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Additional Information

# Magnetic molecularly imprinted polymer for the simultaneous selective extraction of phenoxy acid herbicides from environmental water samples

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## Abstract

A selective magnetic molecularly imprinted polymer (MMIP) was synthesized with 4-chloro-2-methylphenoxyacetic acid as template and 4-vinylpyridine as monomer in presence of vinylized magnetite nanoparticles. Scanning electron microscopy, nitrogen adsorption-desorption isotherms, Fourier transform infrared spectrometry and vibrating sample magnetometry were applied to characterize the resulting material. The synthesized MMIP was applied as sorbent in magnetic molecularly imprinted solid-phase extraction (MMISPE) for selective extraction of a mixture of the five herbicides (4-chloro-2-methylphenoxyacetic acid (MCPA), 4-(4-chloro-2-methylphenoxy)butyric acid (MCPB), mecoprop (MCP), fenoxaprop (FEN) and haloxyfop (HAL)). Several parameters affecting the extraction conditions were optimized to achieve the best extraction performance. The best MMISPE combined with HPLC-DAD gave detection and quantification limits between 0.33-0.71  $\mu\text{g L}^{-1}$  and 1.1-2.4  $\mu\text{g L}^{-1}$ , respectively, were obtained. The precision of the whole method provided RSD values below 7.3%, and the accuracy was demonstrated by the analysis of several water samples of different origins, with recoveries ranged from 77 to 98%. Moreover, a remarkable re-usability of the MMIP sorbent, more than 65 uses without losses in extraction capacity, was obtained.

**Keywords:** phenoxyacid herbicides, magnetic molecularly imprinted solid-phase extraction, molecularly imprinted polymer, magnetic nanoparticles, HPLC, water samples.

## 1. Introduction

Phenoxy acids herbicides, which derive from phenoxyacetic acid (Fig 1), have been widely used in agriculture since the 1950s to control annual and perennial broad-leaved weeds in a wide range of crops due to their high selectivity and strong herbicide activity. Because of their high solubility in water and low sorption in soil, in regions with intensive agricultural activities, these herbicides can easily permeate into surface and groundwater [1]. Their endocrine activity to humans and animals, and irreversible and cumulative impact on ecosystems makes water pollution control mandatory in order to preserve the environment from the presence of these herbicides[2].

These pollutants are conventionally determined by chromatographic and related techniques [3], including gas chromatography (GC) [4,5], liquid chromatography (LC) [6–17] and capillary electrophoresis (CE) [18], although other techniques have also been developed such as photochemically induced fluorescence [19] or chemiluminescence [20]. Nevertheless, these herbicides are present in aqueous systems at trace levels; hence, in most of developed analytical methodologies, sample pretreatment steps are required for achieving a pre-concentration of compounds and removal of matrix interferences. In this context, different sample preparation techniques including QuEChERS [12–14], liquid–liquid microextraction [15], solid-phase microextraction [5], and solid-phase extraction (SPE) [4,8,10,11,17,21–25] have been employed, being the latter the most commonly applied. However, limited selectivity is the usual shortcoming present in most of these conventional extraction sorbents. This drawback can be solved by the development of selective and efficient sorbents as molecularly imprinted polymers (MIPs) sorbents, extensively cross-linked polymers containing specific recognition sites for analytes of interest [26]. Indeed, MIPs have been successfully used as stable and low-cost sorbents in SPE, the so-called molecularly imprinted SPE (MISPE), for the selective extraction and clean-up of target analytes in complex samples. In recent years, some MIPs have been developed for the extraction of phenoxyacid herbicides using 4-vinylpyridine (4-VP) [2,26–28] or methacrylic acid (MAA) [29] as functional monomer, and a phenoxyacid herbicide or a related compound as template (dummy template). The MIPs prepared in these works have used bulk or precipitation polymerization methods, which can show low adsorption capacity and slow mass transfer [30]. Additionally, most of these methodologies rely on the use of conventional SPE formats such as cartridge or dispersive mode, which can be time-consuming and laborious.

As a promising sample pretreatment technique, magnetic SPE (MSPE) has received much interest due to its sustainability, high adsorption efficiency, fast separation process, easy operation and low cost. The combination of the selectivity of MIPs and the advantageous characteristics of MSPE gives rise to magnetic molecularly imprinted solid-phase extraction (MMISPE) techniques. These MMIPs not only exhibit excellent selective binding for target compounds, but also can be quickly separated and easily recovered from the samples by an external magnet, thus avoiding the associated challenging issues of conventional SPE (blocking/clogging of sorbent) and dispersive SPE (centrifugation or filtration steps) [31]. Besides, MMIPs, which prepared by using surface imprinting

technique, can overcome the problems brought by MIPs prepared by traditional polymerization approaches [32].

In the preparation process of MMIPs, magnetite nanoparticles (NPs) have been commonly used as the core-shell magnetic materials, due to their suitable features (easy preparation, functionalization, and operation) [33,34]. Thus, several one-step surface functionalization procedures of  $\text{Fe}_3\text{O}_4$  by incorporating diol-based reagents (such as PEG) and vinylized reagents [35] for further MIP synthesis have been described.

Indeed, in recent years, MMIPs have been widely used as selective adsorbents to extract several target solutes from complex matrices, including herbicides [36–39]. In the specific case of phenoxyacid herbicides analysis, the use of MMIPs as selective extraction supports has been scarcely studied [37]. These authors synthesized magnetic multi-walled carbon nanotubes (MWCNTs) MIPs using phenoxyacetic acid as the dummy-template for selective separation of four (MCPA, 4-chlorophenoxy acetic acid, 2,4-dichlorophenoxy acetic acid and 2-(2,4-dichlorophenoxy) propionic acid) of these herbicides in cereals. However, some issues such as laborious preparation process and homogeneous decoration of CNTs with magnetic NPs combined with sophisticated and expensive instrumentation (UPLC-MS/MS detection) were presented. Additionally, certain analytical aspects (reproducibility and reusability of material) were not mentioned.

The aim of this work was to describe a rapid and economic synthetic protocol for MMIPs preparation along with superparamagnetic and stable particles ( $\text{Fe}_3\text{O}_4$ ) using 4-chloro-2-methylphenoxyacetic acid (MCPA) as template, 4-vinylpyridine (4-VP) as functional monomer, ethylene glycol methacrylate (EGDMA) as cross-linker, and acetonitrile as porogenic solvent. The same magnetic polymer synthesized in the absence of herbicide was used as reference polymer (MNIP). The resulting polymers were characterized by scanning electron microscopy (SEM), nitrogen adsorption measurements, Fourier transform infrared spectroscopy (FT-IR), and vibrating sample magnetometry (VSM). Several features of MMISPE protocol for the extraction of five phenoxyacid herbicides were investigated in detail. The best MMISPE conditions were applied to the extraction of these pollutants from environmental water samples coupled with HPLC-DAD analysis. To our knowledge, it is the first application of MMIPs for simultaneous determination of phenoxyacid herbicides that could be interesting to guarantee an environmental control of these pollutants and assure the human safety.

