

Highly selective enrichment and direct determination of imazethapyr residues from milk using magnetic solid-phase extraction based on restricted-access molecularly imprinted polymers

Shicong Jia^{1,2}, Yanqiang Zhou¹, Jianmin Li¹, Bolin Gong^{1*}, Shujuan Ma², Junjie Ou^{2*}

¹School of Chemistry and Chemical Engineering, Key Laboratory for Chemical Engineering and Technology, State Ethnic Affairs Commission, North Minzu University, Yinchuan, P. R. China

²CAS Key Laboratory of Separation Science for Analytical Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

***Corresponding author.**

Email addresses:gongbolin@163.com (B. Gong)

Email addresses:junjieou@dicp.ac.cn (J. Ou)

Preparation of Fe₃O₄

Fe₃O₄ nanoparticles were synthesized by co-precipitation method. FeCl₃ • 6H₂O (6.75 g) was dissolved in deionized water. Anhydrous ethanol (250 mL) was added and transferred to the volumetric flask (500 mL). Take the above solution, increase the temperature to 50 °C, then add hydroxylamine hydrochloride (0.43 g), and after reacting for 10 min, adjust the pH (9-10) with ammonia water. After magnetic stirring for 30 min, 10 mL of oleic acid was added, and after standing for 20 min, the temperature was raised to 70 °C, and magnetic stirring was performed for 60 min, followed by cooling to room temperature, and slowly adding hydrochloric acid to adjust pH=4. The synthesized Fe₃O₄ nanoparticles were magnetically separated, washed with anhydrous ethanol and acetone 3-5 times, dried under vacuum, and then used.

Synthesis of Fe₃O₄@SiO₂ Nanoparticles

Fe₃O₄@SiO₂ nanoparticles were synthesized according to the literature. Fe₃O₄ nanoparticles (0.6 g) were uniformly dispersed in a mixture of ethanol (320 mL) and deionized water (80 mL). After sonicating the mixture for 20 min, ammonia (10 mL) and TEOS (2 mL) were added. After mechanical stirring at 40 °C for 6 h, Fe₃O₄@SiO₂ nanoparticles were separated with a strong magnet, washed with ethanol 3-5 times, then dried under vacuum and stored for later use.

Preparation of Fe₃O₄@SiO₂@NH₂ Nanoparticles

Amine functionalization of Fe₃O₄@SiO₂ nanoparticles according to methods reported in the literature. Fe₃O₄@SiO₂ nanoparticles (0.4 g) were dispersed in

anhydrous toluene (50 mL), and the mixture was sonicated for 15 min before adding APTES (4 mL). The mixture was stirred under N₂ gas protection at 120 °C for 24 h. Fe₃O₄@ SiO₂@NH₂ nanoparticles were washed 3-5 times with anhydrous toluene and acetone, respectively, separated and dried under vacuum.

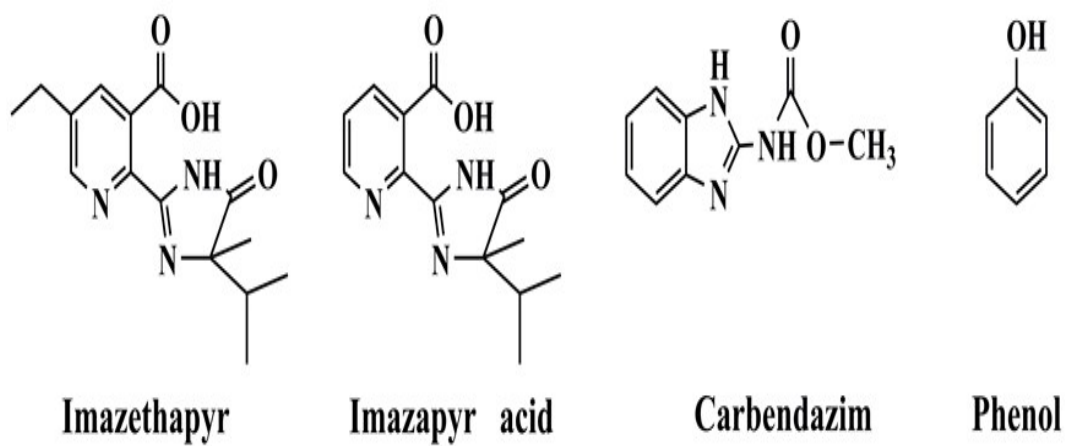


Figure S1. The structures of imazapyr (IM), imazapyr acid, carbendazim and phenol.

