



Solid phase extraction of carbamate pesticides with porous organic polymer as adsorbent followed by high performance liquid chromatography–diode array detection

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ABSTRACT

A solid phase extraction (SPE) method with a porous organic polymer as adsorbent was established for the extraction of five carbamate pesticides (metolcarb, carbaryl, isoprocarb, bassa and diethofencarb) from milk, white wine and juice samples prior to high performance liquid chromatography–diode array detection. The main factors affecting the SPE were optimized, including sample volume, sample loading rate, sample solution pH, desorption conditions and cartridge reusability. Under the optimal conditions, a good linearity existed in the range from 1.0 to 320.0 ng mL⁻¹ for milk and white wine samples and from 0.5 to 160.0 ng mL⁻¹ for juice sample with the correlation coefficients between 0.9956 and 0.9998. The method recoveries of the carbamates were 82.0%–110.0%. The limits of detection were 0.12–0.40 ng mL⁻¹ for milk and white wine samples, and 0.06–0.20 ng mL⁻¹ for juice sample. The adsorption mechanism of the adsorbent was investigated by the extraction of different types of organic compounds (carbamates, benzoylurea insecticides, endocrine disrupting chemicals and polycyclic aromatic hydrocarbons) with the adsorbent. The results showed that the existence of the hydrogen-bonding between the adsorbent and the analytes is favorable for the adsorption and strong hydrophobicity seems to have an adverse effect.

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1. Introduction

Due to their broad biological activity, low bioaccumulation and mammalian toxicities, and relatively short lifespan [1,2], carbamate pesticides are widely used in agriculture. Although carbamate pesticides can disintegrate to some extent, their residues still can be found in some food stuffs because of their excessive use [3]. The pesticide residues in food and animal feed can then enter the human system by direct consumptions of the contaminated food such as juice, wine, milk, etc [4,5]. Because carbamate pesticides are strong endocrine disruptors and central nervous system toxins, they can harm humans and animals at low doses [6–9]. Therefore, it is necessary to establish rapid and sensitive methods for the determination of the carbamates residues.

Several analytical techniques have been used for the determination of carbamate pesticides in real samples, for example,

electrochemical biosensor [10], gas chromatography (GC) [11] and high performance liquid chromatography (HPLC) [12]. For the real sample analysis, a suitable pretreatment technique is often necessary to enrich the pesticides before instrumental analysis due to the low concentration of the pesticides residues in food products. To achieve a necessary enrichment for the analytes, a variety of sample pre-treatment techniques have been reported, such as dispersive liquid-liquid microextraction (DLLME) [13], micro-solid phase extraction (μ -SPE) [9], liquid phase microextraction (LPME) [14], solid phase extraction (SPE) [15–17] and magnetic solid phase extraction (MSPE) [1,18]. Among them, SPE is known as one of the most commonly used sample preparation methods due to its low cost, automation, good repeatability and environmental friendliness compared with traditional liquid-liquid extraction [19,20].

In SPE, it is the key to choose a suitable adsorbent to effectively adsorb the target analytes. Up to now, some different adsorbents, such as carbon nanotube and its composites [21,22], graphene [1,23], metal organic frameworks [24], ordered mesoporous silicas [25] and polyaniline-modified zeolite [26], have been used for the extraction of some carbamate pesticides. In recent years, porous