## 2. Materials and methods

### 2.1. Chemicals and reagents

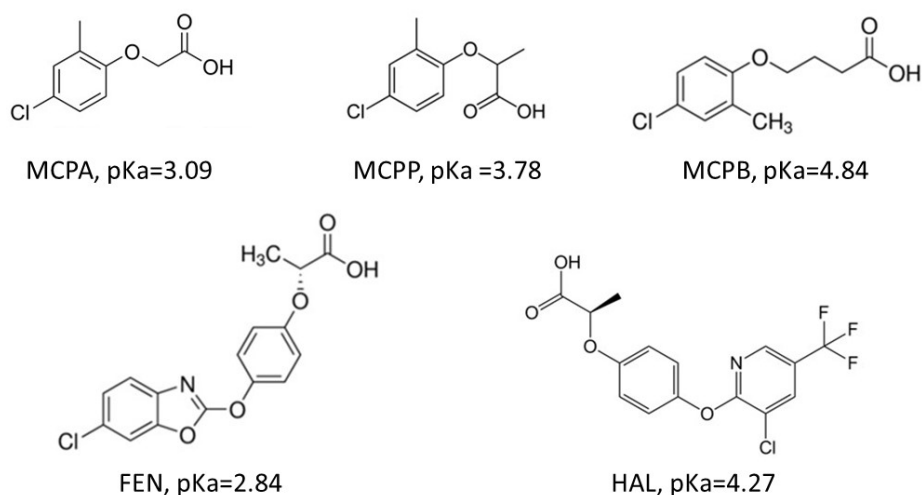
The phenoxyacid herbicides, 4-chloro-2-methylphenoxyacetic acid (MCPA), 4-(4-Chloro-2-methylphenoxy)butyric acid (MCPB), 2-(4-chloro-2-methylphenoxy)propionic acid (MCP, mecoprop), fenoxaprop (FEN) and haloxyfop (HAL), were purchased from Riedel de Haën (Seelze, Germany), (Fig 1).

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and phosphoric acid were acquired from Panreac (Barcelona, Spain), ethylene glycol dimethacrylate (EGDMA) and ammonia from Scharlab (Barcelona, Spain), and 2,2'-azobis(2-methylpropionitrile) (AIBN) from Fluka (Buchs, Switzerland). Moreover, acetic acid (AcH), vinyltrimethoxysilane (VTMS), 4-vinylpyridine (4-VP), and organic solvents such as ethanol, methanol (MeOH), dichloromethane, acetone and acetonitrile (ACN) were purchased from Merck (Darmstadt, Germany). Anhydrous- $\text{N}_2$  was supplied by Abelló Linde (Valencia, Spain).

Nylon or PTFE Phenex Filter Membranes (0.22  $\mu\text{m}$ , 13 mm) from Phenomenex (Madrid, Spain) were employed to filter solutions prior to chromatographic analysis. 160 mL centrifuge polypropylene tubes used for the MSPE were purchased from Brand (Wertheim, Germany).

Ultra-pure water was obtained with a Puranitty TU6 water purification system (VWR, Bedford, MA, USA), and a JP Selecta oven (Barcelona, Spain) was used for polymerization and drying of the resulting materials.

Stock solutions (1000  $\mu\text{g mL}^{-1}$ ) of each herbicide were prepared in ACN and kept at 4°C. Test mixtures composed of the five herbicides at the appropriate concentration were daily prepared by diluting the stock standard solutions with Milli-Q water.



**Fig 1.** Chemical structures and dissociation constants of phenoxyacid herbicides investigated in this study.

## 2.2. Instrumentation

The morphology of the materials was characterized using a scanning electron microscope (S-4800, Hitachi, Ibaraki, Japan) equipped with EMIP 3.0 software from Rontec (Normanton, UK) for image data acquisition. Also, transmission electron microscopy (TEM) images of magnetic materials were obtained using a Jeol (Tokyo, Japan) model JEM-1010 microscope operated at 100 kV. Surface area and pore size values were calculated by nitrogen adsorption-desorption isotherms at 77 K recorded on a Micromeritics (Norcross, GA, USA) ASAP-2020 automated instrument.

Fourier-transform infrared (FTIR) spectra of materials were carried out using a Tensor 27 spectrometer from Bruker (Bremen, Germany). It was constituted by a DLaTGS detector and a Dura Sample IR II attenuated total reflection (ATR) accessory from Smiths Detection Inc. (Warrington, UK) equipped with a nine-reflection diamond/ZnSe DuraDisk plate.

Vibrating sample magnetometry (VSM) data were taken at 300 K in the range from  $-20,000$  Oe ( $-2$  T) to  $+20,000$  Oe ( $+2.0$  T) using a Quantum Design MPMS-XL 7 SQUID magnetometer (San Diego, USA).

Chromatographic determination of phenoxyacid herbicides was performed using an Agilent 1260 Infinity instrument (Agilent Technologies, Madrid, Spain) equipped with a quaternary gradient pump, a solvent degasser system, an autosampler, a Zorbax Eclipse Plus C18  $3,5\ \mu\text{m}$   $100 \times 4,6$  mm (Agilent Technologies, Madrid, Spain) column, and a diode-array detector. An OpenLAB CDS LC ChemStation from Agilent (B.04.03) controlled the chromatographic system.

## 2.3. Synthesis of vinylized MNPs

First, the synthesis of MNPs was carried out in a nitrogen atmosphere following the coprecipitation method described in a previous work [40]. Briefly, in a three-neck beaker  $11.2$  mmol of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $5.6$  mmol of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were dissolved in  $180$  mL of Milli-Q water. The solution was heated to  $50^\circ\text{C}$  and  $12.5$  mL of concentrated ammonia were added with vigorous agitation. After  $30$  min at  $50^\circ\text{C}$ , the temperature was raised to  $90^\circ\text{C}$  and remained for  $30$  min. Afterwards, MNPs were magnetically retained at the bottom of the beaker, washed with water and ethanol, and dried in an oven at  $60^\circ\text{C}$ .