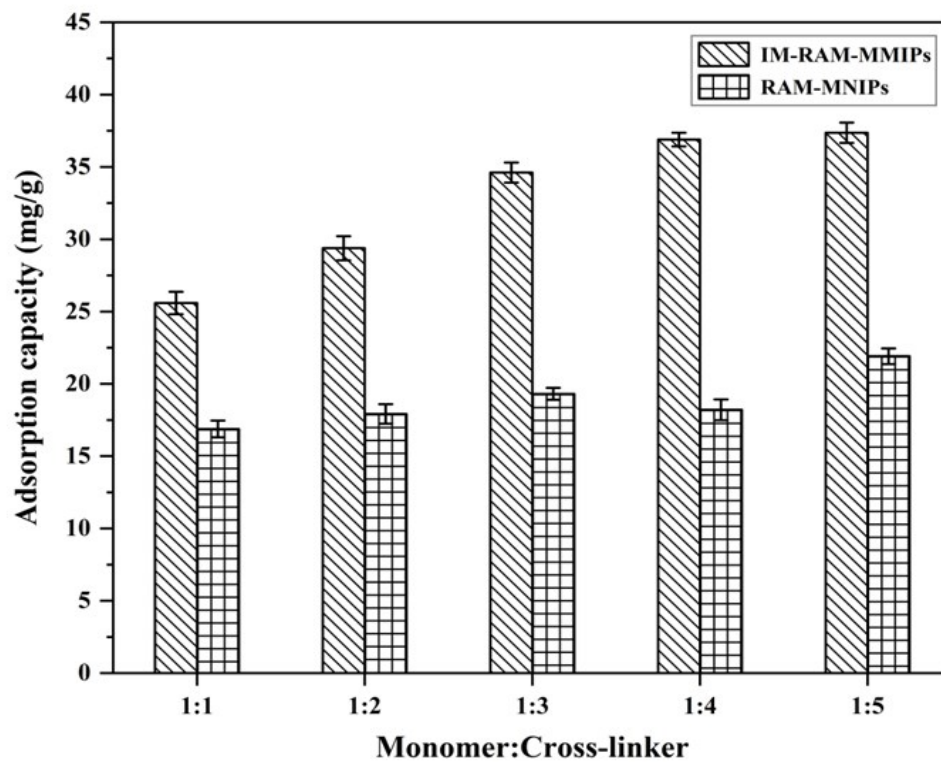


Figure S2. Adsorption capacity of IM-RAM-MMIPs and RAM-MNIPs for IM at different molar ratios of functional monomer to cross-linker.

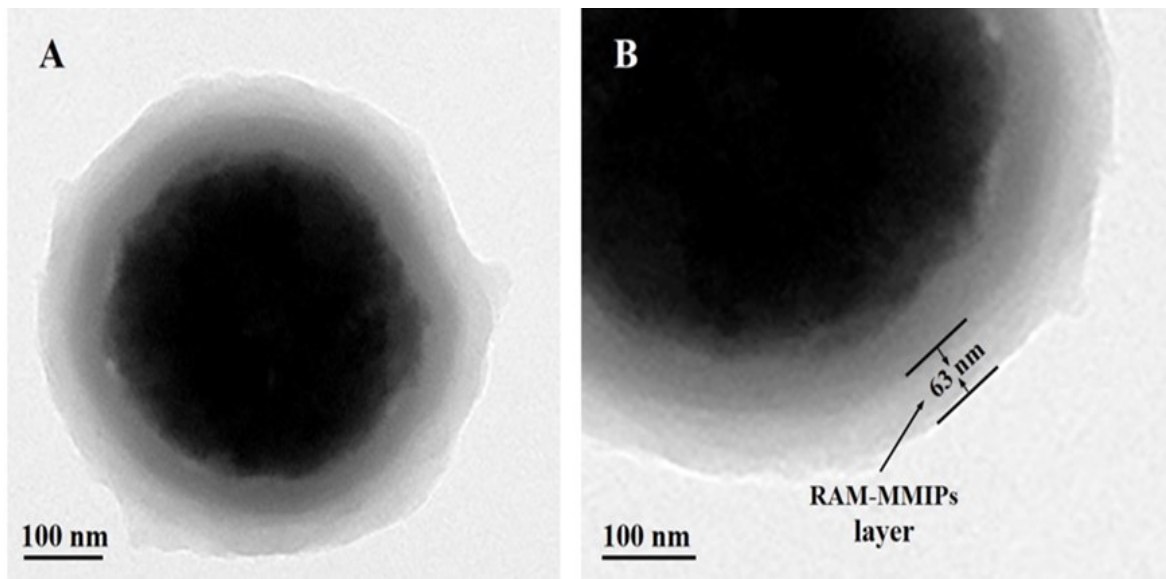


Figure S3. TEM images of IM-RAM-MMIPs.

