

# Zr-MOF modified cotton fiber for pipette tip solid-phase extraction of four phenoxy herbicides in complex samples

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## ARTICLE INFO

### Keywords:

Phenoxy herbicides  
Zirconium-based metal organic framework  
Functionalized cotton fiber  
Pipette tip  
Extraction  
Response surface methodology

## ABSTRACT

Phenoxy herbicides are widely applied in agricultural weeding. The determination of herbicides is important in environmental protection, agricultural production, food safety, and public health. In this study, a facile and efficient analytical method was proposed for the trace detection of phenoxy herbicides in soil, cucumber, and tap water samples by coupling pipette tip solid phase extraction (PT-SPE) with high performance liquid chromatography. UiO-66-functionalized cotton (Cotton@UiO-66) was packed into pipette-tip as sorbent to fabricate extraction device. The modification of UiO-66 on cotton fiber was confirmed using scanning electron microscope, Fourier transform infrared spectroscopy, and X-ray diffraction. The main factors affecting the adsorption of Cotton@UiO-66 for four phenoxy herbicides were evaluated by response surface methodology in detail. Under optimized conditions, Cotton@UiO-66 displayed excellent properties in the extraction of phenoxy herbicides with good peak shape. Linear ranges of 4-chlorophenoxyacetic acid, dicamba, 2,4-dichlorophenoxyacetic acid, and 2-(2,4-dichlorophenoxy) propionic acid were 1.4–72 µg/L, 5.6–280 µg/L, 2.8–140 µg/L and 3.2–160 µg/L (RSDs < 6.3%), respectively. The recoveries were between 83.3 and 106.8% with RSDs < 6.7%, with detection limits ranging from 0.1 µg/L to 0.3 µg/L. The results show that Cotton@UiO-66 in PT-SPE is an effective method for monitoring phenoxy herbicides in complex samples.

## 1. Introduction

Phenoxy herbicides belong to the hormone herbicide family that possess properties such as relatively low toxicity, easy to manufacture, good water solubility and efficiency (Chávez-Moreno et al., 2012). Commonly used phenoxy herbicides, dicamba (DICA) (Guo et al., 2016), 4-chlorophenoxyacetic acid (4-CPA) (Han et al., 2017), 2,4-dichlorophenoxyacetic acid (2,4-D) (Li et al., 2017a), and 2-(2,4-dichlorophenoxy) propionic acid (2,4-DP) (Paszko et al., 2016) are often employed in weeding, and affect almost every physiological process of plant growth. However, leaves and roots can absorb herbicides due to overuse and excess residues. Gill and Garg (2014) reported that only 0.1% of the total employed pesticides get to the target organism in agricultural activities, with the residual herbicides entering the natural circulation system (Lima, 2018; Székács et al., 2015). The accumulation of phenoxy herbicides in plant's internal systems eventually enter the human body and cause further potential toxicity, including neurotoxicity, acute toxicity, reproductive damage, soft-tissue sarcomas and non-

Hodgkin's lymphomas (Kelly and Guidotti, 1989). To protect human health and safety, the European legislation presented legal provisions that the maximum contaminant concentration of phenoxy herbicides in drinking water is between 10 ng/mL and 70 ng/mL (European Commission, 2008). Hence, it is highly desirable to monitor trace-levels of phenoxy herbicides in agriculture related samples, such as soil, groundwater, and vegetable.

Given the low concentration and complex sample matrix of herbicides in practical samples, proper sample pretreatment is essential prior to chromatographic separation and detection. General preparation technologies for sample preparation include solid phase extraction (SPE) (Liu et al., 2019), solid-phase microextraction (SPME) (Li et al., 2019a), liquid-liquid extraction (LLE) (Gure et al., 2014), liquid-liquid microextraction (LLME) (Yuan et al., 2018), magnetic solid-phase extraction (MSPE) (Wang et al., 2019), dynamic liquid-liquid-liquid microextraction (Spietelun et al., 2014), salt de-emulsification dispersive liquid-liquid microextraction and back-extraction (SD-DLLME-BE) (Yue et al., 2016), molecularly imprinted polymers (MIPs) (Liang et al.,

**Abbreviations:** 4-chlorophenoxyacetic acid, 4-CPA; dicamba, DICA; 2,4-dichlorophenoxyacetic acid, 2,4-D; 2-(2,4-dichlorophenoxy) propionic acid, 2,4-DP; *N,N*-dimethylformamide, DMF; pipette tip solid phase extraction, PT-SPE; relative standard deviation, RSD; Zirconium-based metal organic framework, Zr-MOF

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<https://doi.org/10.1016/j.ecoenv.2020.110764>

Received 16 January 2020; Received in revised form 11 May 2020; Accepted 13 May 2020