Then, vinylization of MNPs was made following the method described by Shao and co-workers [41]. Thus,  $0.5$  g of the MNPs were dispersed in  $125$  mL of ethanol and sonicated for  $15$  min. After that,  $4$  mL of ammonia and  $4$  mL of VTMS were added to the MNPs dispersion, and this solution was mechanically agitated overnight at room temperature under a  $\text{N}_2$  air flow. Then, the vinylized magnetite nanoparticles (VMNPs) were washed with ethanol and dried in an oven at  $60^\circ\text{C}$  for  $2$  h.

#### 2.4. Synthesis of magnetic MIP

The synthesis of the MMIP was carried out as follows. Firstly, a pre-polymerization mixture was prepared by mixing 0.2 mmol MCPA as template, 0.8 mmol 4-VP as monomer, and 5 mL of ACN as porogen. The solution was stirred for 2 h in the dark. Subsequently, 5 mL of VMNPs dispersion (1 wt% in ACN), 4 mmol EDMA (crosslinker) and 0.1 mmol AIBN (initiator), were added to the pre-polymerization mixture. The final polymerization mixture was sonicated for 3 minutes, degassed with nitrogen for 5 minutes to remove oxygen, and incubated at 65°C for 24 h.

After that, the MMIP were collected magnetically washed with MeOH:AcH solution (90:10, v/v) until there was no template in the washing solution being detected by HPLC-DAD. The MMIP was finally washed with methanol and dried in an oven at 60°C.

The MNIPs was prepared using the same procedure, but in the absence of the template.

#### 2.5. Sample preparation

Water samples from different sources (tap, fountain, irrigation well and marsh) were collected. The samples were stored in the amber glass bottles and kept at 4°C. Before extraction, the pH of samples was properly adjusted at pH 3.0 and filtered with 0.22- $\mu$ m nylon filters (Phenomenex, Torrance, CA, USA).

#### 2.6. MMISPE protocol

The MMISPE experiments were all performed in 160 mL polypropylene tubes. 50 mg MMIPs were placed into the tube and conditioned with 2 mL of water, which was magnetically decanted with the aid of neodymium magnet. Then, 75 mL of a real sample solution or a working standard solution was added into the tube and orbitally shaken (or stirred) for 1 h. After discarding the supernatant solution, 2 mL of 0.02 mM ammonia solution was used to wash the polymer with adsorbed analytes. Following the removal of the liquid, the target compounds were desorbed with 2 mL of MeOH/AcH (90:10, v/v) under stirring for 5 min. The collected eluent was filtered and used for chromatographic analysis.

#### 2.7. Chromatographic analysis

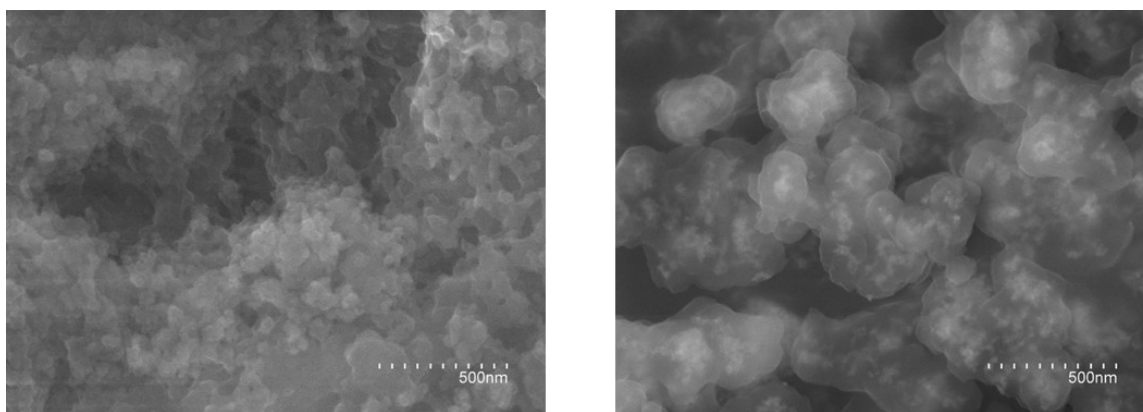
The chromatographic conditions for the analysis of the five phenoxyacid herbicides were obtained using a gradient elution program with aqueous containing phosphoric acid acid (25 mM) (A) and ACN (B) at a flow rate of 1 mL min<sup>-1</sup>. The specific gradient elution program was 45-70% ACN in 6.0 min, and this composition was kept for 0.5 min. Afterwards, the composition returned to initial conditions (45%B) in 1 min, and it was kept for 4 min more. The injection volume was 20  $\mu$ L and detection wavelength was set at 230 nm.

### 3. Results and discussion

#### 3.1. Preparation and characterization of MMIP

In the preparation of MMIPs, the amount of modified MNPs entrapped within the polymer is one of the most critical variables affecting the performance of the MNIP. In a previous work developed by our group [42], MMIPs prepared with 0.5 wt% MNPs gave mechanical stable polymers with a suitable response to a magnetic field. Concerning to template/functional monomer/cross-linker molar ratio selected, previous works have synthesized conventional MIPs [26,29], using 4-VP as monomer and EDMA as cross-linker, in the proportion 1:4:20, which is also a common proportion in literature. Consequently, the MMIP in this work was synthesized using the aforementioned reagents and amounts.

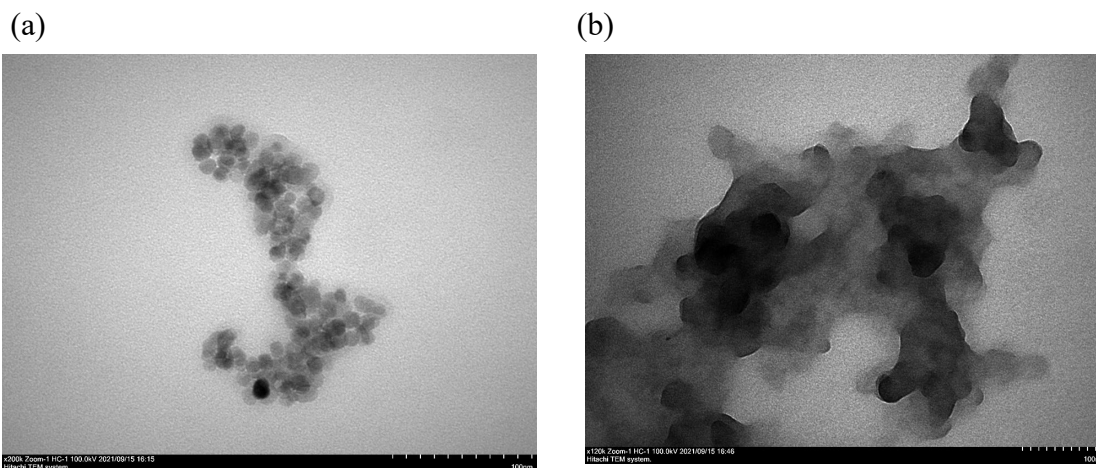
The surface morphology of both MMIP and MNIP, prepared via surface imprinting polymerization method, was characterized by using scanning electron microscopy (SEM). As shown in Fig. 2, the size of particles of MMIP was lower than those obtained for the control polymer (MNIP). These differences could be due to that template molecules had some influence on the growth of particles during the synthesis procedure, and consequently affecting the polymer microstructure.