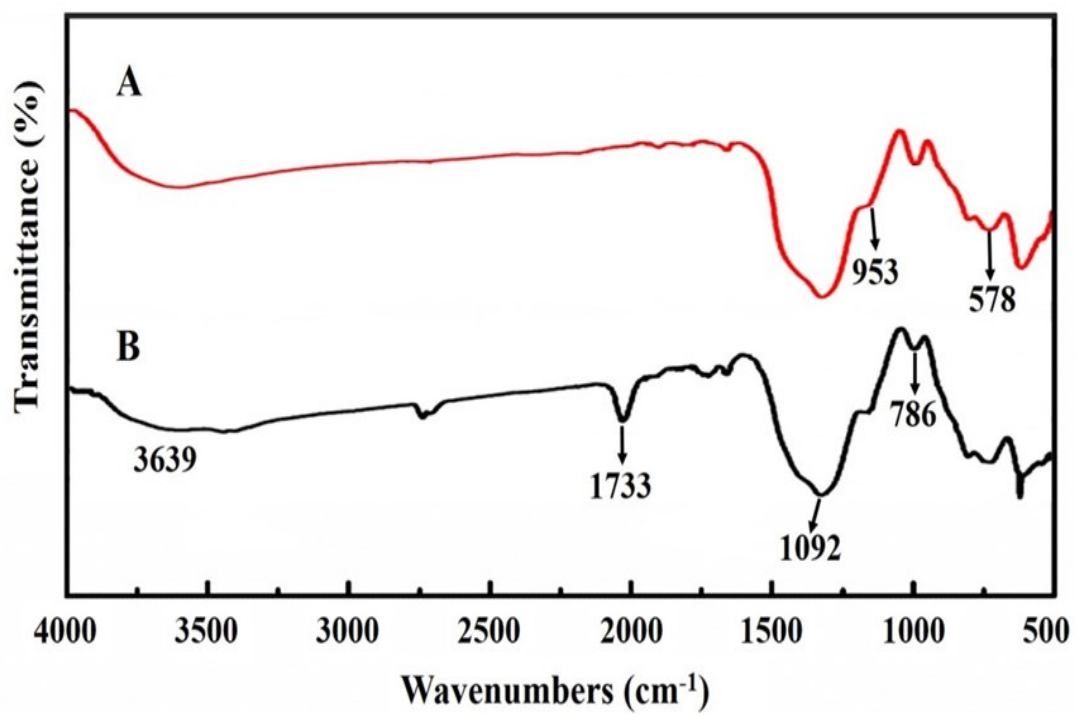


Figure S4. Fourier transform infrared (FT-IR) spectra of (A) Fe₃O₄@SiO₂ and (B)

IM-RAM-MMIPs.

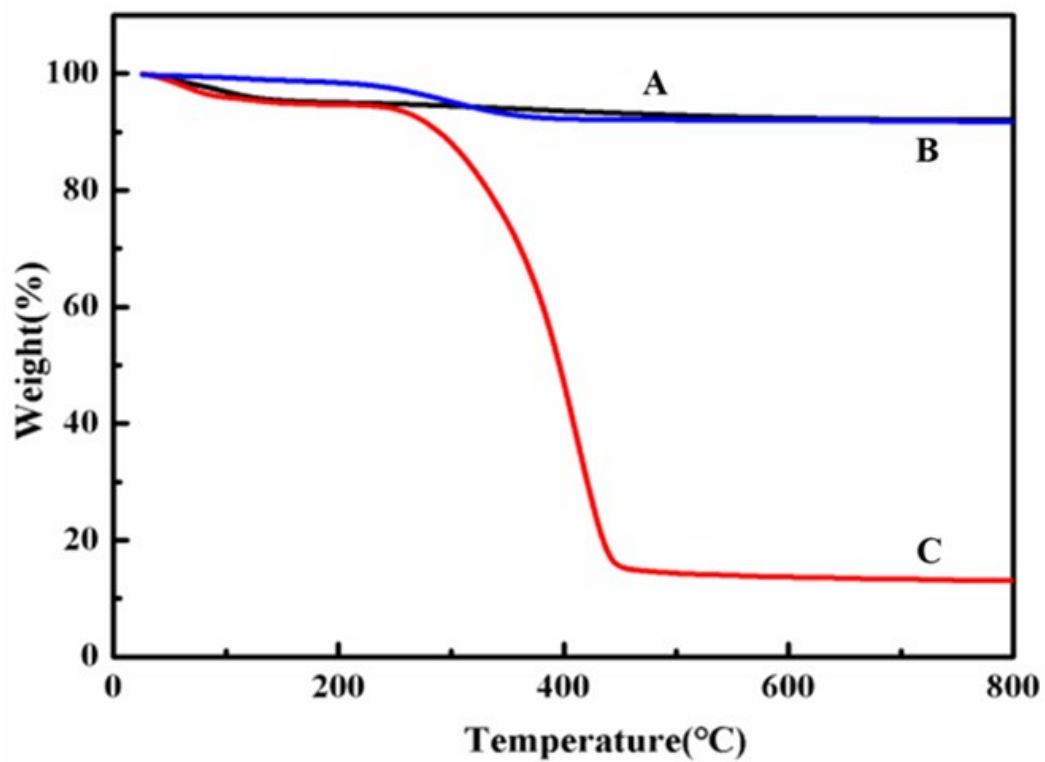


Figure S5. Thermogravimetric analysis curves of (A) Fe_3O_4 , (B) $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and (C) IM-RAM-MMIPs.

