ORIGINAL PAPER

Magnetic dispersive solid-phase extraction of triazole and triazine pesticides from vegetable samples using a hydrophilic-lipophilic sorbent based on maltodextrin- and β-cyclodextrin-functionalized graphene oxide

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Abstract

Maltodextrin- and β-cyclodextrin-functionalized magnetic graphene oxide (mGO/β-CD/MD), a novel hydrophilic-lipophilic composite, was successfully fabricated and used for the co-extraction of triazines and triazoles from vegetable samples before HPLC–UV analysis. mGO/β-CD/MD was synthesized by chemical bonding of β-CD and MD to the surface of mGO, using epichlorohydrin (ECH) as a linker. The successful synthesis of mGO/β-CD/MD was confirmed by characterization tests, including attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), vibrating sample magnetometry (VSM), thermogravimetric analysis (TGA), energy-dispersive X-ray spectroscopy (EDX), Brunauer–Emmett–Teller (BET), and Barrett-Joyner-Halenda (BJH) analyses. The hydrophobic cavity of β-CD and a large number of hydroxyl groups on the MD structure contributed to the co-extraction of mentioned pesticides with a wide range of polarity. Under the optimized condition (sorbent amount, 30 mg; desorption time, 10 min; desorption solvent volume, 300 µL; desorption solvent, methanol/acetonitrile (1:1) containing 5% (v/v) acetic acid; extraction time, 20 min; and pH of sample solution, 7.0), good linearity within the range 1.0–1000 µg L^{-1} ($r^2 \geq 0.992$) was achieved. Extraction efficiencies were in the range 66.4–95.3%, and the limits of detection were 0.01–0.08 µg L^{-1}. Relative recoveries for spiked samples were obtained in the range 88.4–112.0%, indicating that the matrix effect was insignificant, and good precisions (intra- and inter-day) were also achieved (RSDs < 9.0%, $n = 3$). The results confirmed that the developed method was efficient for the determination of trace amounts of pesticides in potato, tomato, and corn samples.

Keywords β-Cyclodextrin · Magnetic solid-phase extraction · Functionalized graphene oxide · Maltodextrin · Triazine herbicides · Triazole fungicides · Vegetable samples

Introduction

Farmers typically use a variety of pesticide combinations to achieve desired grain, vegetable, and fruit quality. Among pesticides, triazines and triazoles are widely used in agricultural practice. The main physicochemical properties of triazines and triazoles are their solubility in water and stability for a long time under a wide range of environmental conditions, leading to the endangerment of water, food, and ecological resources throughout the food chain [1]. Considering the toxicity of these chemicals, it is vital to establish a high-sensitivity pesticide analysis method.

Various determination techniques, including high-performance liquid chromatography (HPLC), fitted with a mass spectrometer (MS) [2], or diode array detector (DAD) [3], gas chromatography (GC) [4], and GC coupled to MS (GC/MS) [5], have been used in recent years for analysis of pesticide residues in environmental samples and agricultural products. However, instrumental analysis cannot determine trace amounts of pesticides in the mentioned samples due to their low concentration and complex sample matrices. As a result, before instrumental analysis, an effective method that is typically based on a reliable

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sample pretreatment procedure is needed [6]. Extraction of pesticides from various samples have been reported by solid-phase extraction (SPE) [7], liquid–liquid extraction (LLE) [8], stir bar sorptive extraction (SBSE) [9], dispersive solid-phase extraction (d-SPE) [10], matrix solid-phase dispersion (MSPD) [11], and magnetic solid-phase extraction (MSPE) [12]. Among all derivates of SPE, MSPE has gotten a lot of attention due to its advantages of high adsorption performance, easy operation, quick separation, time saving, low cost, and low consumption of toxic organic solvents [13]. As the sorbent material plays a vital role, designing and developing high-performance sorbents became a strong challenge to achieve effective methods. Non-magnetic materials have the potential to increase sorbent dispersibility and adsorption performance [13]. Therefore, to provide an affinity toward the target pesticides, hybrid materials have been synthesized [13–16]. Graphene oxide (GO), a derivative of graphene, has various groups on basal plane and its edges, including phenol, hydroxyl, carboxyl, and epoxide groups. These functional groups bring better dispersibility and easier modification for GO [17]. GO and aromatic compounds could interact with each other through hydrophobic interactions, Van der Waals forces, hydrogen bonds, π-π interactions, and other non-covalent interactions.

β-Cyclodextrin (β-CD) as a natural cyclic oligosaccharide is obtained from starch via CD saccharin invertase [18]. It is a well-known reality that CDs can form inclusion complexes with various organic molecules, especially aromatics, through host–guest interactions in its hydrophobic cavity [18]. β-CD is a biocompatible, cheap, and environmentally friendly alternative for sorbents fabrication. Therefore, it has been used to develop different sorbents due to its strong recognition and enrichment functions [18–21]. MDs are carbohydrates derived from maize starch and are a group of oligosaccharides composed of glucose with a dextrose equivalent (DE) value lower than 20 [22]. They have a large number of hydroxyl groups; therefore, they possess hydrophilic structures. MD could be solved in aqueous solution easily leading to interact with other materials better in reaction solution, while other hydrophilic polymers could not be solved in aqueous solution easily such as cellulose and chitosan. MDs can interact with analytes via hydrogen bonding. As a result, combining MDs with other materials will improve the dispersibility and efficiency of corresponding materials while also expanding their application range [23]. Consequently, MD, incorporation in sorbent structure, could enhance the extraction efficiency toward hydrophilic analytes. Today, it is important that synthesized sorbents are economically viable, but many synthetic compounds mentioned above are expensive and most of them are non-degradable. To prepare low-cost and effective sorbent, materials that are originated from nature could be utilized. A potential family of these materials is dextrians which are biocompatible, cheap, and environmentally friendly.

In this study, a new and high performance sorbent composed of MD and β-CD modified mGO (mGO/β-CD/MD) was fabricated. mGO was prepared via the coprecipitation method. MD and β-CD were grafted on mGO through a chemical bond via epichlorohydrin (ECH), using a simple synthesis method. mGO modification through a chemical bond improves its stability and reusability. The fabricated sorbent was applied to extract triazines (atrazine (ATZ), tribenuron methyl (TRB), and metribuzin (MET)) and triazoles (cyproconazole (CYP), tebuconazole (TEB), penconazole (PEN), and diniconazole (DIN)) with different polarities from vegetable samples. To the best of our knowledge, this is the first time that a sorbent based on β-CD and MD was fabricated and applied for the simultaneous extraction of 7 pesticides with a variety range of polarity from potato, tomato, and corn samples.