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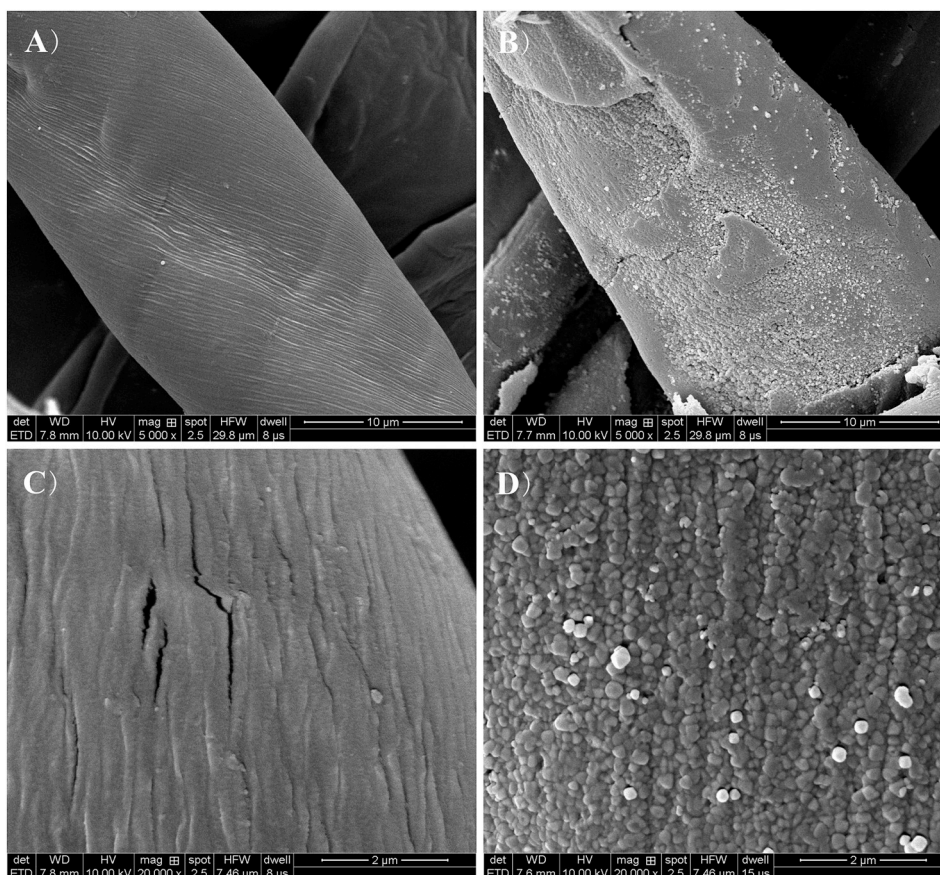


Fig. 1. SEM morphology of bare cotton fiber (A and C), UiO-66 modified cotton (B and D); A) and B) under 5000-times magnification; C) and D) under 20,000-times magnification.

2019) and dispersive solid phase extraction d-SPE (Koesukwiwat et al., 2008) etc. Among these techniques, SPE is the preferred method because of its advantages in solvent consumption, simplicity and sensitivity. More importantly, SPE retains the convenience of introducing new materials as sorbents, responding to increasing demands for practical approaches. For example, Kamaraj et al. (2017) prepared an environmentally friendly and low-cost graphene-nanosheets with few-layer as potential adsorbent material for the removal of five phenoxy herbicides in drinking water. Li et al. (2019a) fabricated a highly hydrophobic polymer monolithic column for online extraction of four chlorophenoxy acid herbicides in rice grains. Therefore, sorbent preparation is the key factor for the effective extraction of phenoxy herbicides.

Zirconium-based metal-organic frameworks (Zr-MOFs) (Cavka et al., 2008) are tetrahedral or octahedral caged structures formed by  $Zr^{4+}$  clusters ( $Zr_6O_4(OH)_4$ ) and carboxyl organic (Hu et al., 2015). UiO-66 is one of the most attractive Zr-MOFs, because of its good chemical resistance and pH tolerance, unprecedented thermal stability, high porosity and large specific surface area (Piscopeo et al., 2015). UiO-66 is the most widely used Zr-MOF in the field of extraction. Li et al., 2017 described a hydrothermal method for the growing of porphyrinic Zr-MOF on the surface of stainless steel to extract nitrated polycyclic aromatic hydrocarbons. Lin et al. (2018) synthesized several Zr-MOFs with unique structures and high porosity, such as UiO-66, MOF-802, and MOF-808. UiO-66 is usually immobilized for practical applications of sorbent material (Li et al., 2019b). For different inspection purposes, UiO-66 can be coated onto different carrier substrates, for example, stir bar (You et al., 2017), stainless steel (Wu et al., 2018), magnetic particles (Li et al., 2018) etc. Cotton made of polymer cellulose (Martinez-Sanz et al., 2017), possesses advantages for crystal growth, such as abundant hydroxyl groups on surface, large specific surface area, steady

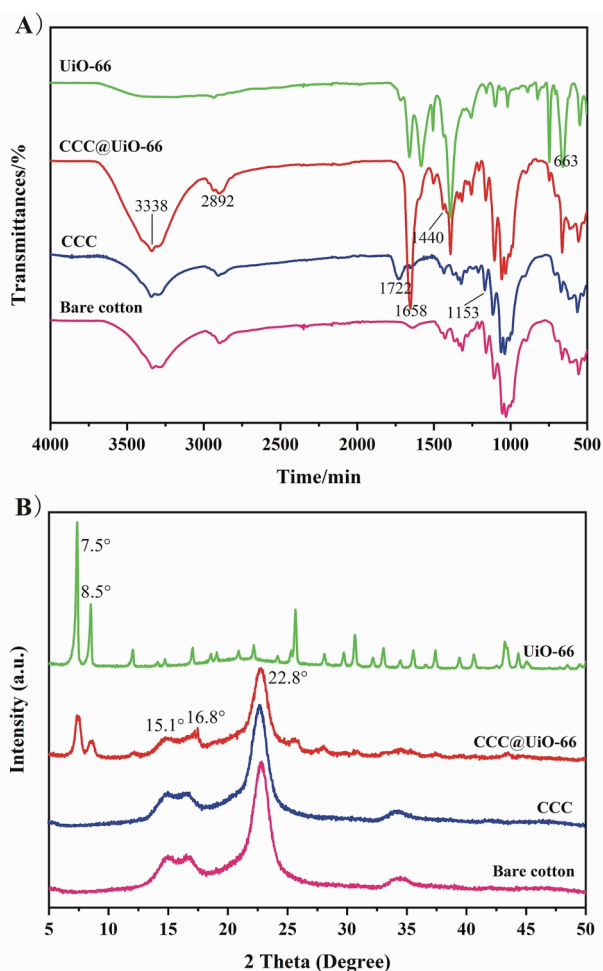
chemical resistance, easy biodegradability, and environmentally friendliness (Wang et al., 2018). Furthermore, functionalized cotton can be used as sorbent for numerous applications, using both extraction mode and loading volume. Cotton fiber can be also thermally esterified with citric acid to fabricate carboxyl modified cotton (Gong et al., 2007), which supplies active sites for growing Zr-MOF according to our previous research (Bao et al., 2019).