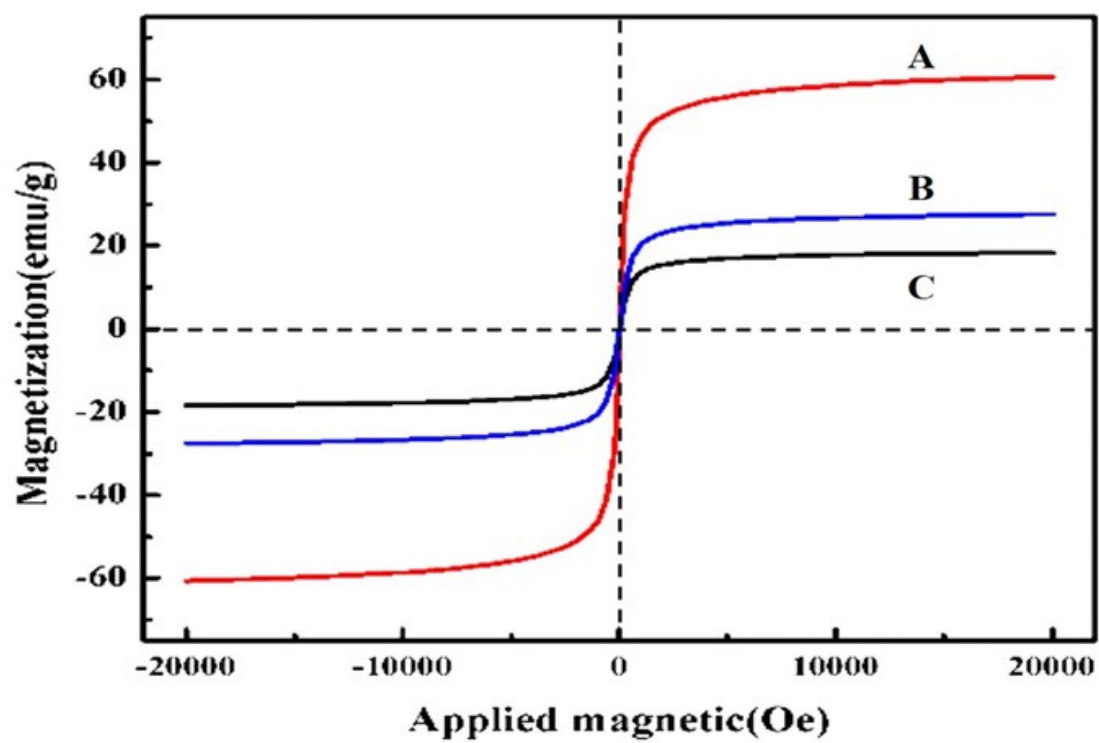


Figure S6. Magnetization curves of (A) Fe_3O_4 , (B) $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and (C) IM-RAM-MMIPs.

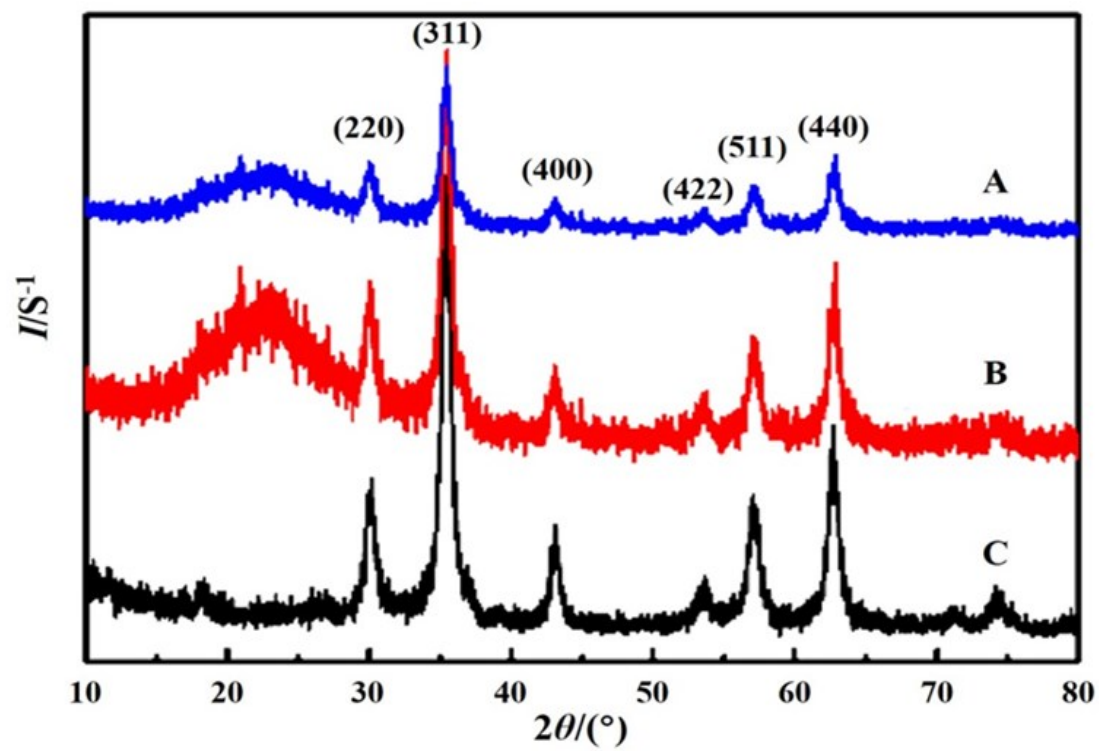


Figure S7. XRD patterns of (A) IM-RAM-MMIPs, (B) $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and (C) Fe_3O_4 .