Experimental

Reagents

TRB (95%), MET (97%), ATZ (99%), CYP (95%), TEB (97%), PEN (97%), and DIN (95%) were purchased from Ariashimi Company (Tehran, Iran). ECH, sodium chloride (NaCl), sodium hydroxide (NaOH), sodium hydrogen carbonate (Na$_2$HCO$_4$), and graphite were obtained from Merck (Darmstadt, Germany). H$_2$SO$_4$ (98%), ammonia solution, methanol (MeOH) (HPLC grade), and acetonitrile (ACN) (HPLC grade) were purchased from Dr. Mojallali (Tehran, Iran). MD ($DE=4$–7), β-CD, iron (II) chloride tetrahydrate (FeCl$_2$.4H$_2$O), iron (III) chloride hexahydrate (FeCl$_3$.6H$_2$O), KMnO$_4$, H$_3$PO$_4$ (85%), and H$_2$O$_2$ (30%) were purchased from the Sigma-Aldrich (Bornem, Belgium). Ultrapure water was prepared by the Millipore Milli-Q gradient water purification system.

Solutions

The stock standard solution (1000 mg L^{-1}) of each analyte was prepared by dissolving an appropriate amount of each analyte in ACN. The standard solutions were stored in a refrigerator at 4 °C and dark condition. A fresh 100.0 mg L^{-1} standard solution containing the seven pesticides was prepared in ACN every week and kept at 4 °C. The working solutions at different concentrations were prepared by dilution of the standard solution with ultrapure water.

Preparation of vegetable samples

The fresh vegetables, including corn, tomato, and potato, were purchased from local markets (Tehran, Iran), and homogenized with high-speed homogenizer after being cut into bits. Each homogenized sample (10.0 g) was accurately transferred into a 50-mL centrifuge tube and spiked with specific amounts of analytes mixed standard solution. The centrifuge tube was then filled with 10 mL of ACN. The mixture was ultrasonicated for 30 min, followed by centrifugation at 6000 rpm for 3 min. The collected supernatant was then evaporated with a rotary vacuum evaporator before redissolved by 25 mL ultrapure water in a centrifuge tube [9].

Apparatus and analytical conditions

Information about the analytical conditions, characterization instruments, and other apparatus is provided in the Electronic Supplementary Material (ESM).

Synthesis of the sorbent

GO and mGO were prepared following a previously reported procedure and the detail is provided in the ESM.

Synthesis of ECH-functionalized mGO

To achieve a homogeneous suspension, 0.5 g of the resulting mGO was ultrasonically dispersed in 200 mL of ultrapure water. The pH of the suspension was then adjusted to 9.5 by adding an appropriate amount of NaOH solution. After that, 10 mL of ECH was applied to the suspension dropwise. The reaction mixture was stirred magnetically at 60 °C for 3 h. The solid product was separated by an external magnet and washed with ultrapure water (3 times). The final product was epoxy-functionalized mGO [23].

Synthesis of mGO/β-CD/MD

The epoxy-functionalized mGO (0.5 g) was dispersed in 200 mL carbonate buffer and then 0.2 g of β-CD and 0.2 g of MD were added to the solution. The pH of the mixture was adjusted to about 10. After stirring of solution at 60 °C for 3 h, the product was isolated with a magnet and washed three times with warm water [23]. Synthesis procedure is illustrated in Fig. 1.
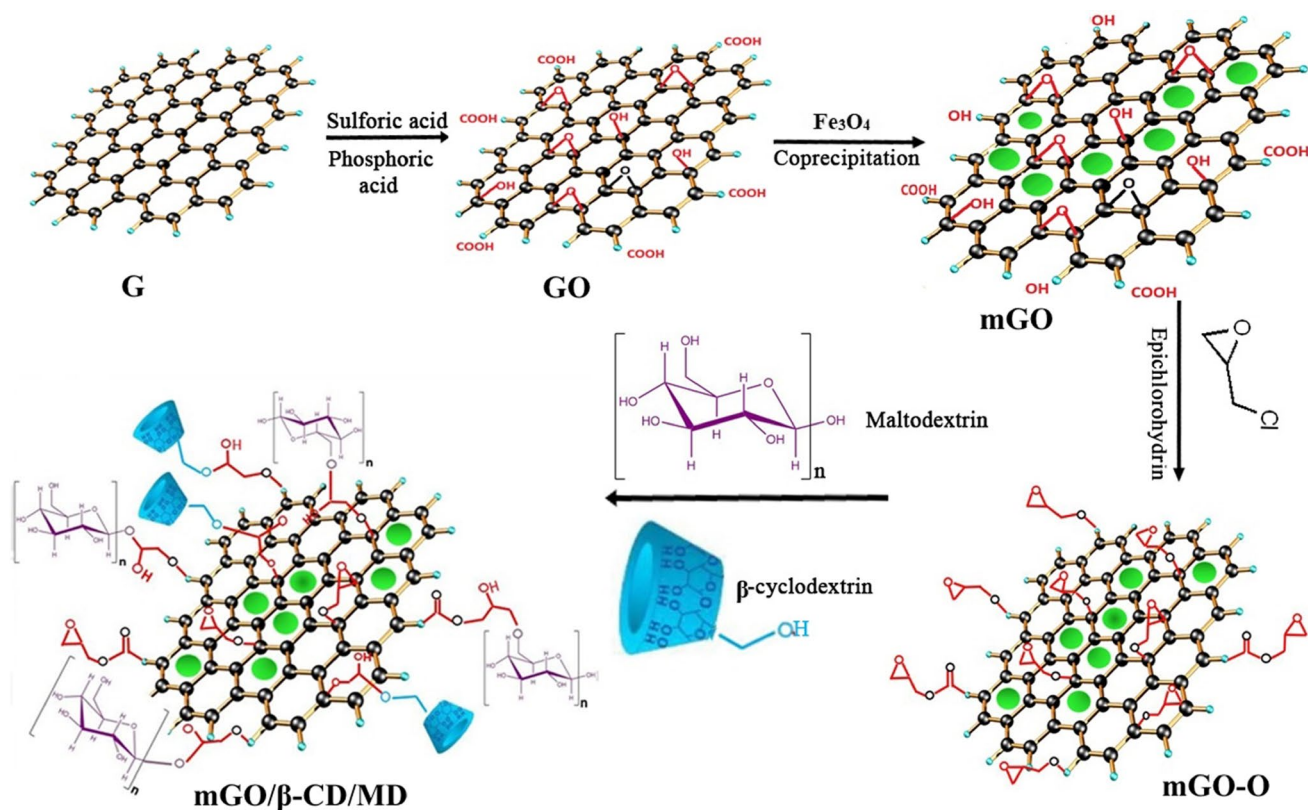