In this work, UiO-66 coated cotton fiber is fabricated to introduce as the sorbent for the selective adsorption of some pesticides. The synthesis of Zr-MOF modified cotton fiber sorbents has been improved. The cost estimate of the sorbent is about 0.2 dollar per gram. Zr-MOF supplies a large number of both Zr-O groups and benzene rings. The formation of Zr-O-H bond,  $\pi$ - $\pi$  interaction and hydrophobic interaction are considered the specific interactions between the fabricated sorbent and phenoxy herbicides. The selectivity of the Cotton@UiO-66 is investigated by monitoring trace-level of four phenoxyacetic acid herbicides in practical samples. The results confirm the good applicability of Cotton@UiO-66 in PT-SPE mode for the determination of phenoxy herbicides.

## 2. Materials and methods

### 2.1. Materials and reagents

All reagents were used as received. Anhydrous citric and zirconium (IV) *n*-propoxide (ca. 70% in 1-propanol), four phenoxyacetic acid herbicide standards including 4-chlorophenoxyacetic acid (4-CPA), 2,4-dichlorophenoxyacetic acid (2,4-D), 2-(2,4-dichlorophenoxy) propionic acid (2,4-DP), and dicamba (DICA) were bought from Aladdin Reagent (Shanghai, China). Purified terephthalic acid (PTA) was purchased from Shanghai Yuanye Biotechnology (Shanghai, China). Acetic acid,



**Fig. 2.** A) FT-IR spectrum and B) XRD patterns of UiO-66 powder, UiO-66 modified cotton, COOH-terminated cotton, and bare cotton fiber from top to bottom, respectively.

hydrochloric acid and *N,N*-dimethylformamide (DMF) were bought from Kermel Reagent (Tianjin, China). The cotton fiber was bought from Heze Health Materials Factory. All above chemical reagents were of analytical grade. HPLC grade Acetonitrile was purchased from Merck Company (Darmstadt, Germany). Methanol and phosphoric acid were bought from TEDIA (Fairfield, OH, USA). Soil and tap water were obtained from Chinese herbal garden in Xi'an Jiaotong University. Cucumber was purchased from a local Huarun Supermarket.

## 2.2. Instruments

Separation experiments of target compounds were performed on Shimadzu LC-2040C 3D (Tokyo, Japan). SEM (Quanta FEG 250) (USA) was used for the characterization of apparent morphology of Cotton@UiO-66. FT-IR (Nicolet 6700, Thermo Fisher, USA) was used to record the functional group change of Cotton@UiO-66. The wavenumber recorded in the spectra ranged from 4000 to 500  $\text{cm}^{-1}$ . X-ray diffraction results were collected by X-ray diffractometer (LabX XRD-6100, Shimadzu) with the  $2\theta$  ranged from 5° to 50°.

## 2.3. Preparation of Cotton@UiO-66 packed pipette-tip

The modification of cotton fiber was fabricated according to our previously reported work (Bao et al., 2019). Experimental details are presented in Supplementary Material. Firstly, plentiful free carboxyl groups were bonded on cotton using citric acid, which supplied

chemical sites to coordinate with metal ions. Secondly,  $\text{Zr}_6\text{O}_4(\text{OH})_4$  clusters were anchored on cotton coated with carboxyl groups. Thirdly, UiO-66 was generated and immobilized on cotton- $\text{Zr}_6\text{O}_4(\text{OH})_4$ . In brief, 1000.0 mg of carboxyl modified cotton was added to 190.0 mL of solution containing UiO-66 precursor (262.2  $\mu\text{L}$  of 70% zirconium propoxide [ $\text{Zr}(\text{OnPr})_4$ ] and 14.8 mL of acetic acid), and stirred for 2 h at room temperature. Then, 190.0 mg of PTA (1 mg/mL) was added to the above mixture, and stirred for an additional 16 h. The fabricated Cotton@UiO-66 was washed with methanol and DMF for several times, respectively, and dried in oven for further use. For the extraction device, 20.0 mg of Cotton@UiO-66 was weighed and packed into 200  $\mu\text{L}$  pipette-tip. The pipette-tip packed with Cotton@UiO-66 was flushed with methanol, and dried.