Figure S8. Water contact angle profiles of IM-RAM-MMIPs.

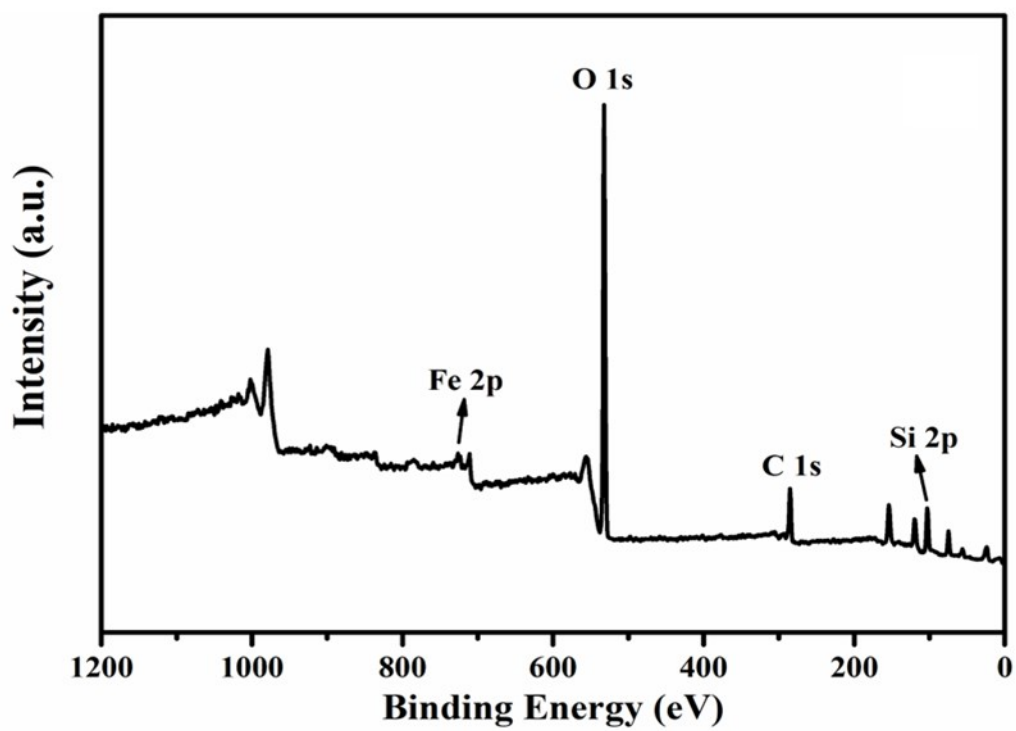


Figure S9. XPS spectra of survey scan of IM-RAM-MMIPs.

