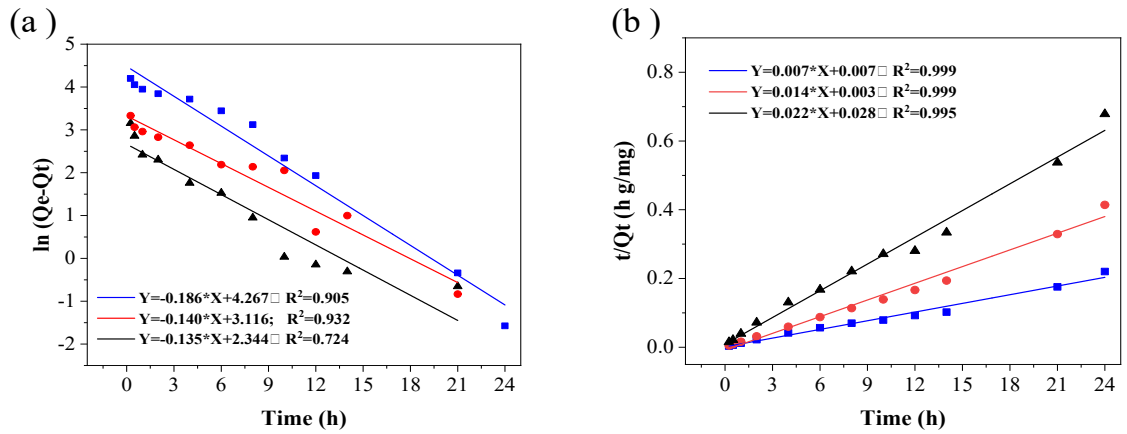

(a)
ln (Qe-Qt)
Time (h)
Y=-0.186*X+4.267□ R²=0.905
Y=-0.140*X+3.116; R²=0.932
Y=-0.135*X+2.344□ R²=0.724
(b)
t/Qt (h g/mg)
Time (h)
Y=0.007*X+0.007□ R²=0.999
Y=0.014*X+0.003□ R²=0.999
Y=0.022*X+0.028□ R²=0.995

Figure S4

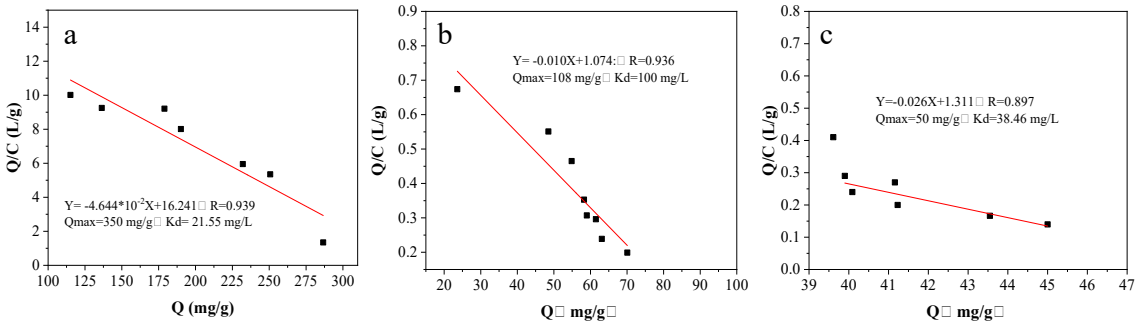

a
Y= -4.644*10-2X+16.241 R=0.939
Qmax=350 mg/g Kd= 21.55 mg/L
Q/C (L/g)
Q (mg/g)
b
Y= -0.010X+1.074: R=0.936
Qmax=108 mg/g Kd=100 mg/L
Q/C (L/g)
Q mg/g
c
Y=-0.026X+1.311 R=0.897
Qmax=50 mg/g Kd=38.46 mg/L
Q/C (L/g)
Q mg/g