Fig. 1 Synthesis procedure of mGO@β-CD@MD

Extraction procedure

The sample solution (25 mL, pH = 7) was transferred to a centrifuge tube. Then, appropriate amount of sorbent (30 mg) was added to the sample solution and was stirred by an overhead stirrer for 20 min at 500 rpm to reach the equilibrium. Then, the sorbent was separated from the suspension using an external magnet, and the supernatant was decanted. After that, the analytes were desorbed from the sorbent by adding 300 μL of a mixture of MeOH and ACN (1:1, v/v) containing 5% (v/v) acetic acid (HAc) by ultrasonication for 10 min. Finally, 20 μL of the eluent was injected into the HPLC–UV for further analysis of the analytes.

Results and discussion

Choice of materials

The sorbent components are important variable affecting the extraction performance. In this regard, GO was chosen due to broad delocalized π-π electron system, its functional groups, and high surface area. Its functional moieties could react with any linker agents such as epichlorohydrin, and could be modified easily. Consequently, GO was preferred to other materials. Using Fe_3O_4 nano particles in sorbent's structure caused magnetic properties. Therefore, synthesized sorbent could be separated by an external magnet easily. In the next step, mGO surface was modified with β-CD and MD, using epichlorohydrin as a linker. Epichlorohydrin was used, since it could react with mGO and dextrins rapidly in a mild reaction condition. β-CD was chosen for mGO surface modification, since it could enhance the extraction efficiency of the sorbent toward some analytes with specific size. Since CDs can form inclusion complexes with various organic molecules, especially aromatics, through host–guest interaction in its hydrophobic cavity, using β-CD in sorbent structure could be beneficial for extracting analytes with appropriate size. MD was chosen as a modifier, as it has many hydroxyl groups which can interact via hydrogen bonding. MD has a hydrophilic nature which could enhance the sorbent capability for hydrophilic analytes extraction. Besides, MD can be solved in aqueous solutions easily rather than other hydrophilic polymers such as cellulose and chitosan.

Characterization of sorbent

The ATR-FTIR analysis was employed to prove the chemical structure of the final sorbent. In Fig. S1A, the stretching vibration of the OH group is characterized by a wide band of about 3600 cm^{-1}. The peaks at 1387 cm^{-1}, 1626 cm^{-1}, and 1726 cm^{-1} are attributed to C-O, C=C, and C=O stretching

vibrations, respectively [6]. The characteristic peak at 587 cm^{-1} was the stretching vibration of Fe–O-Fe, which proves the presence of Fe_3O_4 [13]. In Fig. S1B, the characteristic absorption peak of β-CD and MD is a broad band in 1200–900 cm^{-1}. As shown in Fig. S1C, dextrins and mGO/β-CD/MD have very similar spectra, with all of the dextrin's characteristic peaks at 940 cm^{-1}, 1029 cm^{-1}, 1075 cm^{-1}, and 1160 cm^{-1}. The peak at 940 cm^{-1} is correlated with R-1,4 bond skeleton vibrations. The asymmetric glycosidic vibration of (C–O–C) is responsible for the large band at 1140 cm^{-1}; the coupled v (C–C/C–O) stretch vibration has peaks at 1080 cm^{-1} and 1030 cm^{-1}, respectively [24]. Besides, the spectrum of the final sorbent illustrates a significant change compared to that of the mGO. The spectrum of the mGO/β-CD/MD contains all of the specific peaks of β-CD and MD in the fingerprint regions (1200–900 cm^{-1}). As a consequence of all of the above findings, β-CD and MD have been successfully grafted onto the mGO.

The morphological characteristics of synthesized materials were investigated using the FESEM technique, which was presented in Fig. 2. Figure 2A illustrates a typical sheet-like with smooth surface and crumpled shape of GO. As shown in Fig. 2B, the Fe_3O_4 nanoparticles (NPs) were well distributed on GO sheets. Besides, these images show that the Fe_3O_4 NPs had been assembled on the surface of the GO that is related to their large specific surface area, high surface energy, and their superparamagnetic behavior. Grafting β-CD and MD was performed via ECH as a linker, leads to having a lamellar structure with wrinkled forms, which could be seen in Fig. 2C and D. As shown in Fig. 2D, the surface of the mGO/β-CD/MD is rougher than that of mGO, which reveals that many β-CD and MD clusters had been assembled on the surface of the GO layers. Energy-dispersive spectrum (EDS) analysis of mGO is shown in Fig. 2E. It represents the peaks associated with Fe, C, and O elements with mass ratios (w%) of 23%, 41.17%, and 35.58%, respectively. The EDS pattern of the mGO/β-CD/MD nanocomposite (Fig. 2F) represents the peaks corresponded to Fe, C, and O with the mass ratio (w%) of 10.8%, 48.2%, and 41%, respectively. EDS mapping of synthesized sorbent was also presented in Fig. S2 and proves well distribution of Fe_3O_4 NPs within the composite structure and the successful synthesis of the sorbent.