**Fig 2.** SEM micrographs of the materials: (a) MMIPs and (b) MNIPs. Magnification scale at 30,000  $\times$ .

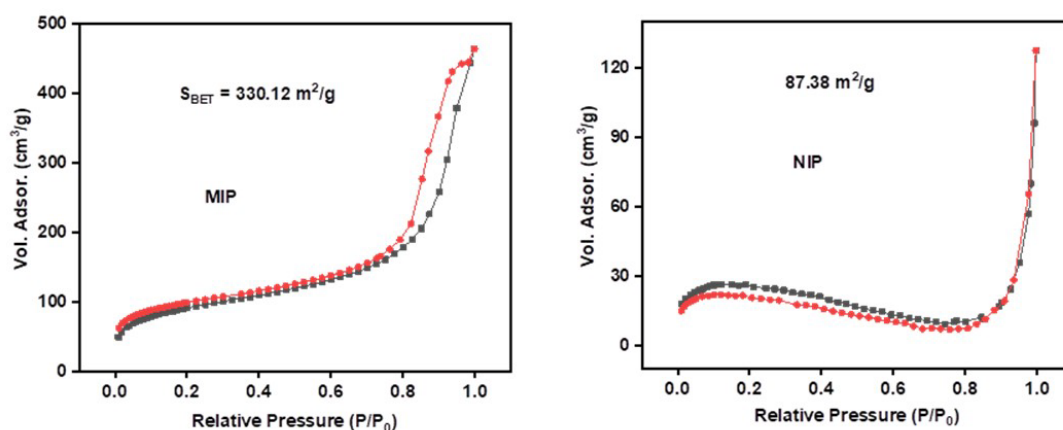
Additionally, the morphological structure of the MMIPs were investigated using TEM (Fig. 3). As it can be observed, TEM images of the magnetic core containing agglomerations of  $\text{Fe}_3\text{O}_4$  NPs gave an average diameter of about 12-13 nm. As shown in Fig. 3B, the particle size of MMIPs was larger (around 30-50 nm), thus indicating that MIP were successfully synthesized by binding of functional monomer and crosslinking agent on magnetite surface.





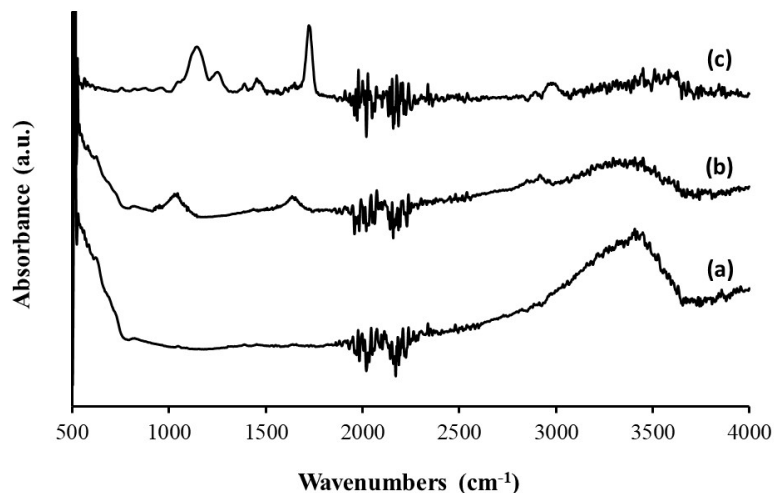
**Fig 3.** TEM images of: (a) MNPs and (b) MMIPs.

The textural properties of materials were also studied by nitrogen adsorption–desorption measurements (Fig. 4). The results showed that the specific surface area of MMIPs ( $330.1 \pm 1.4 \text{ m}^2 \text{ g}^{-1}$ ) was higher than that of MNIPs ( $87.4 \pm 0.3 \text{ m}^2 \text{ g}^{-1}$ ). Furthermore, MMIP gave a pore diameter larger than the, corresponding MNIP (8.3 and 4.0 nm for MMIP and MNIP, respectively). From these results, it can be derived that the formation of selective cavities in the MMIP were successfully produced.



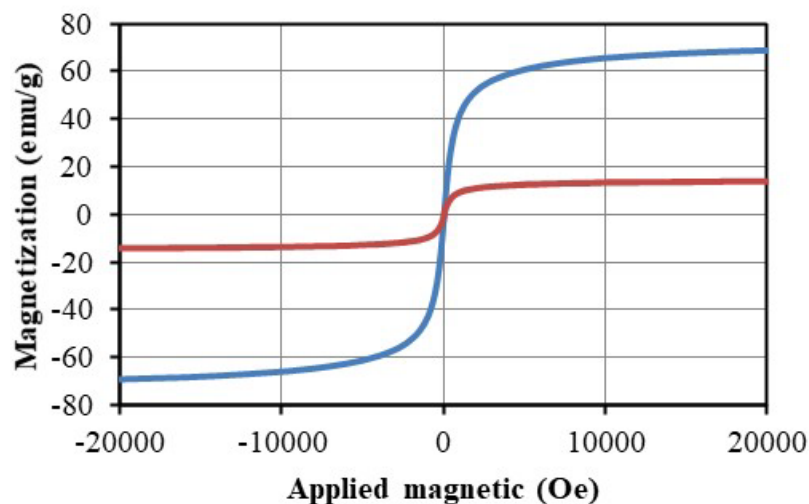
**Fig 4.** Nitrogen adsorption-desorption plots for: (a) MMIP and b) MNIP polymers.