Figure S5

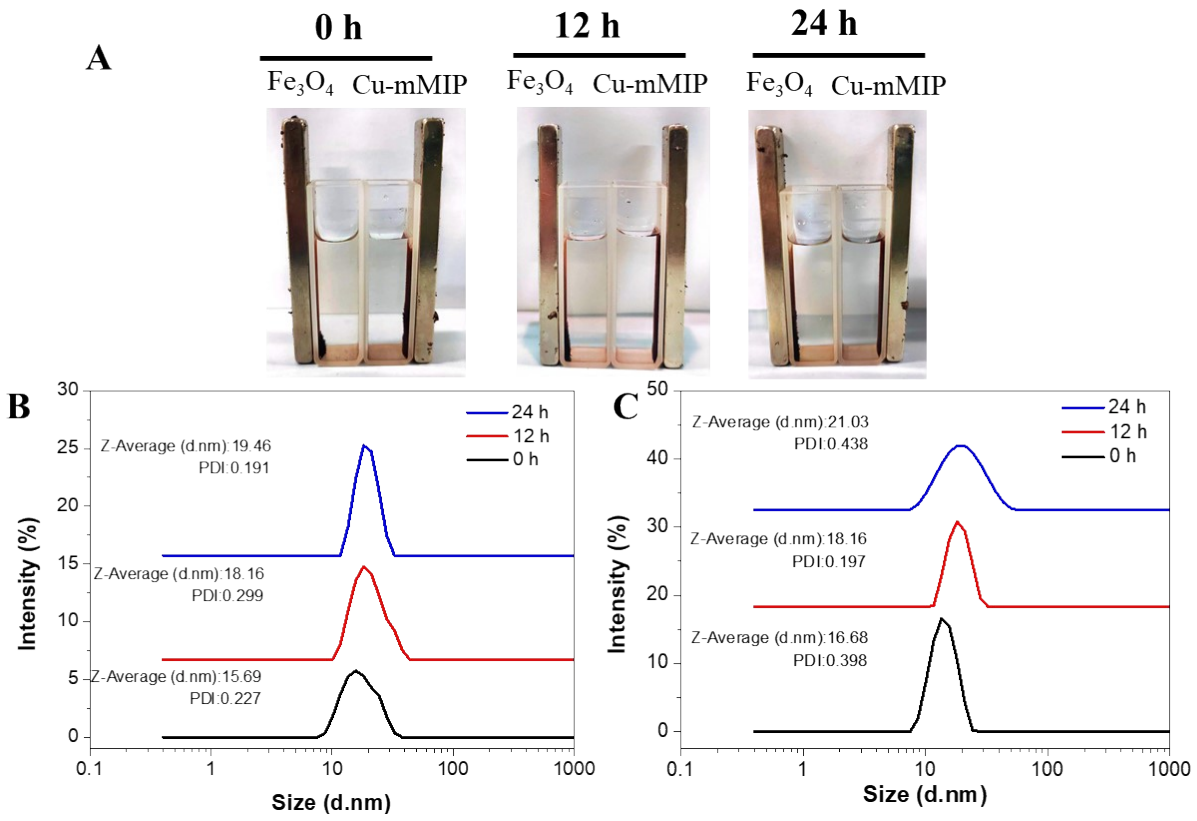

A
0 h
12 h
24 h
Fe3O4 Cu-mMIP
Fe3O4 Cu-mMIP
Fe3O4 Cu-mMIP
B
Z-Average (d.nm):19.46
PDI:0.191
Z-Average (d.nm):18.16
PDI:0.299
Z-Average (d.nm):15.69
PDI:0.227
24 h
12 h
0 h
Intensity (%)
Size (d.nm)
C
Z-Average (d.nm):21.03
PDI:0.438
Z-Average (d.nm):18.16
PDI:0.197
Z-Average (d.nm):16.68
PDI:0.398
24 h
12 h
0 h
Intensity (%)
Size (d.nm)