The amount of β-CD and MD in fabricated mGO/β-CD/MD composite was determined using thermogravimetric analysis (TGA). As shown in Fig. 3, the weight loss in the region of 20–140 °C was related to removing residual water. As reported in the literature by Dong et al. [22], MD weight loss took place at about 250 °C, and according to another report by Hădărugă et al. [25], β-CD weight loss took place in 328 °C. As shown in Fig. 3, the weight loss area between 140 and 360 °C was attributed to the decomposition of β-CD and MD, which was estimated to be 17 wt%. The weight

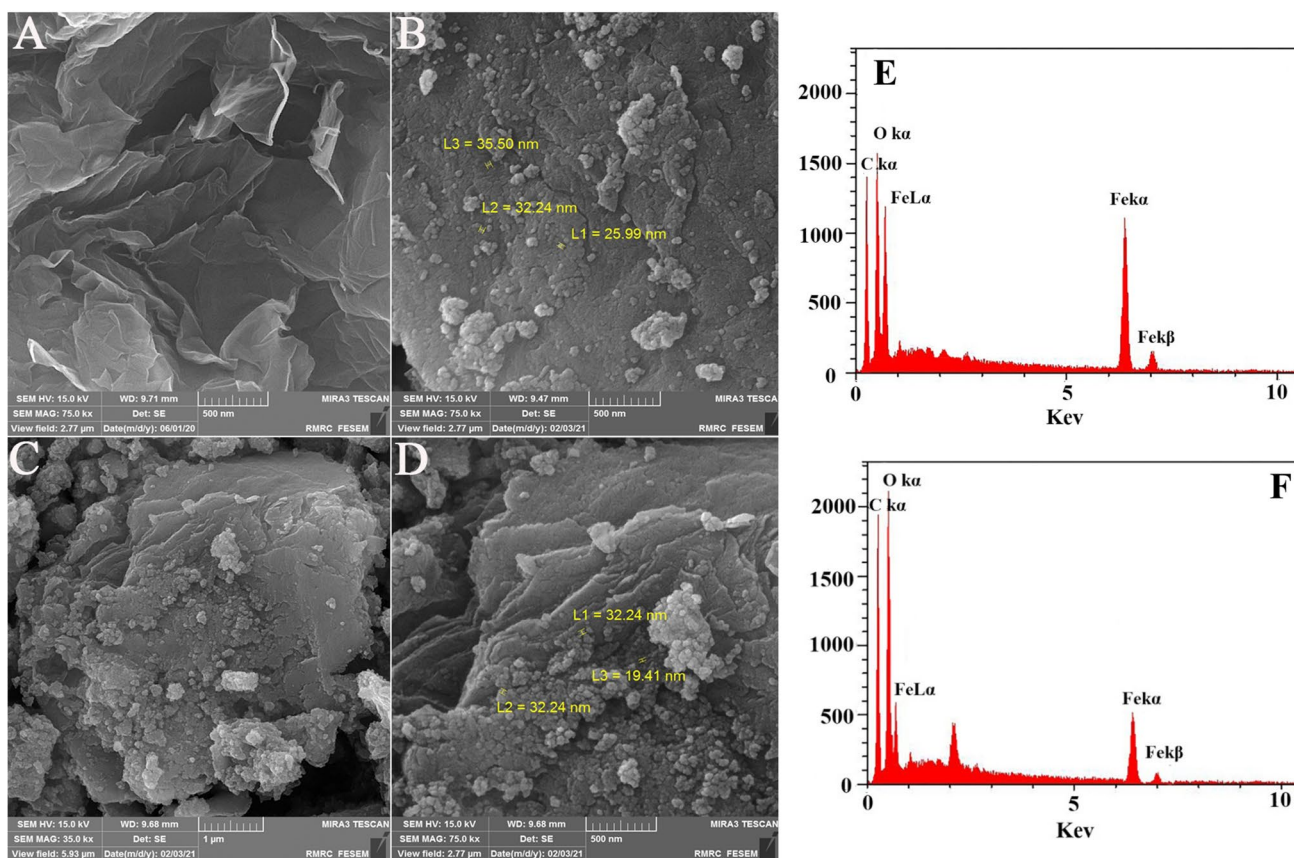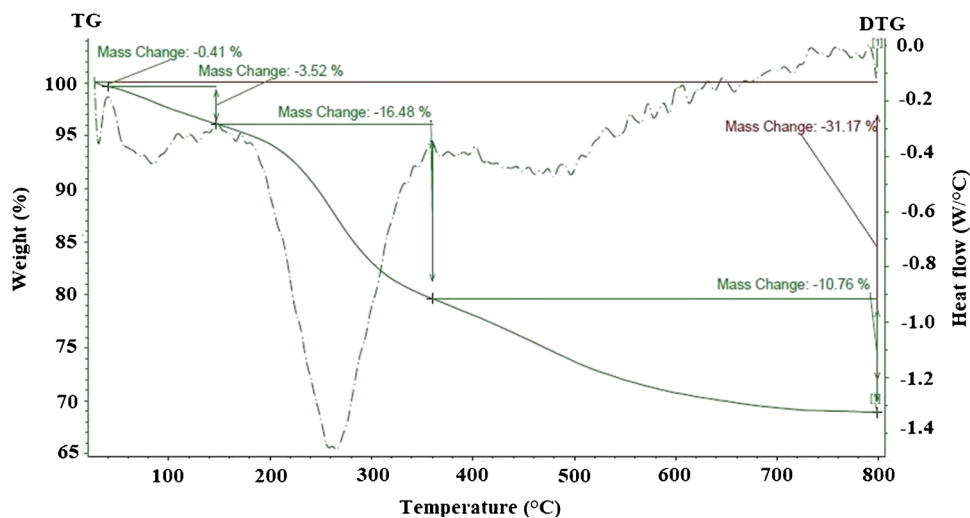**Fig. 2** FESEM images of (**A**) GO, (**B**) mGO, and (**C**, **D**) mGO@β-CD@MD and EDS patterns of (**E**) mGO, and (**F**) mGO@β-CD@MD

Fig. 3 TGA and differential thermogravimetry (DTG) curves of mGO@β-CD@MD

loss region at about 360–600 °C may be attributed to the decomposition of GO residue [26]. XRD and VSM analyses were studied and obtained results are described in detail in ESM and related patterns are illustrated in Fig. S3 and Fig. S4, respectively. Brunauer–Emmett–Teller (BET) and

Barrett–Joyner–Halenda (BJH) analyses have been performed and the nitrogen adsorption–desorption isotherms of mGO, mGO/β-CD, and mGO/β-CD/MD were investigated. Related data and figures are shown in ESM (Fig. S5).