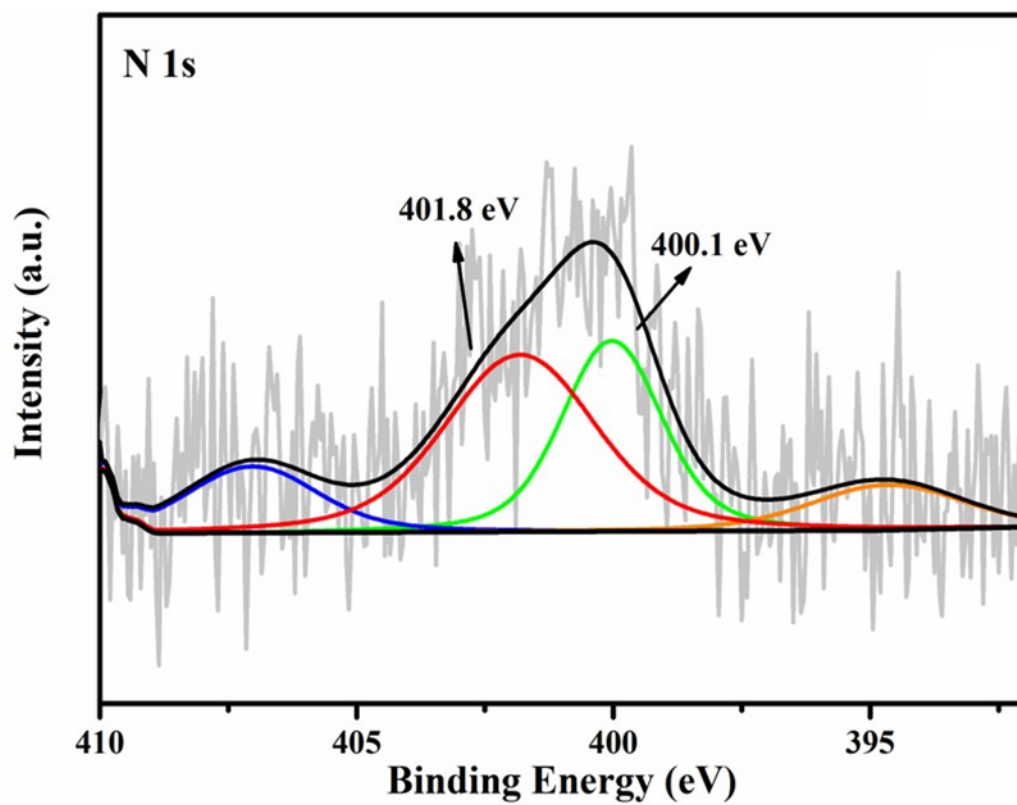


Figure S10. High-resolution scan of N 1s spectra of IM-RAM-MMIPs.

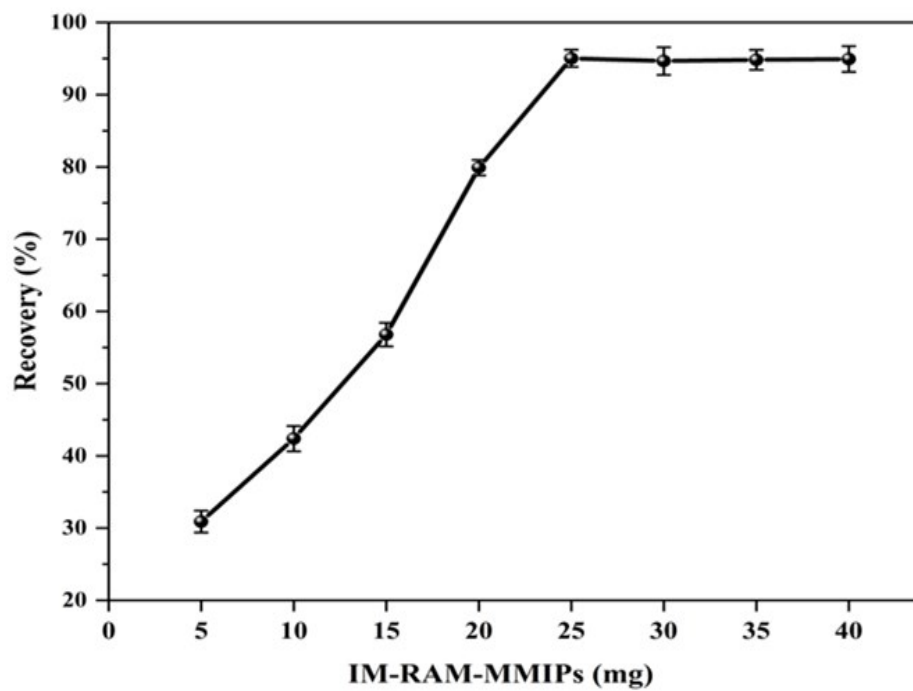


Figure S11. The effect of the amount of IM-RAM-MMIPs on recovery.

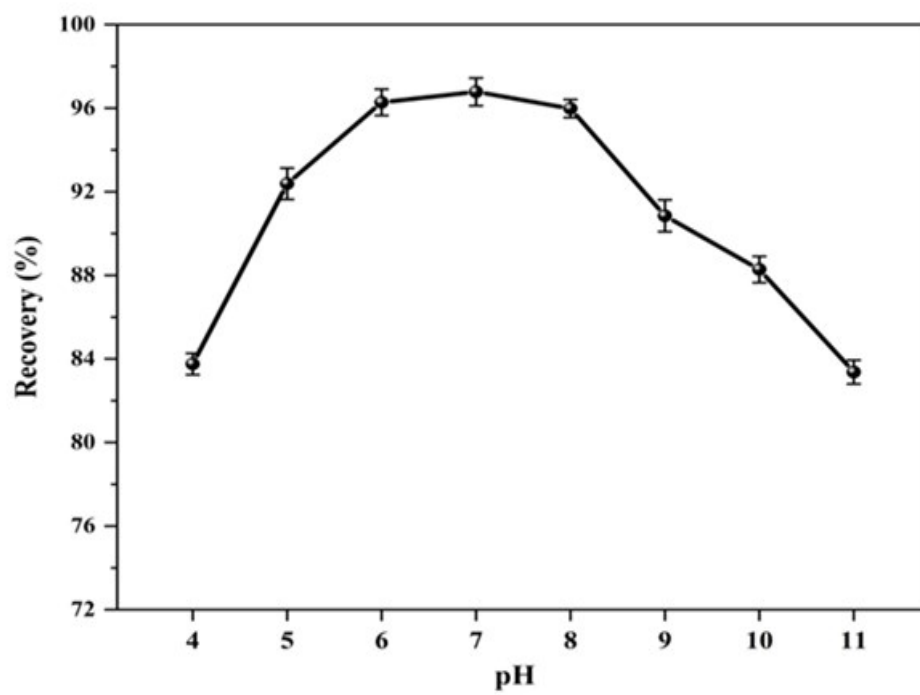


Figure S12. The effect of the pH of milk sample solution on recovery.