## 2.4. Characterization of Cotton@UiO-66

The microscopic morphology of cotton and Cotton@UiO-66 was determined using scanning electron microscopy (SEM). X-ray diffraction (XRD) was applied to confirm the crystal structure of Cotton@UiO-66. The functional groups and the change of chemical bonds in Cotton@UiO-66 were inspected by Fourier transform infrared spectra (FT-IR). The wavenumber ranged from 4000 to 500  $\text{cm}^{-1}$ .

## 2.5. Preparation of complex matrices samples

The proposed method was applied to monitor trace phenoxy herbicides in real samples to verify the feasibility. First, phenoxy herbicides reserve solutions were prepared in volumetric flask using acetonitrile as solvent. The concentrations of 4-CPA, DICA, 2,4-D and 2,4-DP were 28.8  $\mu\text{g}/\text{mL}$ , 112.0  $\mu\text{g}/\text{mL}$ , 56.0  $\mu\text{g}/\text{mL}$ , and 64.0  $\mu\text{g}/\text{mL}$ , respectively.

Surface water samples were obtained from tap water in Xi'an (Shaanxi, China). The collected sample was filtered using 0.22  $\mu\text{m}$  nylon membrane before extraction to remove possible suspended solid. After filtration, the prepared samples were stored at 4 °C for further use.

10.0 g soil sample was added to 50 mL ultrapure water and sonicated for 30 s. Then, the solution was centrifuged for 10 min at 12000 rpm. The supernatant was collected to prepare a real soil sample.

Fresh cucumbers were cleaned and smashed using a portable crusher. 10.0 g cucumbers homogenate and 50 mL of ultrapure water were added into an Eppendorf, sonication time 30 s. After centrifuging at 12000 rpm for 10 min, the supernatant was collected to prepare a real cucumber sample.

For the detection of the spiked sample, the pH value of the sampling solution was first adjusted to pH 3.0 using HCl solution (1.0 mol/L). Then, a specific volume of the phenoxy herbicides standard solution was added to the actual sample.

## 2.6. Cotton@UiO-66-based SPE procedures

For all SPE experiments, 20 mg of Cotton@UiO-66 was weighted and packed in 200  $\mu\text{L}$  pipette-tip to prepare Cotton@UiO-66-based SPE device. The extraction experiments of phenoxy herbicides were performed on Cotton@UiO-66 packed pipette-tip with the assist of a syringe pump. In the sampling step, 20.0 mL of sample solution was loaded at a set rate. Eluent solvent of 500  $\mu\text{L}$  was introduced in the desorption step using a syringe pump. The analytical solution consists of methanol and acetic acid (HAc) solution (50% acetic acid in water). The eluent was obtained and filtered using a 0.22  $\mu\text{m}$  filter membrane to remove particles. The obtained filtered eluent was separated and analyzed by HPLC method.

## 2.7. HPLC analysis

The HPLC system equipped with a degasser system, thermostat-controlled column oven, high-pressure quaternary pump and PDA