Optimization of extraction condition

Type of sorbent

The sorbent type is a critical factor that influences extraction performance. mGO was chosen in this case because of its high sorption potential and excellent magnetic properties of magnetite NPs. As shown in Fig. 4, the extraction capabilities of mGO, mGO/β-CD, and mGO/β-CD/MD were investigated. Experimental conditions were as follow: desorption solvent: ACN, pH of sample solution: 7.0, extraction time: 30 min, desorption time: 14 min, desorption solvent volume: 300 μL, sorbent amount: 35 mg, and salt amount: 0% w/v. The main interaction between mGO and analytes is related to π-π and hydrophobic interactions. Introducing β-CD in sorbent structure creates the ability to form a host–guest inclusion complex [13]. Therefore, the combination of mGO with β-CD would show the synergy of the two materials. As shown in Fig. 4, introducing β-CD increased the extraction efficiency of triazoles more than triazines. Because the atrazine and metribuzin molecules are likely to be too small to create a host–guest inclusion complex with β-CD, while triazoles have a triazolyl group and a benzene ring, they are more likely to form an inclusion complex with β-CD. As a result, β-CD can form an inclusion complex with compounds that contain double aromatic rings of appropriate size and shape. Besides, metribuzin and tribenuron methyl are almost polar analytes and do not have an affinity to be extracted by β-CD. By adding MD in sorbent structure, the extraction efficiency of triazines was enhanced. MD as a polar compound has a large number of hydroxyl groups, therefore, could form hydrogen bond. Introducing MD into the sorbent
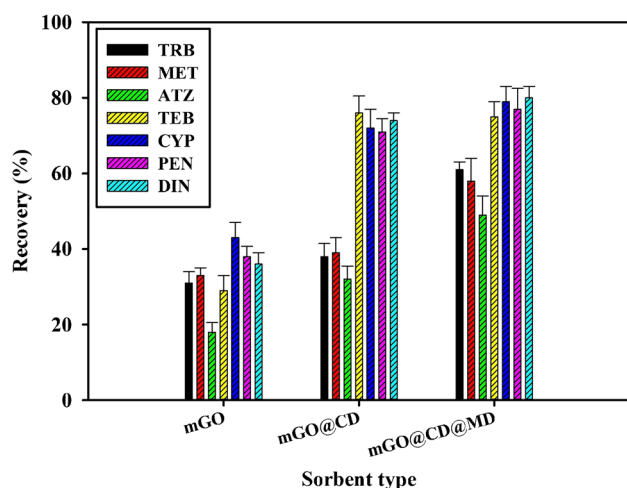
structure could be beneficial for triazines, which have many hydrogen bonding sites and are almost polar. Subsequently, mGO/β-CD/MD showed the best extraction efficiency, and the adsorption mechanism toward the analytes is mainly dominated by the π-π interaction, inclusion complex formation, hydrophobic interaction, and hydrogen bonding. Finally, mGO/β-CD/MD was employed for the extraction of analytes with a wide range of polarity.

Respective data and figures of effective parameters (type of desorption solvent, desorption time, desorption solvent volume, pH of sample solution, ionic strength, sorbent amount, and extraction time) on the extraction efficiency are given in the ESM. The following experimental conditions were found to give best results: sorbent type, mGO@β-CD@MD; desorption solvent type, ACN:MeOH (1:1) containing 5% w/v HAc; (Fig. S6); desorption solvent volume; 300 μL (Fig. S7); desorption time, 10 min (Fig. S8); pH of sample solution; 7.0 (Fig. S9); salt concentration, 0.0% w/v (Fig. S10); sorbent amount, 30 mg (Fig. S11); extraction time, 20 min (Fig. S12).

Reusability of mGO@β-CD@MD

The reusability of mGO@β-CD@MD was investigated by employing the sorbent in adsorption–desorption experiments several times. After the extraction procedure, the sorbent was washed to remove any analyte remnants and prepare it for subsequent extractions. The sorbent was washed with 1 mL of ACN:MeOH (1:1) containing 5% w/v HAc under ultrasonication condition for 10 min, then washed with acetone. Additional extractions were applied to investigate the memory effect, using 300 μL of the desorption solvent followed by HPLC–UV analysis. The sorbent mGO@β-CD@MD could be reused at least four times and lost 10% of its initial extraction efficiency, indicating that the fabricated sorbent was stable and reusable.

Method validation

Under the optimized condition, a series of parameters representing the analytical performance of the proposed method, including the limit of detection (LOD), the limit of quantification (LOQ), linearity, precision, extraction efficiency, and preconcentration factor (PF) were investigated. Ten standard solutions (1.0, 5.0, 10.0, 20.0, 50.0, 100.0, 200.0, 500.0, 700.0, and 1000.0 μg L^{-1}) were used to plot each calibration curve. As summarized in Table 1, all the analytes showed acceptable linearity with satisfactory determination coefficients (R^2) varying between 0.992 and 0.999.

In this study, to determine the LOD, the concentration of studied analytes was reduced to be corresponded to the signal-to-noise ratios of 3. As shown in Table 1, LODs were in the range of 0.01–0.08 μg L^{-1}, and LOQs varied from 1.0

Fig. 4 Effect of sorbent type on the extraction efficiency of pesticides. Extraction conditions: desorption solvent: ACN, pH of sample solution: 7.0, extraction time: 30 min, desorption time: 14 min, desorption solvent volume: 300 μL, sorbent amount: 35 mg, and salt amount: 0% w/v

Table 1 Figures of merit of developed MSPE procedure for analysis of pesticides

Parameter	Concentration[a]	TRB	MET	ATZ	CYP	TEB	PEN	DIN
Linearity[a]		5.0–500.0	10.0–700.0	1.0–700.0	20.0–500.0	5.0–1000.0	1.0–500.0	5.0–500.0
LOQ[a]		5.0	10.0	1.0	20.0	5.0	1.0	5.0
LOD[a]		0.08	0.05	0.01	0.08	0.02	0.05	0.02
R^2		0.999	0.992	0.999	0.996	0.999	0.997	0.999
Intra-day and (inter-day) RSD (%) ($n=3$)	50.0	4.7 (6.6)[b]	7.5 (9.1)	6.2 (9.1)	5.5 (7.2)	4.5 (5.3)	3.9 (5.9)	5.1 (6.3)
	100.0	5.9 (7.2)	6.7 (8.2)	5.5 (7.7)	4.9 (7.8)	6.1 (7.5)	4.5 (7.6)	5.9 (8.1)
	300.0	5.0 (6.7)	6.2 (7.0)	7.5 (9.0)	7.0 (8.2)	4.0 (8.0)	5.0 (5.9)	5.8 (7.8)
Batch to batch RSD (%) ($n=3$)	100.0	8.5	9.6	7.8	8.9	9.9	8.8	8.5
Recovery (%)		77.1	69.4	66.4	85.5	87.4	95.3	92.0
PF		64.0	56.7	55.0	70.0	72.4	79.0	76.4