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organic polymers (POPs), a new class of advanced porous materials, have attracted increased attention from researchers because of their high chemical and thermal stability, diverse structures, good porosity and functionality [27,28]. POPs have been applied in gas storage [29,30], separations [31] and catalysis [32]. Different POPs such as conjugated microporous polymers (CMPs) [33], porous aromatic frameworks (PAFs) [34], covalent triazine frameworks (CTFs) [35] and covalent organic frameworks (COFs) [36] have been synthesized and employed for adsorption. However, the synthesis for most POPs requires noble-metal catalysts, high temperature and environmentally unfriendly solvents, which will increase the cost and environmental pollution. Moreover, the solubility of the organic monomers involved is often low in water, which makes the synthesis of POPs difficult in aqueous solutions. Lately, an environmentally friendly method based on a mild diazo coupling reaction in aqueous solution under mild conditions without the involvement of metal catalysts and templates has been reported [37,38] to prepare *o*-hydroxyazobenzene-based POPs (HAzo-POPs) with relatively high surface area and abundant –OH and –Ph–N=N–Ph– groups. Those POPs can supply intensive hydrogen bonds and large π electron conjugated system and have been successfully applied to CO₂ capture and conversion [37] and the removal and separation of methylene blue [38]. Since the HAzo-POPs possess hydrogen bonding and large π stacking capability, it may serve as an efficient adsorbent for the extraction of some organic compounds. However, there have been few reports on the use of HAzo-POPs as the adsorbent in sample pretreatment.

Recently, we have reported the preparation of a HAzo-POP by the reaction of 2,6-diaminoanthraquinone and *m*-trihydroxybenzene and used it as the SPE adsorbent for the extraction of some phenylurea herbicides [39]. In this work, a HAzo-POP, which was prepared from benzidine and *m*-trihydroxybenzene according to the reported method [37] and designated as BD-THB-POP, was explored as the SPE adsorbent for the extraction of some carbamate pesticides (metolcarb, carbaryl, isoprocarb, bassa and diethofencarb). The BD-THB-POP showed excellent adsorption performance for the carbamate pesticides and finally, a SPE method with the BD-THB-POP as the adsorbent was established for the extraction of the carbamate pesticides from milk, white wine and juice samples prior to high-performance liquid chromatographic detection. Meanwhile, the adsorption mechanism of the BD-THB-POP was explored by using different kinds of compounds including carbamates, benzoylurea insecticides, endocrine disrupting chemicals and polycyclic aromatic hydrocarbons as model analytes.

2. Experimental

2.1. Chemicals and reagents

Benzidine, concentrated hydrochloric acid, sodium nitrite, Na₂CO₃, *m*-trihydroxybenzene, tetrahydrofuran (THF), HPLC-grade acetonitrile, acetone and methanol were all purchased from Huaxin Chemical Reagent Company (Baoding, China). The standards of the carbamates (metolcarb, carbaryl, isoprocarb, bassa and diethofencarb), the benzoylurea insecticides (diflubenzuron, hexaflumuron and flufenoxuron), the endocrine disrupting chemicals (EDCs) (BPA, 4-t-BP, 4-t-OP and NP) and the polycyclic aromatic hydrocarbons (PAHs) (naphthalene, fluorene, acenaphthene, phenanthrene, anthracene, fluoranthene and pyrene) were all purchased from Aladdin Reagent (Shanghai, China). The water used throughout the work was prepared with Molelement 1820D ultra-pure water machine (Chongqing, China). The milk, white wine and juice samples were purchased from a local supermarket (Baoding, China).

2.2. Characterization of the BD-THB-POP

The BD-THB-POP was synthesized according to the reported method [37]. The texture of the BD-THB-POP was observed by both transmission electron microscopy (TEM) with a JEOL model JEM-2011(HR) (Tokyo, Japan) and scanning electron microscopy (SEM) with an S-4800 instrument (Hitachi, Japan). The infrared spectra (IR) were measured with a WQF-510 A spectrometer (Ruili, China). The Brunauer-Emmett-Teller (BET) surface areas were determined from the N₂ adsorption at 77 K using V-Sorb 2800 P (Jinaipu, China). The powder X-ray diffraction (PXRD) measurements were carried out with Cu K α radiation on a Bruker D8 ADVANC (Bruker, Germany).

2.3. Sample preparation

For milk sample, 100 mL milk and 1 g trichloroacetic acid were added in a conical flask, and then the conical flask was shaken on a slow-moving platform for 20 min. After the sample was centrifuged at 9500 rpm for 5 min, the supernatant was collected into a volumetric flask. Then, 5 mL of acetonitrile was added to the sediment phase, which was vortexed for 1 min and then centrifuged. The resulting supernatant was combined to the previous one. The same extraction process with acetonitrile was performed for another time. Then, the supernatant was made to the volume mark with water. Finally, the sample solution was filtered through a 0.45 μ m filter for the subsequent SPE procedures.