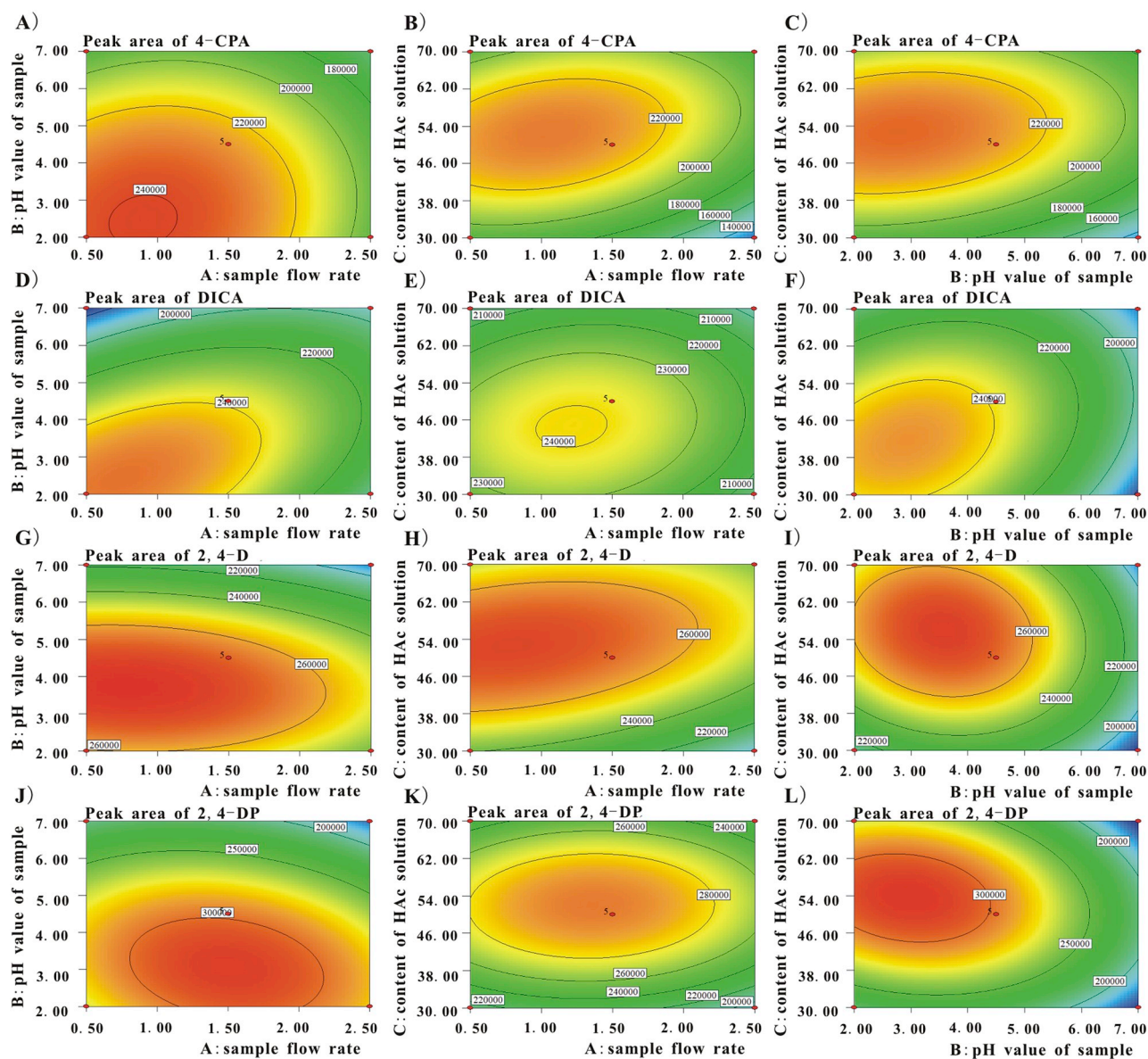


Fig. 3. Response surface plots demonstrating the influence of sample solution: flow rate, pH value, and content ratio of acetic acid on the extraction of 4-chlorophenoxyacetic acid, dicamba, 2,4-dichlorophenoxyacetic acid, and 2-(2,4-dichlorophenoxy) propionic acid.

Table 1

Linear ranges, coefficient of regression ( $R^2$ ), LODs ( $\mu\text{g/L}$ ), LOQs ( $\mu\text{g/L}$ ) and RSDs data of the method.

Analytes	Linear range ( $\mu\text{g/L}$ )	Correlation of regression ( $R^2$ )	LOD ( $\mu\text{g/L}$ )	LOQ ( $\mu\text{g/L}$ )	RSD (%) ( $n = 5$ )	
					Intraday	Interday
4-CPA	1.4–72	0.9980	0.1	0.3	2.6	6.3
DICA	5.6–280	0.9996	0.2	0.7	3.1	4.7
2,4-D	2.8–140	0.9990	0.2	0.7	3.5	4.7
2,4-DP	3.2–160	0.9959	0.3	1.0	1.6	5.0

4-CPA: 4-chlorophenoxyacetic acid, DICA: dicamba, 2,4-D: 2,4-dichlorophenoxyacetic acid, 2,4-DP: 2-(2,4-dichlorophenoxy) propionic acid, LOD: limits of detection, LOQ, limits of quantification, RSD: relative standard deviation.

detector and data collection and handling software. The column used for separation of target compounds was VP-ODS column (C18, 250 mm  $\times$  2.0 mm i.d., 5  $\mu\text{m}$  particle size). This C18 column was purchased from GL Science (Tokyo, Japan). The mobile phase

composed of two solvents, A and B, where acetonitrile was used as solvent A and 0.1% phosphoric acid aqueous was used as solvent B. The gradient elution condition was performed using the following conditions: 0–20 min, 30–50% A. The flow rate controlled by HPLC instrument was set at 0.4 mL/min, and 227 nm was selected as ultraviolet detection wavelength.

### 3. Results and discussion

#### 3.1. Sorbent characterization

##### 3.1.1. SEM

The surface morphology of cotton without modification and Cotton@UiO-66 were investigated by SEM (Fig. 1). Under 5000-times magnification in (Fig. 1A), the surface of bare cotton is relatively smooth with visible fiber structure. While on the surface of Cotton@UiO-66, small particles are observed at the same magnification.

shown in Fig. 1C, without modification the micro surface morphology of bare cotton shows obvious fiber structure. After UiO-66 immobilization on cotton fibers, the Cotton@UiO-66 surface becomes