FT-IR measurements were also conducted in order to confirm the correct synthesis of MMIPs (Fig 5). As shown in curve (a), the absorption band at approximately  $550 \text{ cm}^{-1}$  corresponded to the stretching vibration of Fe-O [43]. After modifying the magnetic core with VTMS (b), a peak around  $1050\text{-}1100 \text{ cm}^{-1}$  due to the stretching bonds of Si-O-Si, and the peak at  $1620 \text{ cm}^{-1}$  attributed to C=C stretching vibrations, which confirmed the introduction of vinyl group to the  $\text{Fe}_3\text{O}_4$  nanoparticles [44,45]. Finally, the absorption peak of the C=O stretching band at approximately  $1720 \text{ cm}^{-1}$  in MMIPs (c) showed that imprinted polymer layer had been satisfactorily prepared on magnetic particles.



**Fig 5.** FT-IR spectra of: (a)  $\text{Fe}_3\text{O}_4$ , (b) vinylized  $\text{Fe}_3\text{O}_4$  and (c) MMIP.

Magnetization value of synthesized materials is a key aspect in magnetic separation process. For this purpose, the magnetic hysteresis loops were obtained with a vibrating sample magnetometer (Fig 6). As it can be seen, the shape and trend of the two magnetization curves were similar and no remanence or coercivity were observed (the curves passed through the origin), indicating that samples exhibited superparamagnetism. The saturation magnetizations ( $M_s$ ) of  $\text{Fe}_3\text{O}_4$  and MMIPs were 70.9 and 14.1  $\text{emu g}^{-1}$ , respectively. The decrease in magnetization value of MMIP can be ascribed to the presence of the molecularly imprinted layer on the surface of MNPs. In any case, this value was high enough for the complete magnetic separation in a short time (30 s) using an external magnet.



**Fig 6.** Magnetization data at 300 K for MNPs (blue) and MMIP material (red) from -20000 Oe to 20000 Oe.

### 3.2. Preliminary experiments. Selectivity of MMIP

Prior to optimization studies of MMISPE, preliminary experiments were simultaneously conducted in both MMIP and MNIP materials to assess their recognition properties. Along these experiments, MCPA was used as target analyte. At this regard, 5 mL of MCPA solution ( $0.25 \mu\text{g mL}^{-1}$ ) in water were loaded onto 50 mg of material for 5 min. Other conditions tested were: 3 min with 1.5 mL of washing solvent and 5 min with 5 mL of MeOH/HAc (90:10, v/v) as the desorption solvent.

During these experiments, it was observed that MCPA was bound both to MMIP and MNIP particles. Such finding is common in molecular imprinting studies and it is attributed to the occurrence of non-selective interactions between target analytes and functional groups distributed in the synthesized materials. Thus, the introduction of a washing step is mandatory to decrease these non-specific interactions and to achieve selective extraction. Different washing solutions (Table 1) were evaluated in order to minimize these unspecific interactions and to achieve proper recoveries and appropriate imprinting factors (IF). As it can be seen, a satisfactory recovery (79.4%) and the best IF value (1.76) was obtained using a 0.2 mM ammonia solution as washing solvent. Consequently, this washing solvent was used for the following studies.

**Table 1.** Effect of the washing solvent in magnetic materials on the recoveries and IF values of MCPA (n=3).

Washing solution	Recovery (%)		<sup>a</sup> IF
	MMIP	MNIP	
Water	95.6 ± 0.4	92.7 ± 1.6	1.03
ACN	54 ± 3	52.5 ± 1.6	1.03
ACN:water 90:10	62.7 ± 1.8	57 ± 5	1.10
ACN:water 70:30	67 ± 5	62 ± 3	1.08
ACN:water 50:50	92 ± 2	87 ± 5	1.06
MeOH	59 ± 4	55 ± 5	1.07
AcH 0.2 mM	87 ± 5	87.7 ± 1.9	0.99
NH <sub>3</sub> 0.2 mM	79.4 ± 0.4	45 ± 10	1.76

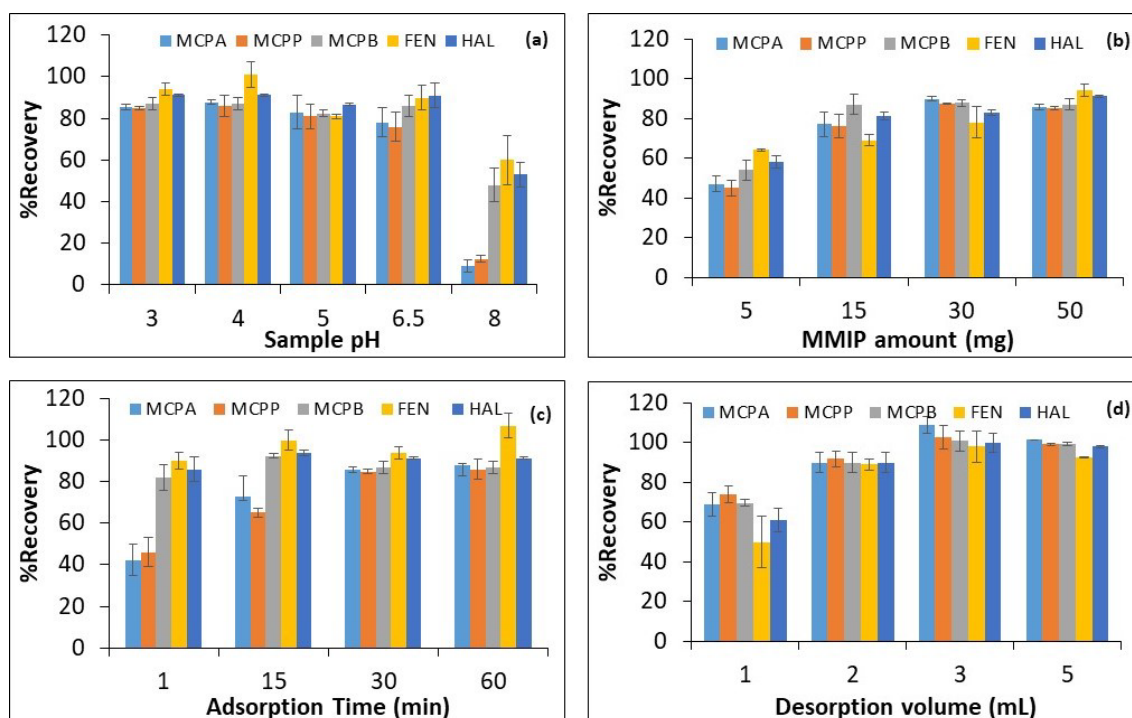
<sup>a</sup> IF was calculated as the ratio of recoveries of the analyte in the MMIP and the MNIP.