For white wine sample, 25 mL of white wine sample was diluted with 75 mL of water prior to the following SPE.

For juice sample, 50 mL of juice sample was diluted with 50 mL of double-distilled water, and the resulting solution was centrifuged and filtered through 0.45 μ m membrane before the following SPE.

2.4. Solid-phase extraction procedures

For the SPE, 20 mg BD-THB-POP was packed into a 3-mL SPE cartridge that was purchased from Agela Technologies (USA). The packed SPE cartridge was conditioned with 5 mL of methanol, 5 mL of acetonitrile, and 5 mL of water, respectively. Then, the sample solution (100 mL) was loaded at a flow rate of 5 mL min⁻¹ on a YGC-8 CNC automatic solid phase extraction instrument. After that, the cartridge was washed with 5 mL of water-acetonitrile mixture (95:5, v/v) and then dried under vacuum. Subsequently, 300 μ L acetonitrile eluent was added into the cartridge to pre-soak the adsorbent for 1 min. Then, the eluate was collected at a flow rate of 0.5 mL min⁻¹. After being filtered through a 0.45 μ m membrane, 20.0 μ L of the eluate was injected into the HPLC system for analysis.

2.5. HPLC conditions

An LC-20AT (Shimadzu, Japan) HPLC system equipped with an SPD-M20 A diode array detector and two LC-20AT pumps was used for the detection. A Centurysil C18 column (250 mm \times 4.6 mm i.d., 5.0 μ m) from Bonna-Agela technologies (Tianjin, China) was used for separations. The mobile phase was a mixture of acetonitrile-water (43:57 (v/v) for white wine and milk samples; 45:55 (v/v) for juice sample) at a flow rate of 1.0 mL min⁻¹. The UV monitoring wavelengths were set at 200, 223, 200, 200, 208 nm for the metolcarb, carbaryl, isoprocarb, bassa and diethofencarb, respectively. The sample injection loop was 20.0 μ L.