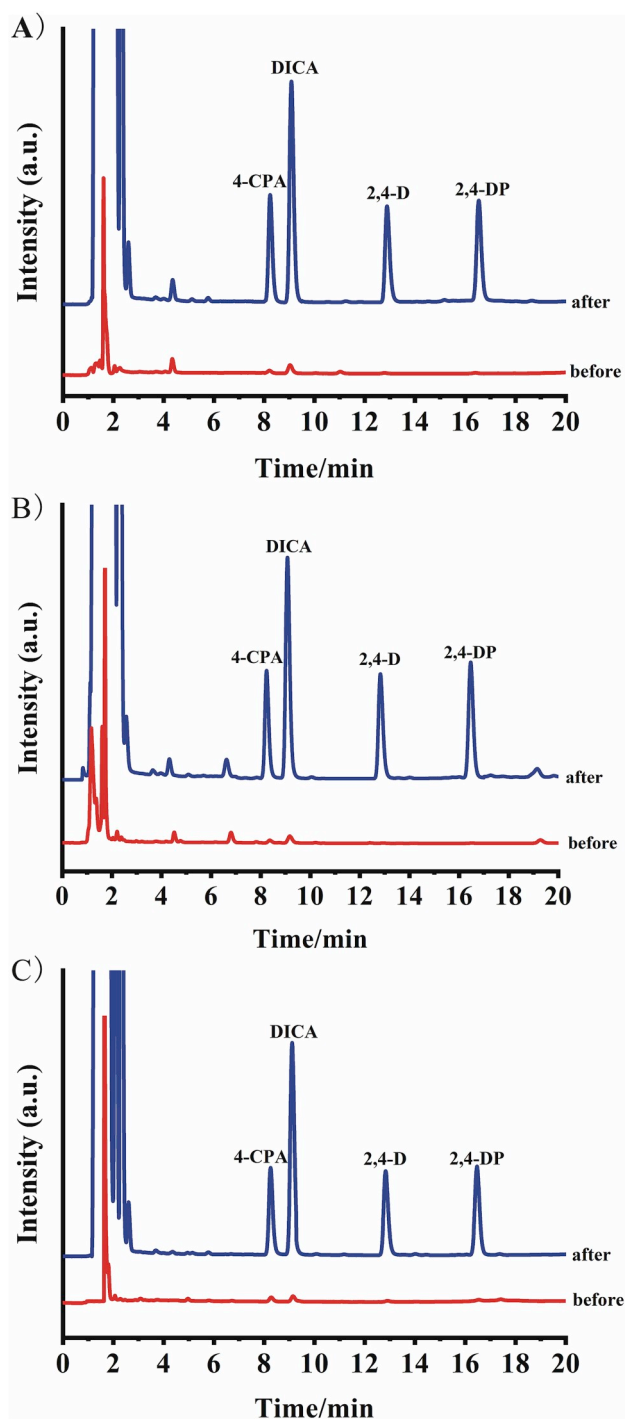


Fig. 4. Chromatograms of A) soil, B) cucumber, C) tap water sample spiked with 50  $\mu\text{L}$  of stock solution before and after extraction using UiO-66 modified cotton.

grainy. At 20000-times magnification (Fig. 1D), abundant particles are examined on the surface of cotton. The results evidence that UiO-66 was successfully formed on cotton without changing its fibrous morphology.

### 3.1.2. FT-IR

The valence bond and structure changes were confirmed by FT-IR spectroscopy. Fig. 2A demonstrates the spectrums of UiO-66 powder, UiO-66 modified cotton, carboxyl cotton and cotton, respectively. The characterized vibration band of OH stretching and absorption bands of

carbonyl are at  $3338\text{ cm}^{-1}$  and  $1658\text{ cm}^{-1}$ , respectively. The peak observed at  $2892\text{ cm}^{-1}$  corresponds to the absorption band of asymmetric C-H stretching vibration. While, the bond at  $1440\text{ cm}^{-1}$  conforms with H-C-H scissoring. These absorption bands reflect the structure of cotton. The IR spectrum of COOH-terminated cotton and UiO-66 functionalized cotton displays characteristic peaks at  $1722\text{ cm}^{-1}$ , which are attributed to the absorption band of carboxyl group. This arose from the citric acid esterification reaction. The signal at  $1153\text{ cm}^{-1}$  conforms with the absorption band of C-H bending vibration. The salient peak at  $663\text{ cm}^{-1}$  refers to Zr-O, which is attributed to the immobilization of UiO-66 crystal. Overall, FT-IR spectra of UiO-66 coated cotton displays absorption peaks corresponding to both cotton and UiO-66. The results further confirm the formation of UiO-66 on cotton fabric.

### 3.1.3. XRD

X-ray diffraction results were applied to confirm the structures of UiO-66 powder, Cotton@UiO-66, carboxyl cotton and cotton, respectively. As shown in Fig. 2B, signal responses at  $7.5^\circ$  and  $8.5^\circ$  in XRD pattern of UiO-66 coated cotton correspond to the characteristic responses of UiO-66 crystal powder. This confirms the formation of crystal of UiO-66 on cotton fiber. Fig. 2B shows intense peaks at  $2\theta = 15.1^\circ$ ,  $16.8^\circ$  and  $22.8^\circ$  of UiO-66 modified cotton correspond to the bare cotton. XRD analysis further confirms the successful fabrication of Cotton@UiO-66.

## 3.2. Optimization of SPE conditions

To gain efficient extraction of four phenoxy herbicides in tap water, soil, and vegetable samples, the main SPE experiment conditions required further optimization. Response surface methodology (RSM) was introduced for the prediction of optimal conditions. In this work, Box-Behnken Center combination test design was used to optimize the SPE parameters of phenoxy herbicides. The variables investigated for RSM include flow rate of the sample solution (0.5–2.5 mL/min), pH value of the sample solution (pH 2.0–7.0) and the percentage of acidic solution (50% HAc in water) in acetonitrile (30%–70%). The response variable was peak area of 4-CPA, DICA, 2,4-D and 2,4-DP. The RSM experiment used a randomization principle to design the experimental sequence, which minimized the influence of unexplained variables in the observed response due to external factors. The regression equation of each response value Y was obtained by RSM test. Analysis of Variance (ANOVA) results were collected to evaluate the significant difference of RSM model. Detailed results are provided in Supplementary Material. The corresponding response surface maps were gained using simulation of RSM software. Fig. 3A-L exhibit the variation trend of response value Y followed with independent variable. On the basis of RSM test, the software provided the optimal parameters for Cotton@UiO-66-SPE device to enrich and detect phenoxy herbicides from complex matrix. The flow rate of sampling, pH value of sampling solution, proportion of HAc solution in eluent solvent was 1.17 mL/min, pH 3.16, 50.7%, respectively.

The impact of sample flow rate was two-sided in the extraction process. The values of flow rate of sampling increase from 0.5 to 2.5 mL/min, while the trend of extraction increases first and then decreases. The results could be attributed to the interaction between phenoxy herbicides and adsorbent. Although high flow rate can improve operation time, it could also lead to loss of phenoxy herbicide compounds due to incomplete adsorption. While low flow rate can result in a decrease of target analytes due to back-extraction during long extraction times. Hence, the influence of

sample flow rate of this method was evaluated by RSM. The best condition predicted by RSM was 1.17 mL/min.

