*Analytical Methods*

**Supporting Information**

# Trace detection of methcathinone in sewage using targeted extraction based on magnetic molecularly imprinted polymers coupled to liquid chromatography-tandem mass spectrometry

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## Part 1. Experimental

### 1.1 Materials and instrumentation

Hexahydrate ferric chloride ($FeCl_3 \cdot 6H_2O$), Ferrous chloride tetrahydrate ($FeCl_2 \cdot 6H_2O$), 3-aminopropyltriethoxysilane (APTES), tetraethyl orthosilicate (TEOS), ethanol, acetic acid, polymer poly (acrylic acid, PAA), ammonium acetate, acetonitrile, formic acid and ammonium hydroxide ($NH_3 \cdot H_2O$) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Cathinone, methamphetamine, ketamine, methcathinone, morphine, cocaine and amphetamine were supplied by the institute of criminal science and technology of Changsha Public Security Bureau. All chemicals commercially available are of analytical grade. All aqueous solutions were prepared with ultrapure water (18.2 MΩ·cm, Millipore).

Fourier transform infrared spectra (FT-IR) were performed on 850 spectrophotometer (Tianjin Gangdong SCI.&TECH. CO,.LTD). Transmission electron microscopy (TEM) imaging was performed with HT7800 Hitachi TEM system at 300 kV. AB SCIEX TRIPLE QUAD™ 5500+ (LC-MS/MS) was employed to quantify methcathinone.

LC-MS/MS conditions were as follows: mobile phase: 20 mmol ammonium acetate in acetonitrile and 0.1% formic acid in ultrapure water (70:30). Separation performed on a Zorbax Eclipse Plus C18 column (150 mm×2.1 mm, 3.5 μm) (Agilent, America). Injection volume: 5 μL. Elution was performed at a flow rate gradient of 0.25 mL/min for 10 minutes with the column oven temperature was set to 40 ℃. Mass spectrometric conditions: electrospray ionization positive ion mode (ESI+). Vcap: 4500 v; drying gas: nitrogen with flow rate at 10 L/min, temperature 500 ℃; Collision gas: Helium, collision energy: 10/22 v. Declustering potential: 85 V for methcathinone. Precursor/product ion: 164/146 (CE: 10v), 164/130 (CE: 34v) for methcathinone.

## Part 2. Experiment

### 2.1 Synthesis of $Fe_3O_4$

Briefly, 10 mg PAA was dispersed in 30 mL ultrapure water in 100 mL three-necked flask and then deoxidized with nitrogen flow for 30 minutes and heated to 75 ℃ according to the literatures. Meanwhile, 0.584 g $FeCl_3 \cdot 6H_2O$ and 0.222 g $FeCl_2 \cdot 4H_2O$ dispersed into 1 mL diluted hydrochloric

acid (1 M). The mixed iron precursor was then quickly injected into the hot polymer solution with violently stirred under nitrogen atmosphere, and then added with 15 mL $NH_3 \cdot H_2O$ (28%) to adjust pH. The solution turned black immediately upon addition of ammonia and the resulting mixtures were refluxed for 40 minutes at 75 ℃. After cooling down, the black product was washed by ultrapure water and ethanol three times with the aid of external magnetic field and dried at 60 ℃ for 4 h.

2.2 Preparation of silica coated $Fe_3O_4$

The nano-sized magnetic $Fe_3O_4$ was synthesized by modified high temperature coprecipitation approach according to literature. Then, 20 mg $Fe_3O_4$NPs were dispersed into a mixture containing 12 mL ethanol and 3 mL water and ultrasonicated for 20 minutes. Then 0.1 mL $NH_3 \cdot H_2O$ and 0.3 mL TEOS were added into the mixture and vibrated for 12 h at room temperature. The obtained $Fe_3O_4$NPs@$SiO_2$ was washed with hydrochloric acid (1 M), ethanol and ultrapure water to remove incomplete products with the help of external magnetic and then dried at 60 ℃ for 4 h.

