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Preparation of magnetic superhydrophilic molecularly imprinted resins for detection of triazines in aqueous samples

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ABSTRACT

In this work, magnetic superhydrophilic molecularly imprinted resins (MMIRs) were prepared for the determination of triazines in aqueous samples combined HPLC–MS/MS. The amino functionalized magnetic nanoparticles were introduced into superhydrophilic molecularly imprinted resins based on one-pot condensation of resorcinol, melamine and formaldehyde. The obtained MMIRs exhibited magnetic responsiveness, superhydrophilic and selective feature. The MMIRs were directly used as adsorbents for selective enrichment and separation of six triazines in juice and lake samples under an applied magnetic field. The detection limits of triazines are in the range of 0.02–0.07 $\mu g\,L^{-1}$ (except for simazine, 0.38 $\mu g\,L^{-1}$). At the spiked level (5 $\mu g\,L^{-1}$), the recoveries are in the range of 85–101% with the RSDs $\leq$7%. This work provided a novel and efficient approach for the detection of triazines in aqueous samples.

1. Introduction

Triazine herbicides have been widely used to increase the yield of crops in agriculture. However, high stability and abuse of triazines have led to the diffusion and accumulation in food and environment. Researches demonstrated that triazines are harmful to human health, such as cancer, birth defects and hormonal disorder [1–4]. In the past decades, a variety of pretreatment and quantification methods have been used for enrichment and detection of triazines in food and environment samples, including gas chromatography (GC) combined air-assisted liquid–liquid microextraction (LLE) [5], dispersive liquid–liquid microextraction followed by high-performance liquid chromatography (HPLC) [4], high performance liquid chromatography-tandem mass spectrometry (HPLC–MS/MS) combined solid phase extraction (SPE) [2], etc. However, the conventional LLE and SPE methods often lack selectivity. Molecularly imprinted polymers (MIPs) with memory function of shape, size and functional groups to template molecules [6], have been applied as selective materials for extraction of triazines [7–10]. In particular, MIPs combine HPLC–MS/MS have been received excellent performance [9].

Although molecular imprinting technology has made great progress in the detection of triazines, most MIPs are often prepared and used in organic environments [7,9,10]. This significantly limits the detection of triazines in aqueous samples such as beverages and environmental waters. Up to now, various strategies have been attempted to prepare MIPs for the detection of triazines in aqueous samples. Sambe et al. utilized glycerol dimethacrylate and glycerol monomethacrylate as hydrophilic monomers to synthesize a hydrophilic restricted access media MIPs for the detection of triazines in river water [11]. Xu et al. prepared a double water-compatible MIPs with water-compatible core and hydrophilic polymer brushes to enrich the triazines in river and tap water [12]. Qiao et al. prepared water-compatible MIPs by water/oil/water suspension polymerization to detect triazines in environmental water [13]. The above methods shared some strategies to prepare MIPs used to detect triazines in aqueous samples, while the preparation methods more or less have some drawbacks, involving cumbersome multi-step graft or swelling process, difficult to obtain hydrophilic allylic monomer, requiring nitrogen

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and lower yield. It is necessary to exploit an effective strategy for synthesizing hydrophilic imprinted material by a simplicity and reliability method.

Recently, more and more reports utilized non-allylic monomers or non-radical polymerization strategies to produce MIPs used in water. Some researchers used polysaccharides (e.g. sodium alginate, chitosan and gelatin) to prepare water-compatible MIPs. The polysaccharides with many hydrophilic groups can be used as hydrophilic monomers to form multiple hydrogen bonds with the targets or can be used as cross-linker for self-assembly [14–16]. Some researchers used poly-dopamine or polyethyleneimine (PEI) as hydrophilic monomer or cross-linker to prepare water-compatible MIPs because the poly-dopamine and PEI are hydrophilic, biocompatible and multifunctional [17–20]. In addition, more and more attentions have been paid to prepare water-compatible molecular imprinted resins (MIRs) by the condensation of aldehyde, amino and hydroxyl groups. The preparation process also avoids the use of allylic-monomer and the auxiliary of nitrogen, more important, the hydrophilic raw materials are very common. Yang et al. utilized the condensation of glyoxal, urea and formaldehyde to produce glyoxal-urea-formaldehyde gel as hydrophilic monomer to prepare water-compatible MIRs [21]. Guo et al. and Wang et al. prepared water-compatible MIRs utilizing water-soluble melamine-urea-formaldehyde (MUF) gel as hydrophilic monomer [22,23]. However, the preparation methods needed a longer time to solidify and required grinding and sieving. Lv et al. synthesized hydrophilic molecularly imprinted resorcinol-formaldehyde-melamine resin to extract sulfonamides in milk [24]. However, in addition to our previous report [25], there have been no reports of hydrophilic MIRs for the detection of triazines. The application of the above MIRs often requires time consuming and laborious processes such as centrifugation, filtration or column loading. When a magnetic component is introduced into hydrophilic MIRs, the obtained magnetic hydrophilic molecularly imprinted resins (MMIRs), not only possess magnetic characteristic, but also have specific recognition function on the triazines in aqueous samples.