Another important factor that has effect on the efficiency of extraction was the pH value of sampling solution. It not only influenced the existing forms of phenoxy herbicides, but also the surface binding

**Table 2**  
Recoveries and RSDs (n = 5) of four phenoxy herbicides for cucumber, soil and surface water samples.

Analytes	Added ( $\mu\text{g/L}$ )	Cucumber		Soil		Surface water	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
4-CPA	0	N.D.	–	N.D.	–	N.D.	–
	14.4	87.3	5.6	106.8	6.4	91.7	1.7
	43.2	106.0	4.7	95.5	4.5	95.5	4.5
	72.0	97.6	4.2	85.8	1.3	90.7	6.5
DICA	0	N.D.	–	N.D.	–	N.D.	–
	56.0	93.6	2.1	104.7	2.9	103.8	3.0
	168.0	94.8	4.2	85.9	2.5	83.3	5.9
	280.0	104.3	6.7	90.2	3.4	93.6	2.4
2,4-D	0	N.D.	–	N.D.	–	N.D.	–
	28.0	96.2	4.4	97.2	1.4	96.3	4.5
	84.0	106.4	1.2	91.9	5.1	103.5	3.6
	140.0	95.3	3.5	97.2	4.2	105.4	2.1
2,4-DP	0	N.D.	–	N.D.	–	N.D.	–
	32.0	96.4	1.6	95.8	1.7	94.0	3.7
	96.0	95.5	4.8	90.2	3.2	102.6	1.6
	160.0	89.2	4.2	97.4	6.7	102.1	5.0

N.D.: not detected or lower than LOD, 4-CPA: 4-chlorophenoxyacetic acid, DICA: dicamba, 2,4-D: 2,4-dichlorophenoxyacetic acid, 2,4-DP: 2-(2,4-dichlorophenoxy) propionic acid, RSD: relative standard deviation.

sites of UiO-66. As the pH changed, the dissociation states of the phenoxy herbicides also changed, which further influenced the adsorption efficiency of Cotton@UiO-66 towards phenoxy herbicides. Therefore, the effect of pH value on the extraction efficiency of phenoxy herbicide was investigated by varying pH value of sampling solutions from pH 2.0 to 7.0. As shown in Fig. 3, as pH increases the peak areas enhance for phenoxy herbicides until an optimal value is obtained at pH 3.0. A further increase in pH resulted in the decrease of phenoxy herbicides. After the prediction of RSM, the optimum pH value of the sampling solution is pH 3.0. Similarly, the pH of the desorption solution also affects the desorption of the phenoxy herbicides adsorbed on UiO-66. Therefore, the influence of acetic acid percentage in desorption solvent was explored. Desorption solvent consisted of acetic acid solution and acetonitrile. The optimal content of acetic acid solution predicted by RSM was 50.7%.

Detailed ANOVA results for extraction model are given in Supplementary Material. All model terms in Table S1, Table S2, Table S3, and Table S4 showing  $p$ -value < 0.05 are considered significant.  $F$ -values of 5.90, 7.30, 14.46, 20.12 indicate that the model is significant.

To verify the reliability of the RSM prediction results, the above optimum conditions were applied to phenoxy herbicides enrichment experiments. Considering the feasibility of the actual operation, SPE conditions were changed to 1.0 mL/min, pH 3.0, 50% for sample flow rate, sample solution pH value, and percentage of acetic acid solution in eluent, respectively.

### 3.3. Evaluation the proposed method

To evaluate the proposed Cotton@UiO-66 method, parameters of methodology such as linearity, limits of detection (LOD), limits of quantification (LOQ), and accuracy for the determination of four phenoxy herbicides were examined in Table 1. According to the optimized conditions, linearity data was obtained by versus concentration of plotting peak area. As can be seen in Table 1, the calibration curves of all phenoxy herbicides show excellent linearity, with coefficient of regression ( $R^2$ ) in the range of 0.9956–0.9990. LODs varies from 0.1 to 0.3  $\mu\text{g/L}$  at  $S/N = 3$ . Excellent linearity range with Cotton@UiO-66 pipetted syringe SPE extraction coupled with HPLC is 1.4–72  $\mu\text{g/L}$  for 4-CPA, 5.6–280  $\mu\text{g/L}$  for DICA, 2.8–140  $\mu\text{g/L}$  for 2,4-D, and 3.2–160  $\mu\text{g/L}$  for 2,4-DP. The intraday and interday precision using Cotton@UiO-66 pipetted syringe SPE was evaluated under optimum conditions. It can be seen that all RSDs are less than 6.3%. The results reveal the good stability and applicability of the proposed method.

### 3.4. Analysis of phenoxy herbicides in complex samples

To confirm the practicality of the proposed method, complex matrices were used to determine the existence of 4-CPA, DICA, 2,4-D, and 2,4-DP in this study. The spiked concentrations were set at three levels of low, middle and high for the real samples. In Fig. 4, the small phenoxy herbicides peaks are close to invisible in the real samples of cucumber, tap water and soil added stock solutions before the extraction. However, the peak areas increase significantly after the extraction using Cotton@UiO-66. Meanwhile, non-target analytes are not extracted. The specific interactions, such as Zr–O–H bonds, hydrophobic interaction and  $\pi$ - $\pi$  interaction between the UiO-66 on cotton and the four phenoxy herbicides, make up this selectivity adsorption. After repeating five times, recoveries of the spiked cucumber, tap water and soil samples are 87.3%–106.0%, 85.8%–106.8% and 83.3–103.8%, respectively (Table 2).