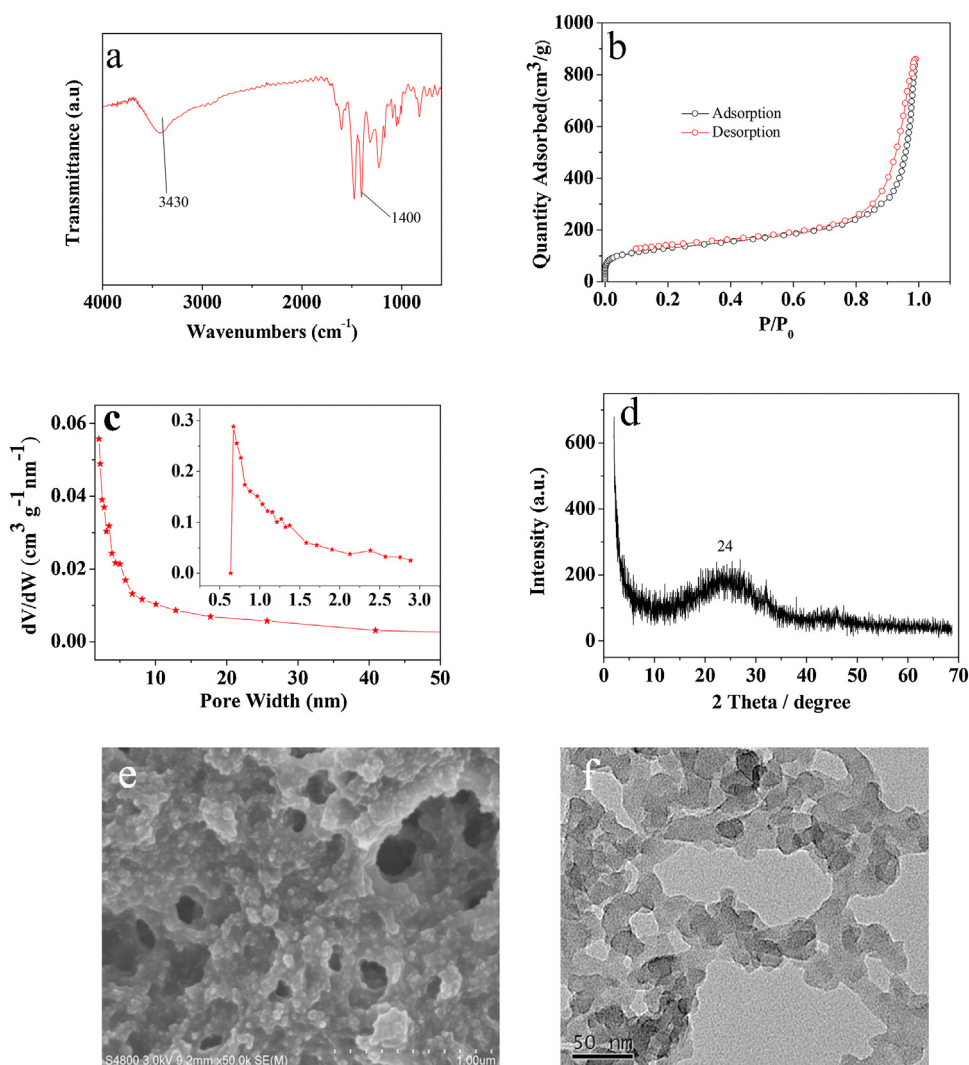


Fig. 1. Characterization of the BD-THB-POP. (a) FT-IR spectra; (b) Nitrogen adsorption-desorption isotherm; (c) Pore size distribution; (d) PXRD patterns; (e) SEM image; (f) TEM image.

3. Results and discussions

3.1. Characterization of the BD-THB-POP

The FTIR spectrum of the BD-THB-POP is shown in Fig. 1a. The peak at the wavenumber of 1400 cm^{-1} from the asymmetric vibration of the -N=N- bond and the broad peak around 3430 cm^{-1} from the Ar-OH group can be seen clearly, which are in good agreement with the literature result [37].

The surface areas and the pore structure of the BD-THB-POP were studied by N_2 adsorption-desorption isotherms measured at 77 K and the result is shown in Fig. 1b. According to IUPAC classification, the BD-THB-POP showed a type-IV isotherms and it had a sharply increased uptake at the $P/P_0 < 0.02$, indicating the presence of micropores. In the intermediate section of the relative pressures ($0.1 < P/P_0 < 1$), the BD-THB-POP had an evident hysteresis loop, indicating the existence of mesopores and macropores. According to the N_2 adsorption data, the BET specific surface area of the BD-THB-POP was calculated to be $436\text{ m}^2\text{ g}^{-1}$. The total adsorption average pore width, Barrett-Joyner-Halenda (BJH) median pore width and Saito-Foley (SF) median pore width for the BD-THB-POP are 7.83 nm, 2.02 nm and 0.67 nm, respectively. The pore size distribution of the BD-THB-POP is shown in Fig. 1c.

The crystal structure of the BD-THB-POP was investigated by PXRD. The PXRD graph of the BD-THB-POP (Fig. 1d) only has a very weak diffraction peak at 24° , implying that the polymer was amorphous in nature.

The morphology of the BD-THB-POP was observed by both scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It can be seen from Fig. 1 e and f that the BD-THB-POP was constructed by irregular tiny particles and had a great many irregular holes among the particles, which were consistent with the reported result [37].

3.2. Optimization of SPE conditions

To evaluate the extraction performance of the BD-THB-POP as the SPE adsorbent for the analytes, the key experimental parameters including the sample volume, sample loading rate, sample solution pH, and elution conditions were investigated. All the experiments were performed in triplicate and the means of the results were used for data analysis.