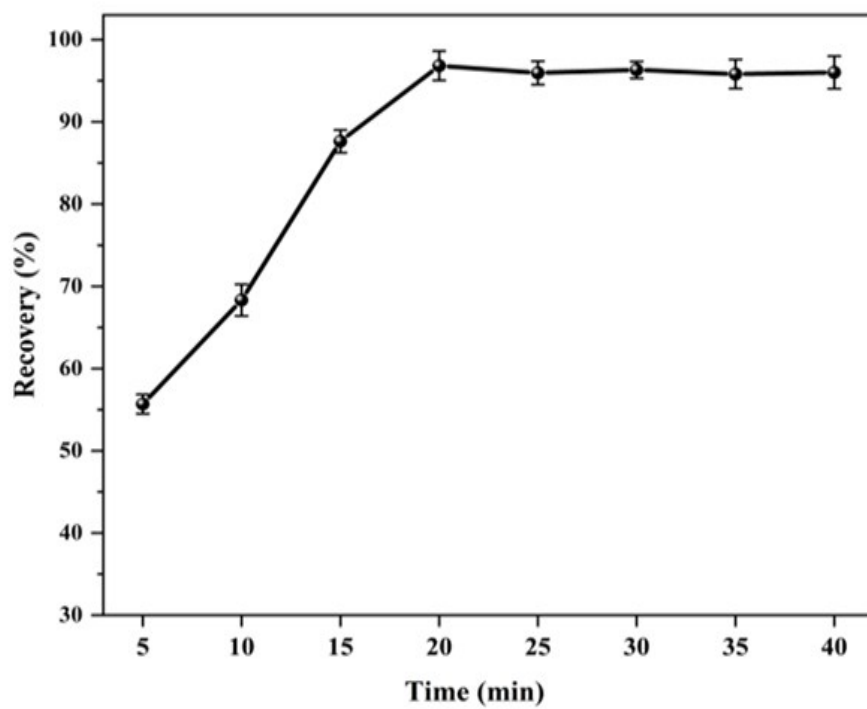


Figure S13. The effect of the ultrasonic extraction time on recovery.

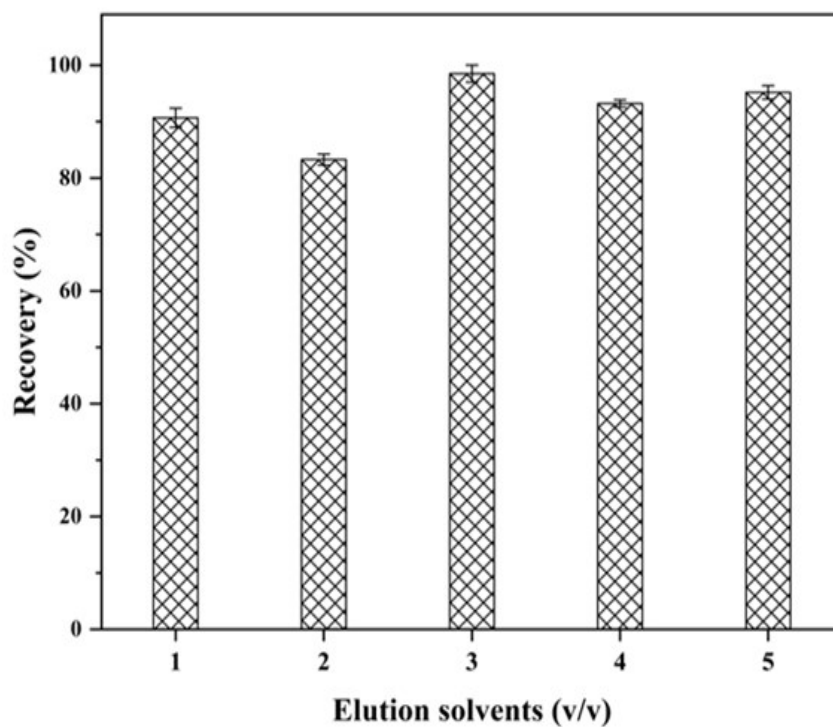


Figure S14. The effect of the elution solvents with different volume ratios on recovery. 1, methanol-acetic acid (7:3); 2, alcohol-ammonium hydroxide (8:2); 3, methanol-ammonium hydroxide (9:1); 4, alcohol-ammonium hydroxide (9:1); 5, methanol-ammonium hydroxide (9:1), Soxhlet extracted.