### 3.3. Optimization of MMISPE protocol

In order to achieve the best extraction recoveries of target analytes, the influence of several experimental variables (such as sample pH, amount of MMIP used, adsorption time, desorption volume, among others) on extraction efficiency was investigated. All the optimization experiments were carried out in triplicate using aqueous solutions containing a mixture of five phenoxyacid herbicides at a final concentration level of  $0.5 \mu\text{g mL}^{-1}$ . The amount of sorbent used in these studies was 50 mg. Other

conditions included: 50 mL sample solution, 5 min of adsorption time, 10 min of desorption time, and 2 mL of MeOH/HAc (90:10, v/v) as the desorption solvent.

The pH of the aqueous sample plays an important role in the adsorption of phenoxyacid herbicides on MMIP, since it can affect its surface and the ionization state of the target molecules. Thus, the effect of pH during the adsorption step was studied in the range 3.0-8.0. As shown in Fig 7a, the recoveries of target compounds were nearly constant and maximum in the pH range of 3.0-4.0. A significant decrease in the extraction was found for pH values above 6.5, which could be related to the extensive deprotonation of carboxyl group of target compounds and the reduction of pyridyl groups ( $pK_a$  (4-VP)  $\sim$  5.5) in the polymeric material, decreasing the ionic interaction with the ionized target analytes. These results indicated that retention in acidic pH ranges took place through hydrophobic effects,  $\pi$ -interaction (between aromatic rings) and electrostatic interactions. According to the obtained results, a pH of 3.0 was selected in all subsequent experiments.



**Fig 7.** Influence of the sample pH (a), MMIP amount (b), adsorption time (c) and desorption volume (d) on the extraction recoveries of phenoxyacid herbicides.

The influence of the amount of sorbent on the recovery of herbicides was also studied (Fig 7b). As can be seen, the recoveries increased from 47-64% to 85-94% with the increasing of the MMIP amount from 5 to 50 mg. Further increasing amount of the polymer did not significantly improve the recoveries. Thus, 50 mg was selected as the amount of sorbent for further studies.

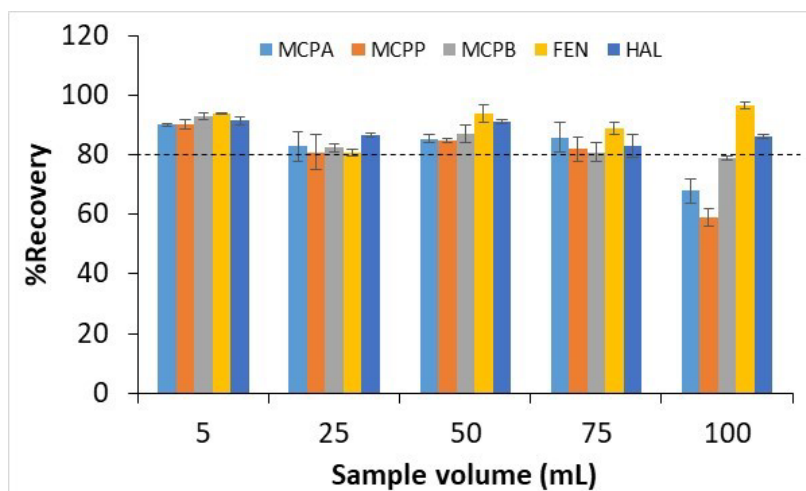
Adsorption time is a key factor that influences the extraction yield and the speed of analysis. The effect of the adsorption time on the recovery of the five phenoxyacids by MMIP was evaluated. According to the obtained results (Fig 7c), the recovery (or recoveries) increased with the adsorption

time and reached a maximum value at 30 min, after which the recoveries remained constant. Therefore, 30 min was selected as the adsorption time for the rest of the experiments.

The choice of a proper desorption solvent is required to desorb target analytes from MMIPs. To this end, MeOH/HAc (90:10, v/v) was selected as eluting solvent, and the minimum volume of this solvent that can efficiently elute the adsorbed analytes was studied (Fig. 7d). The results showed that an eluting volume of 2 mL provided quantitative recoveries of target analytes (between 89-92%), but further increase of the eluting solvent volume did not significantly improve the recoveries. Therefore, 2 mL of MeOH/HAc (90:10, v/v) was chosen for the desorption stage.

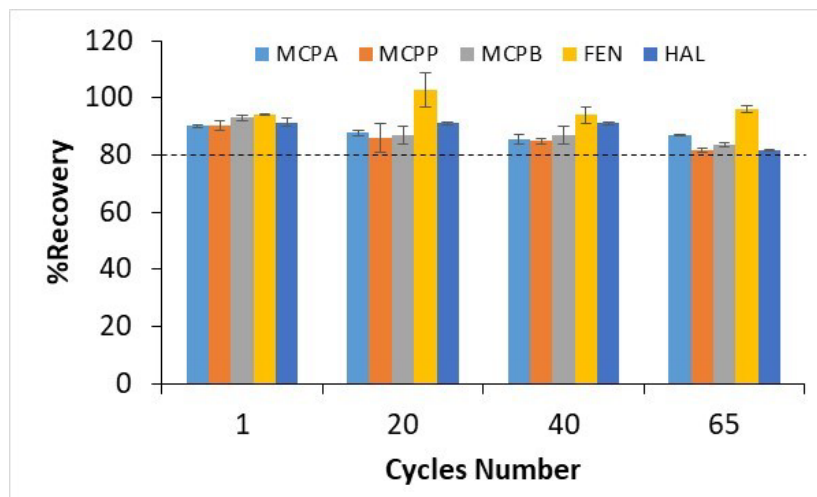
The effect of desorption time was also investigated in the range of 1-15 min and the results showed that 5 min was enough to elute target herbicides from MMIPs. Thus, 5 min of desorption time was used in the following work.

Breakthrough volume was studied by applying MMISPE process to several volumes of standard solutions of target analytes (5-100 mL, final concentration  $0.5 \mu\text{g mL}^{-1}$  for each herbicide). As shown in Fig. 8, satisfactory recoveries (81-89%) up to 75 mL were achieved for all tested analytes, although it required a slight increase in adsorption time up to 1 h. However, higher volumes (100 mL) led to a decrease in the recovery values. Consequently, 75 mL was adopted as the volume for the analysis of real water samples.



**Figure 8.** Influence of breakthrough volume on the efficiency of MMISPE method for extraction of phenoxy acid herbicides. Error bar = SD (n = 3).

Finally, the reusability, a key factor to evaluate the efficiency of sorbents, was considered. This sorbent can be easily reused after washing with MeOH/HAc (90:10, v/v) and MeOH and then dried at  $60 \text{ }^\circ\text{C}$  for 10 min. As shown in Fig. 9, MMIPs could be used at least 65 times without obvious loss of the extraction efficiency, thus indicating the good stability of MMIPs during the extraction process.