## Part 2. Figures and tables

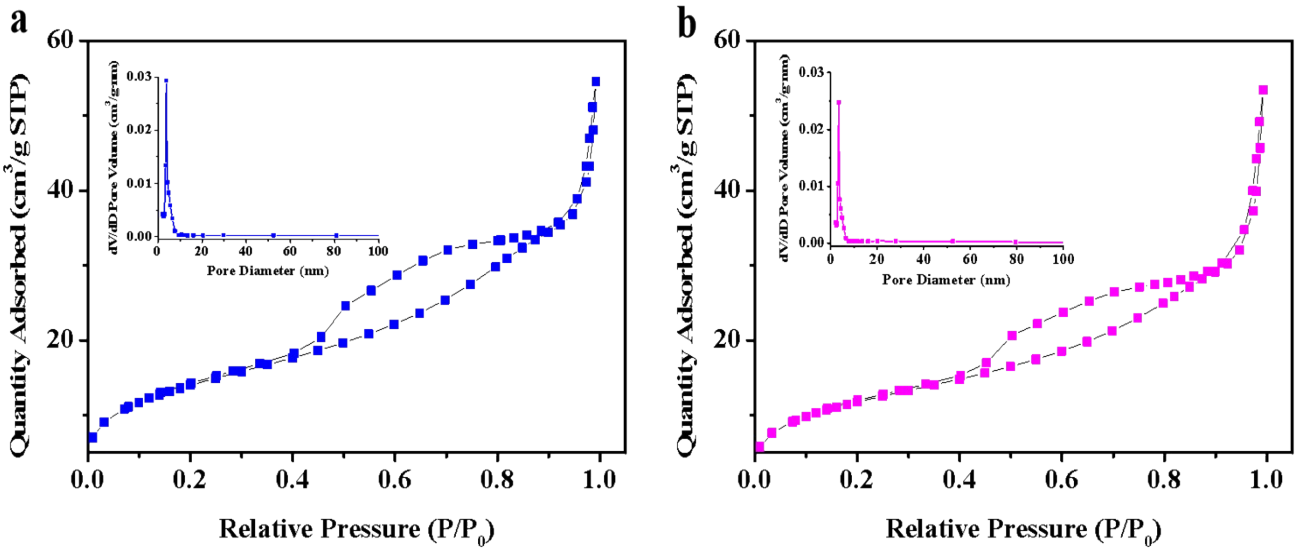


**Fig. S1.** $N_2$ adsorption/desorption isotherms of (a) MMIPs and (b) MNIPs

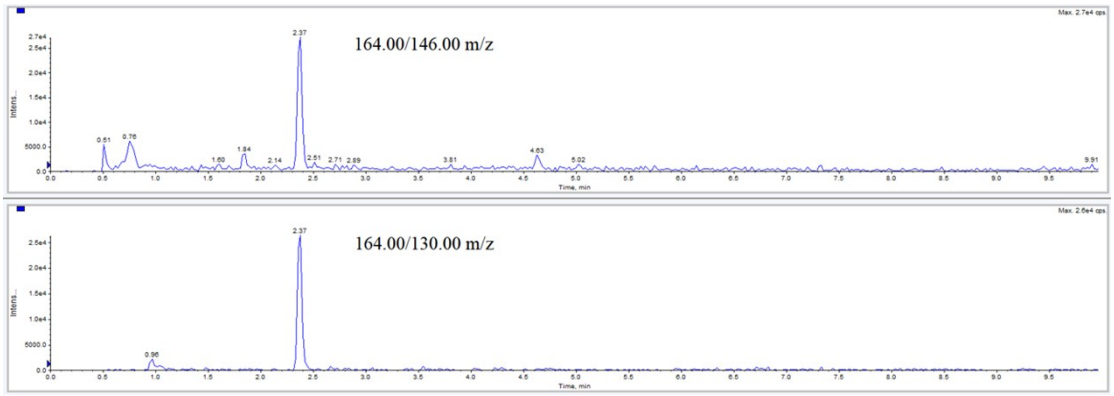


**Fig. S2.** The precursor/product ions of methcathinone by LC-MS/MS.

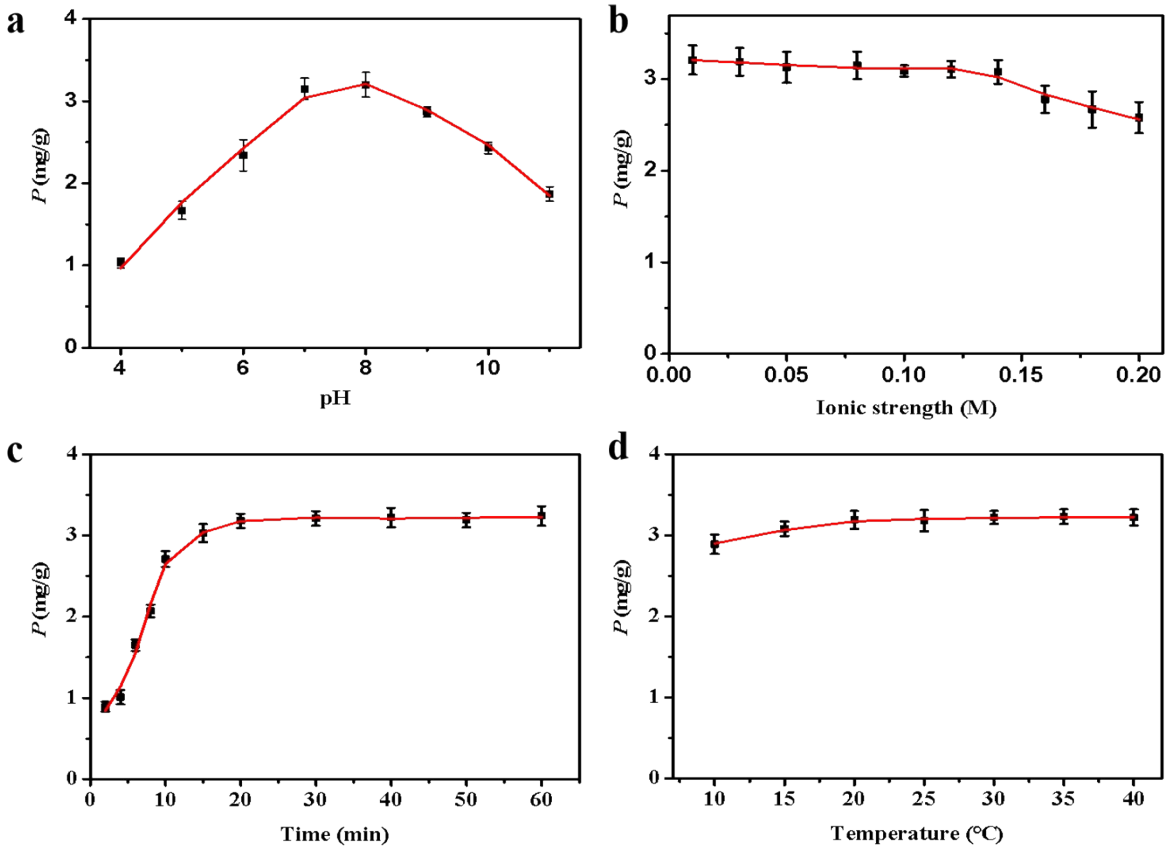


**Fig. S3.** Effect of experimental parameters on the performance of MMIPs for methcathinone adsorption: (a) pH, (b) ionic strength, (c) incubation time and (d)Temperature.

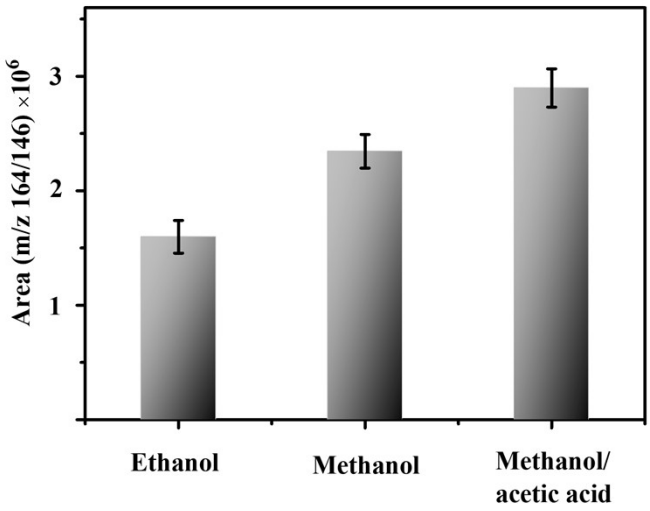


**Fig. S4.** Comparison of the effects of different elution solvents: methanol, ethanol, methanol/acetic acid with 9:1 mixture.

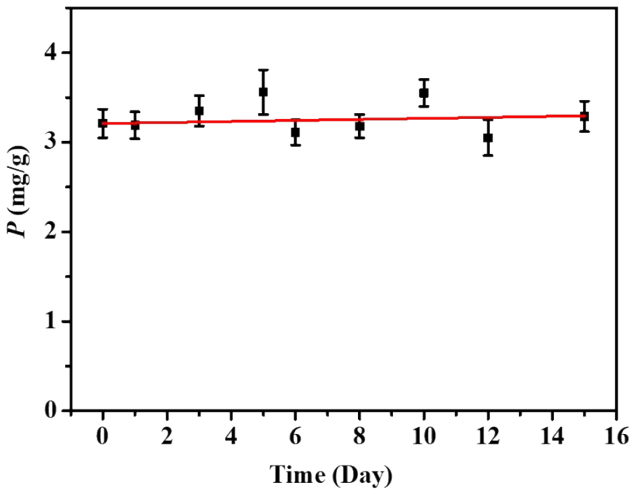


**Fig. S5.** The stability of MMIPs: the trend of adsorption properties of MMIPs within 15 days under the same conditions.

**Table S1.** Specific surface area, volume and pore size of synthesized materials.

| | Pore size / nm | Surface area / $m^2g^{-1}$ | Pore volume / $cm^3g^{-1}$ |
|---|---|---|---|
| MMIP | 7.8875 | 50.8283 | 0.084370 |
| MNIP | 7.7272 | 40.9744 | 0.082571 |

**Table S2.** Validation of methcathinone of spiked samples by the developed MSPE/LC-MS/MS

| Sample | Added (ng/L) | Found* (ng/L) | Recovery (%) | precision RSD (%, n = 3) | |
|---|---|---|---|---|---|
| | | | | Intra-day | Inter-day |
| Wastewater | 20 | 23.34 | 116.7 | 4.77 | 6.89 |
| | 100 | 96.35 | 96.35 | 3.98 | 5.33 |
| | 1000 | 1089.23 | 108.9 | 3.15 | 4.68 |

* Mean of three determinations