



# Water-compatible magnetic imprinted microspheres for rapid separation and determination of triazine herbicides in environmental water



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## ABSTRACT

A novel kind of water-compatible magnetic imprinted cyromazine microsphere (WCMM) was synthesized by water/oil/water suspension polymerization. The obtained WCMM was homogeneously spherical with porous morphology and strong magnetic properties. The microspheres were successfully used as adsorbent in dispersive solid-phase extraction (WCMM-dSPE) to selectively extract cyanazine and atrazine from environmental water. Good linearity of the two analytes was observed in the range from 2.5 to 200.0 ng mL<sup>-1</sup>. The average recoveries at three spiking levels ranged from 84.8% to 104.3% with relative standard deviations (RSD) less than 6.9%. Compared with magnetic non-imprinted particles (WCMN), the proposed WCMM adsorbent of dSPE efficiently improved the efficiency of extracting cyanazine and atrazine from environmental water samples and eliminated the effect of cyromazine leakage on the quantitative analysis of cyanazine and atrazine. The proposed WCMM-dSPE method combined the advantages of magnetic separation, molecular imprinted microspheres and dSPE.

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## 1. Introduction

The increasing widespread use of pesticides, especially triazine herbicides like cyanazine and atrazine, is a serious threat to water quality due to their high solubility in aqueous media [1,2]. While cyanazine is teratogenic and mutagenic in humans, atrazine destroys the cardiovascular and reproductive system [3]. Thus, there is an urgent requirement for the development of high-efficient pre-treatment procedures and high-sensitivity analysis methods to identify and quantify cyanazine and atrazine.

Several methods for the determination of triazines has been developed, such as high-performance liquid chromatography (HPLC) [4–6], gas chromatography (GC) [7,8], gas chromatography-mass spectrometry (GC-MS) [9,10] and HPLC-MS [11,12]. Owing to low levels of analytes in samples and the complexity of the sample matrix, an appropriate sample pre-treatment and enrichment process is needed. Generally, liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are widely used in sample pretreatment processes [13,14]. However, these methods are

time-consuming and large volume of organic solvents are required [15]. Dispersive solid-phase extraction (dSPE), often refers to as the “QuEChERS” (quick, easy, cheap, effective, rugged and safe) method, is very suitable for large volume environmental water sample preparation [16,17]. The separation process of dSPE can be performed by dispersing the adsorbents in a sample solution, thereby increasing the interaction between adsorbent and analyte. The channeling or blocking of SPE cartridges can be effectively eliminated by dSPE. However, the common adsorbents such as primary secondary amine (PSA), octadecylsilane (C<sub>18</sub>), and graphitized carbon black (GCB), all lack the necessary selectivity. Moreover, ordinary dSPE procedures require tedious filtration or centrifugation steps to separate adsorbent particles from the liquid sample.

Magnetic particles for the strong magnetic response have been widely applied in biological field, such as bioseparation, drug delivery and biomolecular sensing [18–20]. Recently it is used as SPE or dSPE adsorbent for environmental sample pretreatment, which make the process of sample pretreatment become easy and effective [21,22]. Graphene-coated magnetic nanoparticles as a new adsorbent of SPE make the process of SPE more efficient [23]. Meanwhile in the field of dSPE, the magnetic particles can be separated only by a magnet, which is time-saving, maneuverability and highly effective. The application of magnetic adsorbent for dSPE is amazing and potential.

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Molecular imprinting is known as a technique for the creation of tailor-made recognition sites able to specifically rebind a target molecule by the shape, size and functional groups [24]. A typical molecular imprinting process usually involves the formation of a complex between template molecules and functional monomer via either non-covalent interactions (such as hydrogen bonds, ionic interactions, hydrophobic interactions, and metal-ion chelating interactions) or reversible covalent bonds (e.g., boronate ester, ketal and acetal, or Schiff base), which is subsequently copolymerized with cross-linkers. After removal of the template molecules, the residue recognition cavities are complementary in size, shape, and functionality to those of template molecules, so it can selectively rebind with the template molecules or its similar structure compounds from a complex matrix [25]. Many kinds of molecularly imprinted polymer (MIP) have been developed [26–30]. Due to regular shape and size, molecularly imprinted microspheres (MIM) become one of amazing MIPs [31]. Recently, magnetic molecularly imprinted polymer attract many researcher's attention, because when the magnetic components be encapsulated into MIP, the resulting composite magnetic MIP not only possess susceptible magnetic characteristics, but also have high selectivity for target molecules [32]. The regular magnetic MIM is a trend of the development of MIP.

The purpose of this study was to develop and validate an analytical method for rapid and selective isolation of cyanazine and atrazine from environment water. A new kind of water-compatible magnetic cyromazine molecularly imprinted microspheres (WCMM), synthesized by water/oil/water suspension polymerization, was employed as the adsorbent of dSPE to improve the selectivity and efficiency of the sample pretreatment procedure. Furthermore, application of a cyromazine template in the polymerization process efficiently eliminated analyte leakage and improved the quantitative analysis. The proposed WCMM-dSPE method combined the quick separation of magnetic particles, the high selectivity of molecular imprinted microspheres and the good clarification, enrichment and high extraction efficiency of dSPE into together. It could be potentially applied for the quantitative determination of triazine in environment water samples.