[a]All concentrations are based on µg L^{-1}

[b]The numbers in parentheses refer to inter-day RSDs

to 20.0 µg L^{-1}. The PF of seven analytes was 55–79 times. PFs were calculated by dividing the slope ratio of the calibration curve obtained by the proposed method by the slope of the direct analysis of the analytes by HPLC–UV. Extraction recovery was calculated using the Eq. 1:

$$ER(\%) = \frac{PF}{PF_{max}} \times 100 \tag{1}$$

Maximum PF was obtained from the ratio of sample solution volume to desorption solvent volume. The extraction recoveries were in the range of 66–95% for the target analytes. The intra- and inter-day relative standard deviations (RSDs) were less than 7.5% and 9.0%, respectively (Intraday and inter-day RSDs, $n=3$ samples at 50.0, 100.0, and 300.0 µg L^{-1} of each analyte). To evaluate the effect of different batches of the sorbent on precision of the method, the batch-to-batch RSD was also studied. For this purpose, three different batches of the sorbent were fabricated and applied for the quantification of target analytes (100.0 µg L^{-1}) in sample solutions. The obtained RSDs were less than 9.9%.

Real samples analysis

Regulatory agencies establish tolerances in treated crops according to good agricultural practices and protect consumer health to guarantee pesticide utilization in the field. Different maximum residue limits (MRLs) are adopted worldwide for different agrarian products [27]. Some MRLs related to our studied analytes in different matrices were tabulated in Table S1 according to national pesticide information center (NPIC) reports.

The practical efficiency of the developed extraction method was investigated by applying it to analyze un-spiked

(blank) and spiked samples, including tomato, potato, and corn samples (Fig. 5). As expected, because of the widespread usage of pesticides in agricultural fields, the target pesticides were observed in selected real samples. The results showed that there were observed 36.0 µg kg^{-1} and 166.0 µg kg^{-1} of DIN in tomato and corn samples, respectively, and 680.0 µg kg^{-1} of ATZ in tomato sample, and 176.0 µg kg^{-1} of TEB in corn sample. To more recognize the compounds that appeared in the retention times of analytes in the chromatogram of HPLC–UV, the real samples were also analyzed by LC–MS/MS after performing the suggested extraction procedure. Related total ion chromatograms are shown in ESM (Fig. S13, S14, and S15 and Table S2). According to the findings, the residue levels in these vegetables were substantially lower than the MRLs, except ATZ value in tomato. Besides, to examine the method's accuracy, the samples were spiked with the analytes at the concentrations of 250.0 and 750.0 µg kg^{-1}, and then they were analyzed by the current method. To calculate relative recoveries (RR %), Eq. 2 was used:

$$RR(\%) = \frac{Cfound - Creal}{Cadded} \times 100 \tag{2}$$

where C_{real}, C_{found}, and C_{added} are the initial analyte concentration in the real sample, the analyte concentrations (µg kg^{-1}) after adding a known amount of the standard to the real sample, and the concentration of a known amount of the standard solution spiked into the real sample, respectively.

The RRs of the spiked samples were within the acceptable range of 88.4–112.0%, with RSDs of 1.8–6.5% ($n=3$). The obtained results were listed in Table 2. As a result, this method based on using mGO/β-CD/MD as a sorbent was

Fig. 5 Typical chromatograms achieved after MSPE from un-spiked and spiked potato, tomato and corn samples (peaks names: (1) TRB, (2) MET, (3) ATZ, (4) CYP, (5) TEB, (6) PEN, (7) DIN)
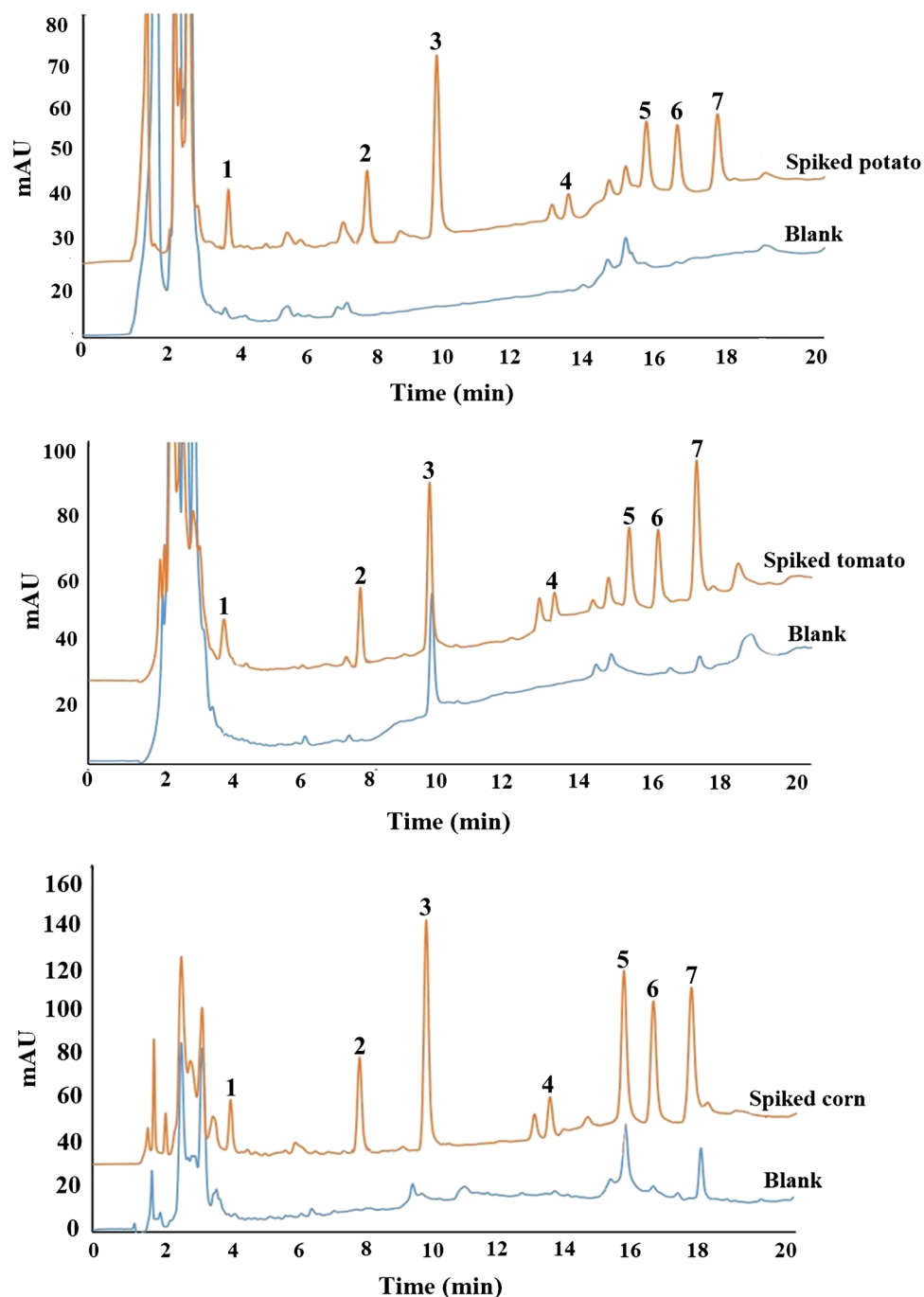
reliable and could be applied for accurate determination of trace amounts of these pesticides in real samples.