### 3.5. Comparison with other methods

As displayed in Table 3, the proposed technique is compared with other reported ones. By comparing the analytical instrument and pre-treatment method, the sorbent type, the amount of sorbent used, real samples, separation time, LOD, linearity and recovery, merits of this method are clearly illustrated. Trace-level of 4-CPA, DICA, 2,4-D, and 2,4-DP are extracted, separated and detected by HPLC couple with PT-SPE. The actual amount of UiO-66 on cotton fiber is much lower, so the cost estimate of the sorbent is much lower. Three practical samples are tested to confirm the good anti-matrix interference ability of the method. Shorter separating time and excellent shape of chromatograms are achieved after optimizing chromatographic condition. Importantly, results of the methodology such as LOD, linearity and recovery exhibit good applicability of the proposed method.

## 4. Conclusion

In summary, the UiO-66 coated cotton was fabricated for the extraction of trace-levels of phenoxy herbicides. The main factors affecting the performance of Cotton@UiO-66 in the extraction of phenoxy herbicides were evaluated by RSM. UiO-66@Cotton packed into a pipette tip exhibited excellent adsorptive selectivity toward 4-CPA, DICA, 2,4-D, and 2,4-DP in practical sample. Linearity of four phenoxy herbicides ranged from 1.4 to 72  $\mu\text{g/L}$ , 5.6–280  $\mu\text{g/L}$ , 2.8–140  $\mu\text{g/L}$  and 3.2–160  $\mu\text{g/L}$  with RSDs < 6.3%, respectively. Monitoring of phenoxy



**Table 3**  
Comparison of current method with other reported ones for the extraction of phenoxy herbicides through related parameter.

Method	Sorbent	Amount of sorbent (mg)	Sample	Separation time (min)	LOD ( $\mu\text{g/L}$ )	Linearity ( $\mu\text{g/L}$ )	Recovery (%)	Ref.
HPLC-UV SPE	MOF-808	30	Juice, tap water	41	0.1–0.5	0.2–250	62.7–105.2	Si et al. (2019)
HPLC-UV SPE	UiO-67	15	Tomato, cucumber, white gourd	42	0.98–1.90	0.3–250	86.1–103.4	Duo et al. (2018)
HPLC-UV SPE	Cationic polyelectrolyte/GO	1000	Spinach, chives	25	0.75–1.5	2.5–200	66.8–99.2	Hou et al. (2020)
HPLC-DAD SPE	Amino modified COF	100	Water	36	0.01–0.06	0.2–100	89.6–102.4	Ji et al. (2019)
HPLC-DAD MMF-SPME	Graphene reinforced monolithic	150	Water, rice	25	0.1–0.12	1.0–200	70.0–118	Pei et al. (2019)
HPLC-DAD SPME	poly (OMA-co-TRIM) monolith	2000	Rice	15	0.9–1.2	5–600	92.9–111.6	Li et al. (2019a)
LC-MS/MS MSPE	CoFe <sub>2</sub> O <sub>4</sub> @ polypyrrole nanoparticles	40	Soil, water	15	0.03–90	$\mu\text{g/kg}$ 0.1–200	80–117	Oller-Ruiz et al. (2018)
UHPLC-MS/MS MSPE-DLLME	magnetic MWNTs	15	Rice, millet, soy, oatmeal, barley	NR	0.19–0.80	1.5–500 ng/g	83.9–102.7	Yuan et al. (2018)
HPLC-PDA PT-SPE	UiO-66 modified cotton	20 (including weight of the cotton)	Soil, cucumber, tap water	18	0.1–0.5	1.4–280	85.8–106.8	This work

SPE: solid phase extraction, MMF-SPME: multiple monolithic fiber solid-phase microextraction, MSPE: magnetic solid phase extraction, PT-SPE: pipette tip solid-phase extraction, ACN: acetonitrile, NR refers to not reported.

herbicides in soil, cucumber and tap water samples, recoveries were in range of 83.3–106.8% with RSDs < 6.7%. The detection limits of phenoxy herbicides ranged from 0.1  $\mu\text{g/L}$  to 0.3  $\mu\text{g/L}$ . The results confirm that the proposed approach is an effective and rapid method for the determination of phenoxy herbicides in complex samples.

### CRedit authorship contribution statement

**Ying Su:** Investigation, Validation, Methodology, Data curation, Software, Writing - original draft, Writing - review & editing. **Sicen Wang:** Supervision, Conceptualization, Funding acquisition, Project administration. **Nan Zhang:** Methodology, Data curation, Writing - review & editing. **Ping Cui:** Data curation, Software. **Yan Gao:** Methodology, Writing - review & editing. **Tao Bao:** Conceptualization, Methodology, Data curation, Writing - original draft, Writing - review & editing, Funding acquisition, Project administration.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Acknowledgments

This research was supported by the National Natural Science Foundation of China (Grant Nos. 81703469 and 81973277), the China Postdoctoral Science Foundation (No. 2017M613157), the World-Class Universities (Disciplines) and the Characteristic Development Guidance Funds for the Central Universities (No. PY3A012) and the Fundamental Research Funds for the Central Universities.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ecoenv.2020.110764>.

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