Figure S6

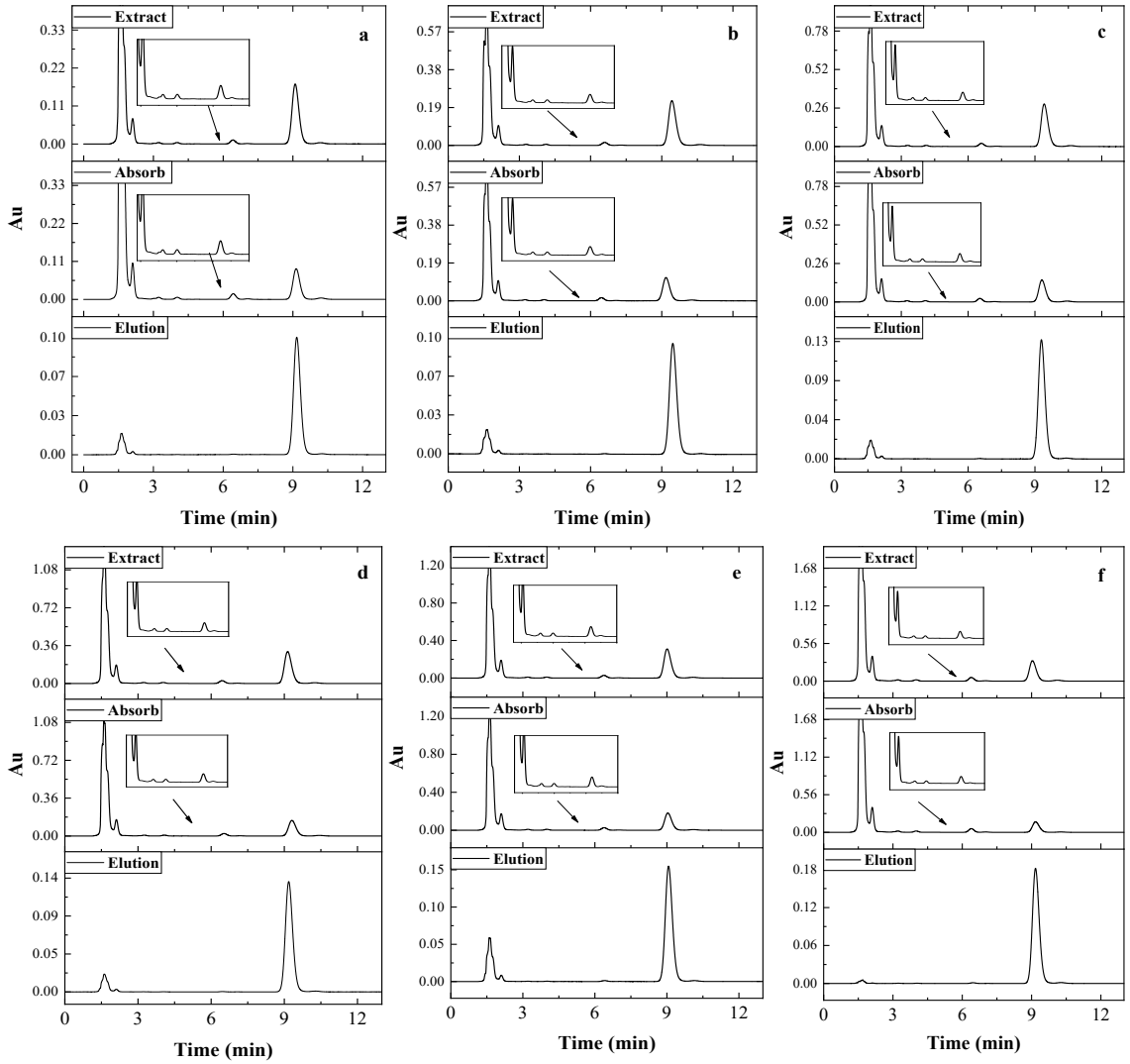
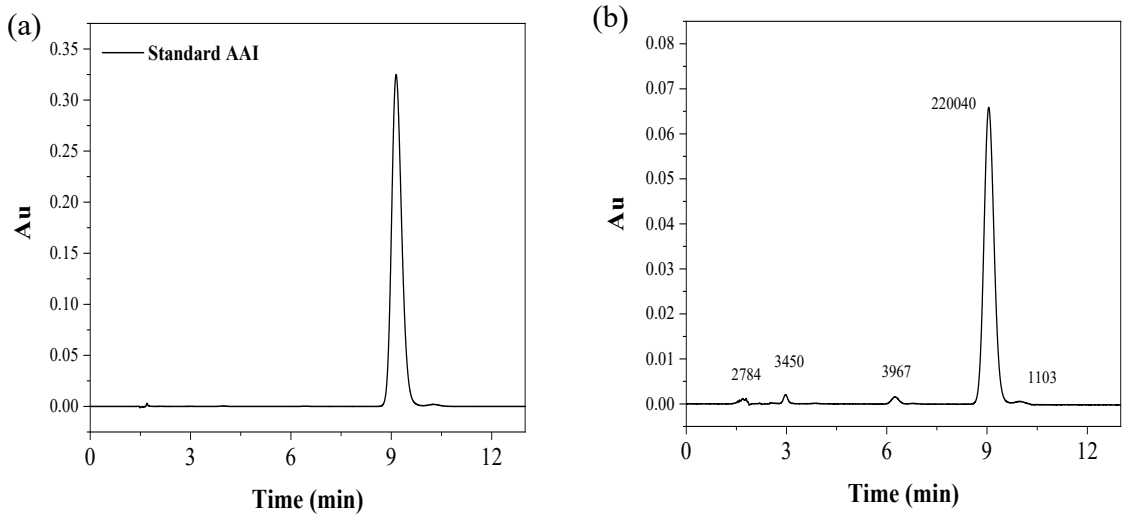


Figure S7



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71 **Figure S8**

72 **Table S1.** Kinetic constants for the Cu-mMIP, mMIP and mNIP

Sorbents	Pseudo-first-order			Pseudo-second-order	
	R^2	K_1 (mL h^{-1})	Qe (mg g^{-1})	R^2	K_2 (g (mg h^{-1}))
Cu-mMIP	0.905	0.186	136.96	0.999	0.007
mMIP	0.932	0.140	72.95	0.999	0.013
mNIP	0.742	0.135	44.65	0.995	0.018

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