Comparison with other methods

The performance of the developed method was compared with other MSPE methods used for triazine or triazole pesticides from the viewpoint of linearity, LOD, RSD, and analysis time. The sorbents listed in Table 3 [4, 12, 19, 28–35] have different natures like metal–organic framework based on magnetic copper (M-MOF-199) [28], zeolitic imidazolate framework based on magnetic zinc (MMP/ZIF-8) [29], magnetic porous organic polymers (MOPs) [4], magnetic partially carbonized cellulose nanocrystals (MPC-CNC) [12], and hydrophilic-lipophilic balanced magnetic NP [30], which were widely used in the field of sample preparation. As tabulated in Table 3, the newly developed mGO/β-CD/MD-based MSPE has provided good detection limits. However, Liu et al. reported MPC-CNC for triazine and triazole pesticides determination followed by UHPLC-MS/MS

Table 2 Analysis of real-food samples

Analyte	Added[a,b]	Potato			Tomato			Corn		
		Found[a]	RR (%)	RSD (%)	Found[a]	RR (%)	RSD (%)	Found[a]	RR (%)	RSD (%)
TRB	0.0	n.d[c]	-	-	n.d	-	-	n.d	-	-
	250.0	259.0 ± 7.5	103.6	2.9	247.0 ± 11.3	98.8	4.6	239.0 ± 9.3	95.6	3.9
	750.0	789.0 ± 27.6	105.2	3.5	739.0 ± 27.3	98.5	3.7	739.5 ± 35.4	99.0	4.8
MET	0.0	n.d	-	-	n.d	-	-	n.d	-	-
	250.0	278.0 ± 11.1	111.2	4.0	262.0 ± 6.5	104.8	2.5	256.0 ± 6.9	102.4	2.7
	750.0	792.0 ± 25.3	105.6	3.2	762.0 ± 30.4	101.6	4.0	761.0 ± 36.5	101.5	4.8
ATZ	0.0	n.d	-	-	680.0	-	6.7	n.d	-	-
	250.0	239.0 ± 6.4	95.6	2.7	872.0 ± 21.8	88.8	2.5	264.8 ± 13.2	105.9	5.0
	750.0	729.0 ± 42.3	97.2	5.8	1368.0 ± 56.0	91.7	4.1	795.0 ± 41.3	106.0	5.2
CYP	0.0	n.d	-	-	n.d	-	-	n.d	-	-
	250.0	221.0 ± 15.0	88.4	6.8	228.0 ± 12.9	91.2	5.7	255.0 ± 16.0	102.0	6.3
	750.0	694.0 ± 34.0	92.5	5.0	687.0 ± 47.4	91.6	6.9	760.7 ± 39.5	101.4	5.2
TEB	0.0	n.d			n.d	-	-	176.0	-	5.9
	250.0	231.0 ± 9.0	92.4	3.9	263.0 ± 7.6	105.2	2.9	445.0 ± 16.0	107.6	3.6
	750.0	765.0 ± 34.4	102.0	4.5	771.0 ± 29.3	102.8	3.8	971.0 ± 42.7	106.0	4.4
PEN	0.0	n.d			n.d	-	-	n.d		-
	250.0	243.0 ± 13.3	97.2	5.5	247.0 ± 10.8	98.8	4.4	275.0 ± 9.6	110.0	3.5
	750.0	742.0 ± 24.5	98.9	3.3	741.0 ± 42.9	98.8	5.8	780.0 ± 42.1	104.0	5.4
DIN	0.0	n.d			36.0	-	6.4	166.0	-	6.6
	250.0	266.0 ± 8.5	106.4	3.2	280.0 ± 14.8	112.0	5.3	416.0 ± 14.5	104.4	3.5
	750.0	745.0 ± 36.5	99.3	4.9	811.0 ± 53.5	108.1	6.6	934.0 ± 55.1	102.4	5.9

[a]The concentrations are based on μg kg^{-1}

[b]These concentrations are reported in initial homogenized vegetable samples, so the spiked concentrations with factor 2.5 are reduced in final sample solution