**Fig 9.** Reusability study of sorbent on the recovery of phenoxyacid herbicides using the optimized MMISPE protocol.

### 3.4. Method validation

The linearity, precision, and limits of detection (LODs) and quantification (LOQs) of the MMISPE-HPLC-DAD method for the five phenoxyacid herbicides were evaluated (Table 2). A linear correlation ( $r > 0.999$ ) between peak area and concentration (from  $0.033$  to  $1 \mu\text{g mL}^{-1}$ ) was achieved for the five phenoxyacid herbicides investigated. The LODs and LOQs (after applying the MMISPE procedure) were experimentally obtained as the concentration of analyte that provided a signal-to-noise ratio (S/N) of 3 and 10, respectively. Thus, the LODs for aqueous samples varied from  $0.33 \mu\text{g L}^{-1}$  to  $0.71 \mu\text{g L}^{-1}$ , whereas the LOQs were in the range  $1.1 \mu\text{g L}^{-1}$  and  $2.4 \mu\text{g L}^{-1}$ .

The intra- and inter-day precision of the developed method was evaluated in three replicate experiments at different spiked concentration levels in blank water. The relative standard deviations (RSDs) were below 7.3%, which indicated a good reproducibility of the MMISPE-HPLC method.

**Table 2.** Figures of merit for the proposed MMISPE-HPLC protocol for determination of the target phenoxyacid herbicides.

Analyte	Regression equation <sup>a</sup>	LOD ( $\mu\text{g L}^{-1}$ ) <sup>b</sup>	LOQ ( $\mu\text{g L}^{-1}$ ) <sup>b</sup>	Precision (%RSD, n= 3)			
				Intra-day			Inter-day
				2.7 $\mu\text{g L}^{-1}$	6.7 $\mu\text{g L}^{-1}$	13 $\mu\text{g L}^{-1}$	13 $\mu\text{g L}^{-1}$
MCPA	$Y = -(0.5 \pm 0.3) + (54.8 \pm 0.7) \cdot X$	0.33	1.1	3.8	3.5	6.3	2.5
MCPD	$Y = -(0.3 \pm 0.2) + (49.9 \pm 0.4) \cdot X$	0.33	1.1	4.3	4.0	4.5	3.8
MCPB	$Y = -(1.2 \pm 0.4) + (57.0 \pm 0.8) \cdot X$	0.48	1.6	2.7	3.5	3.9	4.4
FEN	$Y = (0.8 \pm 0.4) + (44.2 \pm 0.8) \cdot X$	0.71	2.4	5.5	3.2	2.3	5.5
HAL	$Y = (0.00 \pm 0.17) + (48.0 \pm 0.3) \cdot X$	0.53	1.8	7.3	3.6	4.6	6.4

<sup>a</sup>Y = Peak area, X = Concentration expressed as  $\mu\text{g} \cdot \text{mL}^{-1}$

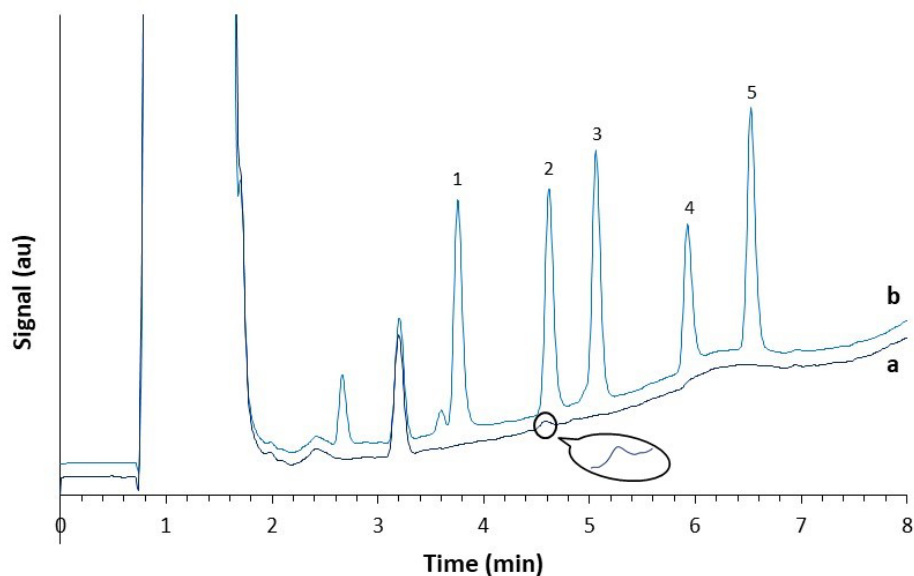
<sup>b</sup>Obtained for the entire method (after applying the preconcentration factor)

### 3.5. Analysis of real samples

Under the optimal conditions, the magnetic MMISPE-HPLC-DAD method was applied to the determination of target herbicides in several water samples. Most of herbicides were not detected in the samples analyzed, although low contents of MCPD (below LOQ) were found in the drinking fountain, irrigation well and marsh water samples. The study of the matrix influence was also considered. In this sense, the recovery values obtained in several matrices were evaluated after spiking the samples at a concentration of  $13 \mu\text{g L}^{-1}$  (Table 3). Recovery values in these water samples were comprised between 77 and 98%, which suggested that the absence of matrix effect. Fig 10 shows the chromatograms of a blank from marsh water and the water sample spiked with the target analytes subjected to pre-treatment using MMIP material. As depicted in Fig. 10a, a small peak at the retention time of MCPD was detected in the blank sample. The identification of MCPD was carried out by comparing its retention time value and absorption spectra with that of the standard, and also by spiking the blank sample with the standard.

**Table 3.** Recovery study of phenoxyacid herbicides in spiked water samples following the recommended MMISPE-HPLC protocol.