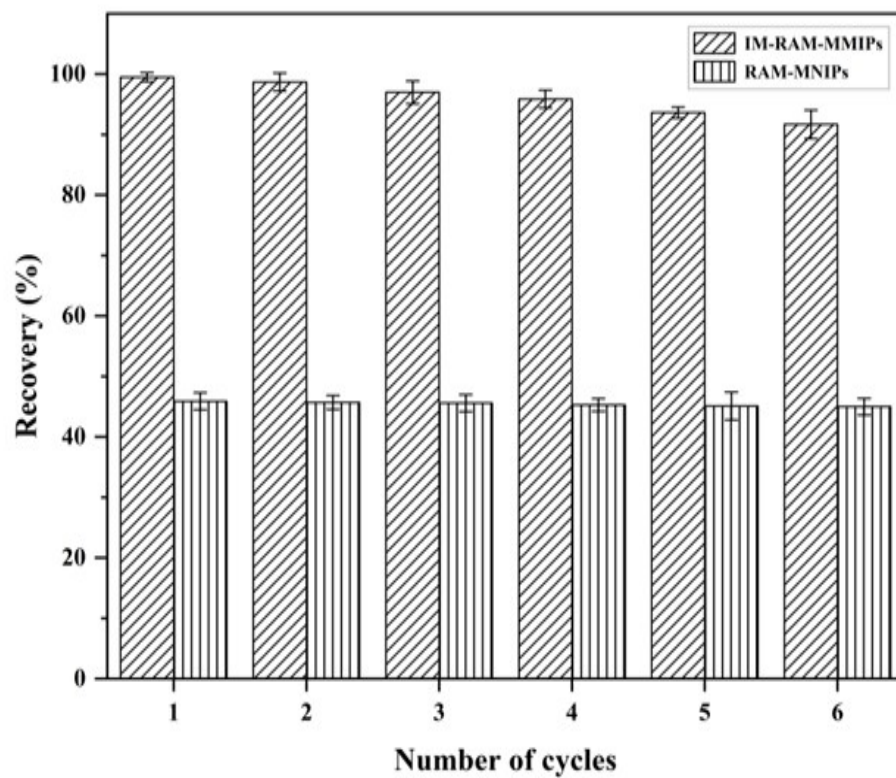


Figure S15. The regeneration ability of the IM-RAM-MMIPs.

Table S1 Specific surface area, pore size and pore volume of IM-RAM-MMIPs and
RAM-MNIPs.

Polymers	Surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume($\text{cm}^3 \text{g}^{-1}$)	Pore size (nm)
IM-RAM-MMIPs	135	0.45	14.5
RAM-MNIPs	113	0.43	13.9

Table S2 Kinetic parameters for the pseudo-first-order and pseudo-second-order models of IM.

Sorbents	Pseudo-first-order model			Pseudo-second-order model		
	K_1 (min ⁻¹)	Q_e (mg g ⁻¹)	R	K_2 (g/mg/min)	Q_e (mg g ⁻¹)	R
IM-RAM-MMIP	0.1207	39.25	0.9747	0.0041	35.39	0.9961
RAM-MNIP	0.1152	25.88	0.9748	0.0032	23.95	0.9941

Table S3 Isothermal parameters for Langmuir and Freundlich models of IM.

Sorbents	Langmuir isothermal model			Freundlich isothermal model		
	K_L (mL mg ⁻¹)	Q_{IMx} (mg g ⁻¹)	R	K_F (mg g ⁻¹)	$1/n$	R
IM-RAM-MMIP	4.12	36.59	0.9975	39.81	0.4473	0.9778
RAM-MNIP	4.05	24.06	0.9971	25.67	0.4525	0.9761

Table S4 The adsorption capacity, IF and SC of IM-RAM-MMIP and RAM-MNIP for IM, imazapyr acid, carbendazim and phenol (n=5).

Adsorbates	$Q_{\text{IM-RAM-MMIPs}}$ (mg/g)	$Q_{\text{RAM-MNIPs}}$ (mg/g)	<i>IF</i>	<i>SC</i>
IM	34.52	18.93	1.83	————
Imazapyr acid	17.03	14.79	1.15	1.59
Carbendazim	12.62	13.81	0.91	2.01
Phenol	2.41	2.73	0.88	2.08

Table S5 Comparison of proposed method with reported methods in MIP.

Absorbents	Protein precipitation methods	Methods	Time (min)	LOD ($\mu\text{g L}^{-1}$)	Recovery (%)	samples	Ref
MIP-SPME fiber	Dichloromethane	SPEM-HPLC	40	0.07-0.29	67.1-99.5 79.1-123	rice peanut	[3]
CMCPS-MIPs	0.1mol L ⁻¹ Ammonium Chloride	SPE-HPLC	180	15	91.1-97.5	soil	[24]
MIP-1VN	0.45 μm Nylon	MISPE-HPLC-PAD	11	5-11	86-107	water rice	[25]
RAM-MMIPs	without	MSPE-HPLC/UV	35	2.13	87.3-102.5	milk	this work