## 2. Experimental

### 2.1. Chemicals and reagents

Cyanazine, atrazine, and cyromazine were obtained from Dacheng pesticide Co. Ltd (Shandong, China). Hydroxyethylcellulose (HEC) was purchased from Guangfu fine chemical industry research institute (Tianjin, China). Acetonitrile, methanol, acetic acid, and ammonia were purchased from Huadong Chemical Reagent Co. (Tianjin, China). Iron(II) chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), iron(III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), oleic acid, methacrylic acid (MAA) and 2,2-azobisisobutyronitrile (AIBN) were obtained from Kermel Chemical Reagents Development Center (Tianjin, China) and trimethylolpropane trimethacrylate (TRIM) was purchased from Sigma–Aldrich (St. Louis, MO, USA). Double-deionized water was filtered through 0.45  $\mu\text{m}$  filter membrane before use.

### 2.2. Instrumentation and experimental conditions

HPLC analysis was performed using a Shimadzu LC-20A system equipped with two LC-20AT solvent delivery units, a SUS-20A gradient controller and a SPD-20A UV-Vis detector (Shimadzu, Kyoto, Japan). A fourier transform infrared (FT-IR) spectrometer (Shimadzu, Japan) was employed to examine the infrared spectra of samples. The morphological evaluation was carried out by scanning electron

micrography (SEM, KYKY-2800B, operating at 25 kV). The analytical column (150 mm  $\times$  4.6 mm I.D.,  $\text{C}_{18}$ , 5  $\mu\text{m}$ ) was purchased from Agilent Technologies Co. Ltd. (California, USA). The mobile phase consisted of water-methanol (45:55, v:v, containing 0.8% acetic acid) at the flow rate of 1.0 mL  $\text{min}^{-1}$ , and the detection wavelength was 224 nm.

### 2.3. Preparation of $\text{Fe}_3\text{O}_4$ magnetic nanoparticles

$\text{Fe}_3\text{O}_4$  magnetic nanoparticles were prepared by coprecipitation method as follows:  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (0.02 mol) and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.03 mol) were dissolved in water (100 mL) by ultrasonic oscillations (500 rpm) for 20 min under nitrogen conditions. As the mixture be heated to 60 °C, ammonium hydroxide (15 mL) was added dropwise into the mixture, causing the color to become black. After 1 h, the obtained magnetic nanoparticles were isolated from the solvent by a permanent magnet and washed several times with deaerated highly purified water and ethanol.

### 2.4. Preparation of WCMM

The water compatible magnetic molecularly imprinted microsphere (WCMM) was prepared by two main steps as follows: (I) Water-in-oil (W/O) inverse emulsion was formed by adding the water phase (10 mL of water solution containing 150 mg of  $\text{Fe}_3\text{O}_4$  nanoparticles) into the oil phase (0.05 g AIBN, 5 mmol of TRIM and 200  $\mu\text{L}$  of oleic acid be dissolved in 2.0 mL of toluene); (II) Water-in-oil-in-water (W/O/W) multiple emulsions was formed by dropping the water-in-oil (W/O) emulsion into ethanol-water (21 mL, 1:2, v:v) solutions that contained 3 mmol MAA, 1 mmol cyromazine and 0.040 g HEC. The mixture was stirred for 20 min and sonicated for 30 min to form the W/O/W form. At the same time nitrogen gas was injected into the above liquid for 20 min to remove the oxygen. The polymerization was performed under agitation of 250 rpm at 70 °C for 24 h. After polymerization, the obtained WCMM particles were washed with methanol-acetic acid (9:1, v:v) and methanol under ultrasonic condition respectively, and then dried under vacuum at 45 °C for 24 h. The water-compatible magnetic non-imprinted microspheres (WCMN) were prepared and processed similarly as above, except that the template molecule (cyromazine) was not added. WCMN were used as the control for comparison in the characterization studies.

### 2.5. Sample pretreatment of dSPE

The environmental water samples were obtained from the local place and stored at 0–4 °C. A sample (20 mL) without filtration and centrifugation was placed into a 20 mL glass bottle, then WCMM (50 mg) was added and thoroughly dispersed in sample by slight shake. After adsorption for 5 min, the WCMM was separated from the water sample by a magnet on the base or wall of the bottle, and then it was washed with deionized water (5.0 mL) and eluted with acetonitrile-acetic acid (5.0 mL, 9:1, v:v). The eluent was evaporated to dryness under nitrogen stream and reconstituted with mobile phase (0.5 mL) for further analysis.

## 3. Results and discussion

### 3.1. Preparation of WCMM

In order to obtain a suitable adsorbent for aqueous sample pretreatment, the water/oil/water suspension polymerization was employed for the preparation of WCMM (Fig. 1). As the core of WCMM, superparamagnetic  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles were the determinant for magnetic induction intensity of WCMM. Their

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