Water samples	Recovery (%) $\pm$ SD (n = 3)				
	MCPA	MCPD	MCPB	FEN	HAL
Mineral	78 $\pm$ 3	78 $\pm$ 3	87 $\pm$ 5	88 $\pm$ 2	82 $\pm$ 5
Tap	77 $\pm$ 3	77 $\pm$ 3	93 $\pm$ 4	87.2 $\pm$ 0.6	85 $\pm$ 3
Drinking fountain	83 $\pm$ 3	83 $\pm$ 4	96 $\pm$ 4	98.0 $\pm$ 1.7	87 $\pm$ 4
Non-potable fountain	96 $\pm$ 7	89 $\pm$ 9	96 $\pm$ 7	86 $\pm$ 6	94 $\pm$ 9
Irrigation well	79.1 $\pm$ 1.4	83 $\pm$ 2	83 $\pm$ 2	89.5 $\pm$ 0.6	85 $\pm$ 2
Marsh water	80.2 $\pm$ 1.8	79.2 $\pm$ 1.8	84 $\pm$ 2	81 $\pm$ 2	86 $\pm$ 3



**Fig 10.** Chromatograms of: (a) marsh water unspiked (blank) and (b) spiked with phenoxyacid herbicides ( $0.04 \mu\text{g mL}^{-1}$ ) after MMISPE optimal procedure. Peak identification: 1) MCPA, 2) MCPP, 3) MCPB, 4) FEN and 5) HAL.

### 3.6. Comparison with other methods

The characteristics of the MMISPE-HPLC method presented in this paper were compared with other recent methods described for the analysis of phenoxyacid herbicides in water samples (see Table 4). As can be seen, most of the methods described include MCPA and MCPP analysis, but MCPB, HAL and FEN analysis were not usually performed. In terms of recoveries and precision, our method presented similar values to the described methods. Concerning sensitivity, the achieved LODs were similar to other reported methods; however, these values were higher compared when more sophisticated and expensive MS systems [21,31] were used. A remarkable feature of our method is the high reusability of the developed MMIP sorbent, which was used more than 65 times without losses in its extraction capacity. This value was superior to other methods [2,46], whereas in most reported studies this information was missing. Additionally, the MMISPE method is easy to operate without any special instrumentation, being the magnetic separation rapid, convenient, and economically attractive.



**Table 4.** Comparison of the proposed method with other recent extraction methods for the analysis of phenoxyacid herbicides in water samples.

Analytes	Water samples	Extraction procedure	Analytical method	Recovery (%)	Precision (%RSD)	LODs ( $\mu\text{g/L}$ )	Sorbent reusability	Ref
2,4-D; 2,4,5-T	River	SPE with BPA-MIP	HPLC-MS-ESI	80-90	-	15 - 34	20 times	[2]
4-CPA; 2,4-D; 2,4-DP; DIC	Tap	PT-SPE with MOF cotton@UiO-66	HPLC-UV	83.3-106.8	< 6.7	0.1 - 0.3	-	[11]
MCPA, MCPP Other 10 herbicides	River	DSPE with MIL-101	UPLC-MS/MS	95.3-105.5	1.4-3.83	0.00018 - 0.00088	-	[21]
MCPP Other 5 herbicides	River and waste	SPE with PMO-STPA and PMO-TEPA	CE-DAD	78.3-107.5	1.9-8.7	0.7 - 1.5	-	[22]
MCPP	Bottled and ground	SPE with MIP	HPLC-UV	65.1-70.5	-	30	-	[29]
4-CPA; 2,4-D; 2,4-DB	Tap, pond, lake and moat	DSPE with V-g-C <sub>3</sub> N <sub>4</sub>	DART-MS	79.9-119.1	0.23-9.82	0.0005 - 0.002	-	[31]
4-CPA; 2,4-D; DIC	Reservoir, lake, drinking and tap	MSPE with Fe <sub>3</sub> O <sub>4</sub> @ZnAl-LDH	HPLC-DAD	79.2-88.6	2.8-8.3	0.1 - 0.2	-	[34]
2,4-DCBA; 2,4-DCPA; 2-(2,4-DCPPA); 3,5-DCBA; 2,4,5-TP	Pond and drain	D-LLLME	HPLC-UV	85-107	< 8.2	0.1 - 0.4	1 time	[46]
MCPA; MCPP; MCPB; FEN; HAL	Mineral, tap, fountain, well and marsh	SPE with MMIP	HPLC-DAD	77-98	2.3-7.3	0.33 - 0.71	> 65 times	This work

**Abbreviations:** 2-(2,4-DCPPA): 2-(2,4-Dichlorophenoxy)-propionic acid; 2,4,5-T: 2,4,5-Trichlorophenoxyacetic acid; 2,4,5-TP: 2-(2,4,5-Trichlorophenoxy)propionic acid; 2,4-D: 2,4-dichlorophenoxyacetic acid; 2,4-DB: 2, 4-dichlorophenoxybutyric acid; 2,4-DCBA: 2,4-Dichlorobenzoic acid; 2,4-DCPA: 2,4-dichlorophenoxyacetic acid; 2,4-DP: dichlorprop: 2-(2,4-dichlorophenoxy)propanoic acid; 3,5-DCBA: 3,5-Dichlorobenzoic acid; 4-CPA: 4-Chlorophenoxyacetic acid; BPA-MIP: Bisphenol-A molecularly imprinted polymer; DART-MS: direct analysis in real time mass spectrometry; DIC: Dicamba: 3,6-dichloro-2-methoxybenzoic acid; D-LLLME: Dynamic liquid-liquid-liquid microextraction; DSPE: Dispersive SPE; Fe<sub>3</sub>O<sub>4</sub>@ZnAl-LDH: MNPs coated with zinc-aluminium layered double hydroxide; ESI: electrospray ionization mass spectrometry; MOF cotton@UiO-66: metal-organic framework UiO-66-funtionalized cotton; PMO-STPA: (styrylmethyl)bis(triethoxysilylpropyl)ammonium chloride; PMO-TEPA: bis(3-triethoxysilylpropyl)amine; PT-SPE: pipette tip SPE; UPLC: Ultra-performance LC; V-g-C<sub>3</sub>N<sub>4</sub>: velvet-like graphitic carbon nitride

## 4. Conclusions

In this study, a selective MMIP sorbent using MCPA as template was synthesized and satisfactorily applied to the extraction of a mixture of five phenoxyacid herbicides in water samples from different origins. Characterization experiments were conducted to evaluate the properties of the synthesized material. Also, a careful choice of the extraction, washing and desorption conditions were investigated to afford a reliable MMISPE method. Combined with HPLC-DAD, MMISPE method is simple, easy to perform in most laboratories and shows a suitable sensitivity, as well as satisfactory recoveries and reproducibilities under optimized conditions. The proposed method avoided the time-consuming steps of centrifugation and filtration required by the traditional sorbents in dispersive and cartridge SPE modes. Besides, the synthesized MMIP exhibited excellent regeneration features and it can be used more than 65 times without any significant loss of extraction capacity. These results indicated that the prepared MMIPs were promising sorbent material for the MSPE of phenoxyacid herbicides at trace levels from environmental water samples.

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