In this work, we introduced amino-functionalized magnetic nanoparticles (Fe_3O_4@NH_2) into the preparation of superhydrophilic molecular imprinted resins based on one-pot condensation of resorcinol, melamine and formaldehyde for the determination of triazines in aqueous samples. Firstly, $FeCl_3 \cdot 6H_2O$ was used as the sole iron source to prepare Fe_3O_4@NH_2 by solvothermal method. Then, the MMIRs were prepared by using resorcinol and melamine as hydrophilic monomer, formaldehyde as hydrophilic crosslinking agent and ametryn, a widely used triazine, as template. Finally, the obtained MMIRs with large amounts of hydrophilic groups were used as magnetic adsorbents to rapid extraction and analysis of six triazines in juice and lake samples followed by HPLC–MS/MS.

2. Experiment

2.1. Chemicals and standards

The standards of ametryn, atrazine, desmetryn, prometryn, propazine and simazine (purity >98%) were provided from the Dr. Ehrenstorfer (Augsburg, Germany). Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), 1, 6-hexadiamine (HDM), anhydrous sodium acetate (NaOAc), ethylene glycol (EG), Melamine, formaldehyde (37 wt.%), resorcinol, sulfamonomethoxine (SDM) and florfenicol (FF) were purchased from the National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Chromatographic grade ACN was purchased from Fisher (Pittsburgh, PA, USA). Deionized water (18.2 $M\Omega\,cm^{-1}$) used throughout the experiment was prepared by a Milli-Q water system (Millipore, Billerica, MA, USA). All other reagents added in the experiment were of analytical grade and used directly as received except for special statement. The chemical structures of analytes are shown in Fig.S1.

Stock solution containing 500 $mg\,L^{-1}$ of each analyte was prepared by methanol. Working solution was obtained by diluting the stock solution with deionized water every day. Both stock and working solutions were stored in a refrigerator in the dark.

2.2. Juice and lake water samples

Peach juice, orange juice and Grape juice (Kangshifu Co., Ltd., Beijing) were purchased from local market in Changchun. Three lake samples were randomly collected from Yan Lake, Qing Lake of Jilin University (Changchun, Jilin Province, China) and South Lake (Changchun, China). All samples were maintained at 4 °C in the dark.

2.3. The preparation of Fe_3O_4@NH_2

The Fe_3O_4@NH_2 was prepared through a solvothermal method according to the reported method with some modifications [17]. Briefly, HDM (11.0 g), NaOAc (5.0 g), $FeCl_3 \cdot 6H_2O$ (3.0 g) were dispersed into EG (60 mL) under magnetic stirring. The obtained homogeneous brown yellow solution was transferred to two Teflon-lined stainless-steel autoclaves and sealed to heat 10 h at 200 °C. The products were washed off the impurities and dried at 60 °C until constant weight.

2.4. The preparation of the superhydrophilic MMIRs

The superhydrophilic MMIRs were prepared as follow: formaldehyde (4.5 mL) and resorcinol (3.303 g) were dissolved in 30 mL of deionized water and stirred for 1 h at 40 °C to form the solution A. Simultaneously, formaldehyde (2.25 mL), melamine (1.261 g) were dispersed in 10 mL of deionized water followed by stirring at 80 °C until the melamine was completely dissolved. Then, Fe_3O_4@NH_2 (0.35 g) and formaldehyde (1 mL) were successively dispersed in the above melamine solution with the help of ultrasound to form the solution B. The solution B was added into the solution A followed by adding 10 mL ametryn acetonitrile solution (0.1 $mol\,L^{-1}$). The mixture was self-assembled at 450 rpm for 40 min. The subsequent condensation was carried out at 80 °C for 14 h and then at 85 °C for 3 h. The products were collected magnetically, washed repeatedly with methanol/acetic acid/water (3:1:1, v/v) until no ametryn was detected by HPLC. After washing off the residual acetic acid, the MMIRs were dried to constant weights. Adopting the same procedures, magnetic superhydrophilic non-imprinted resins (MNIRs) were synthesized in the absence of ametryn. Hydrophilic MIRs were synthesized in the absence of Fe_3O_4@NH_2 (0.35 g) and formaldehyde (1 mL). Hydrophilic non-molecular imprinted resins (NIRs) were synthesized following the same procedure of the MIRs in the absence of ametryn.

2.5. Characterizations of the resins

Fourier transform infrared spectroscopy (FTIR, Nicolet AVATAR 360 FT-IR spectrophotometer) was used to characterize the functional groups. Vibrating sample magnetometer (VSM; JDM-13, Jilin University, Changchun, China) was used to test the magnetic properties. The morphology, X-ray diffraction (XRD) pattern, water contact angle and thermal stability were investigated by field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan), Shimadzu XRD-6100 spectrometer, KRÜSS FM40 Easy Drop