[c]*n.d* not detected

with LOD lower than our method [13]. It may be due to Yi et al. who employed a more sensitive detection instrument (UHPLC-MS/MS) than the instrument used in this work (HPLC–UV) for pesticide detection [12]. Liang et al. reported $Fe_3O_4@SiO_2$-GO/MIL-101 (Cr) composite for extraction of triazines from rice sample. This method depicted similar results to our work [31]. In another work, ionic liquid-based magnetic carbon nanotubes (IL-Fe_3O_4@ MWCNTs) was synthesized and applied for triazoles fungicides (TFs) determination prior to GC–MS analysis. This method showed limited linearity, comparable RSD and LOD values, but shorter extraction time than ours. Prepared sorbent benefits from ILs properties, such as polarity, low volatility associated to nonpolar and ionic interactions. The condensed cyclic structure of ILs makes it to an excellent functional compound to interact with TFs [33]. Su et al. synthesized a core–shell $Fe_3O_4@SiO_2@MOF/TiO_2$ nanocomposite, and used it for TFs extraction from water samples, before HPLC–MS/MS analysis. Developed method provided better repeatability, lower LODs, and shorter extraction time than our work. Low LODs are the results of using HPLC–MS/MS analysis instrument. In this sorbent MOF

and TiO_2 particles play efficient role, since MOF should enable fast molecular diffusion and thus increase the mass transfer rate of the target analytes. TiO_2 immobilized on MOF could improve the relatively weak physisorption forces between analytes and MOF [34]. In a recent study, magnetic porous carbon (Fe_3O_4@PC) was used as a sorbent for TFs determination before HPLC–UV analysis. This method provided wider linearity than our work and good precision. Analytes were extracted in a very short time which may due to sorbent structure and capability. The porous carbon was prepared by incomplete combustion of filter paper loaded with zinc hexahydrate. Synthesized sorbent possesses many pores, large pore volume, and high specific surface area [35]. In this study, natural originated materials which are cheap, degradable, and easily accessible have utilized for mGO modification, while other studies have applied synthetic materials which are expensive and non-degradable. Besides, most of these sorbents were fabricated for specific analytes; in most cases, the analytes were from the same class and had similar polarity. The sorbent of the current study can extract analytes that are from two different classes with different polarities, which was the most outstanding advantage

Table 3 Comparison of proposed method with other MSPE methods for determination of pesticides

Sorbent	Analytes	Matrix	Detection	Linearity (µg/L)	LOD (µg/L)	RSD (%)	Extraction time (min)	Ref
MOPs	TFs	Cucumber, cabbage	GC-FID	0.5–200	0.12–0.19	<6.8	30	[4]
MPC-CNC	Triazines, TFs	Water samples	UHPLC-MS/MS	0.02–10	0.002–0.006	<15.7	16.5	[12]
M-MOF/β-CD	Prochloraz, TFs	Tomato, lettuce	HPLC–MS/MS	1–500	0.25–0.1	<6.7	45	[19]
M-MOF-199	TFs	Water samples	HPLC–MS/MS	0.25–1000	0.05–0.1	9	25	[28]
MMP/ZIF-8	TFs	Water samples	GC–MS/MS	1–400	0.08–0.27	<9.65	11	[29]
Magnetic poly(divinylben-zene-co–N-vinylpyrro-lidone)	Triazines	Water samples	HPLC–DAD	0.20–10	0.048–0.081	<10.5	20.5	[30]
Fe_3O_4@SiO_2-GO/MIL-101(Cr)	Triazines	Rice	HPLC–UV	2–1000	0.01–0.08	8.7	30	[31]
Fe_3O_4@APTES-GO/ZIF-8	TFs	Water, honey, fruit juices	HPLC–DAD	1–1000	0.014–0.109	<6.9	60	[32]
IL-Fe3O4@MWCNTs	TFs	Water samples	GC–MS	0.5–50	0.05–0.22	≤10	8	[33]
Fe3O4@SiO2@MOF/TiO2	TFs	Water samples	HPLC–MS/MS	0.0005–0.5	0.00019–0.0012	≤7.5	10	[34]
Fe3O4@PC	TFs	River water Wheat flour Rice	HPLC–UV	1–1200	0.2–0.3	≤7	5	[35]
mGO/β-CD/MD	Triazines and TFs	Potato, tomato, corn	HPLC–UV	1.0–1000	0.01–0.08	≤7.5	30	This work

TFs triazoles fungicides, *M-MOF-199* magnetic copper-based metal organic framework, *MMP/ZIF-8* magnetic zinc-based zeolitic imidazolate framework, *M-MOF/β-CD* β-cyclodextrin-functionalized magnetic zinc-metal organic framework, *MOPs* magnetic porous organic polymers, *MPC-CNC* magnetic partially carbonized cellulose nanocrystals, *IL-Fe₃O₄@MWCNTs* ionic liquid-based magnetic carbon nanotubes, *Fe₃O₄@PC* magnetic porous carbon

compared to other sorbents. Generally, the results showed the proposed method using mGO/β-CD/MD as a sorbent has provided wide linearity, low LODs, and RSDs compared with other methods, indicating that it had superiorities in sensitivity and repeatability for analysis of pesticides in vegetables.

Conclusion

In this work, we have shown the great potential of β-CD, and MD as biocompatible, cheap, and easily accessible materials to functionalized magnetic mGO as an effective sorbent for triazole fungicides and triazine herbicides co-extraction and determination prior to HPLC–UV. mGO/β-CD/MD was synthesized as a novel hydrophilic-lipophilic magnetic composite, which would exhibit the merits of magnetic GO, β-CD, and MD. Consequently, it was separated fast, had a high surface area, and could be used for the extraction of analytes with different polarities. Synthesized sorbent has the capability to adsorb other species for example pigments

such as methylene blue, crystal violet, and malachite green and other pollutants such as chlorobenzen, polycyclic aromatic hydrocarbons, benzylurea, and organophosphate pesticides and even other matrix species like β-carotene and vitamin C. As synthesized sorbent has β-CD in its structure, it could be employed for adsorption of hydrophobic species with aromatic rings with appropriate size. Due to MD existence in sorbent structure, it can also be used for hydrophilic species. It could be beneficial for analysis of wide range of species in different samples.

All in all, this method was environmentally friendly, convenient, and effective for the simultaneous determination of triazole and triazine pesticides in vegetable samples. As far as we know, this hydrophilic-lipophilic magnetic sorbent based on the dextrins was firstly introduced in the analysis of pesticides. It is the first time that an MSPE procedure using mGO/β-CD/MD as a sorbent and HPLC–UV has been used to extract and analyze triazoles and triazines at the same time. Although synthesized sorbent could not be used in homogenized vegetable and fruit matrix directly, and these kinds of matrix should be pretreated before analysis, since

these matrixes would obstruct the separation of the sorbent and make it less reusable which is the limitation of this method. Besides, the sorbent synthesis procedure is multistep; however, large quantities of the sorbent can be synthesized via one synthetic batch.

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