3.2.1. Effect of the sample volume

When the concentration of the analytes in the sample solution remained unchanged, the sample volume can affect the enrichment factors of the analytes. So, different volumes (20.0–150.0 mL)

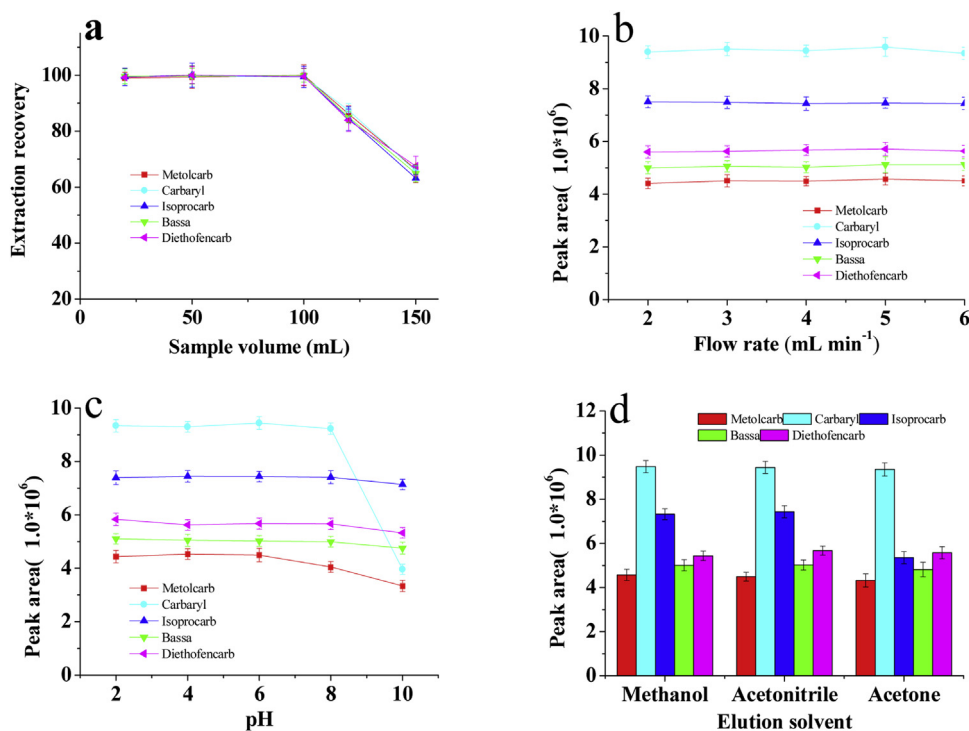


Fig. 2. Effect of different factors on the extraction of the carbamate pesticides. (a) Sample volume; (b) Sample loading rate; (c) Sample solution pH; (d) Elution solvent.

of the aqueous sample solution containing each of the carbamate pesticides at 80.0 ng mL^{-1} were tested to investigate the effect of sample volume. Fig. 2a shows that the extraction recoveries for the carbamates remained almost unchanged when the sample volume was increased from 20 to 100 mL and then was declined after that. Therefore, 100.0 mL sample solution was selected for the experiments.

3.2.2. Effect of the sample loading rate

In SPE, the loading rate of sample solution can affect the whole analysis time, so this factor should be taken into account. The effect of the sample loading rate was studied at the flow rate of 2, 3, 4, 5 and 6 mL min^{-1} respectively. As shown in Fig. 2b, the peak areas of the five carbamates remained almost constant when the loading rate was changed from 2 to 6 mL min^{-1} . In other words, the loading rate had little effect on the adsorption for the carbamates in the investigated range. In this study, 5 mL min^{-1} was selected as the sample loading rate.

3.2.3. Effect of sample solution pH

The pH of sample solution can affect the existing forms and charges of the analytes and therefore can influence the SPE process. In this work, the effect of sample solution pH on the SPE was investigated by adjusting the sample solution to different pH values (2.0, 4.0, 6.0, 8.0 and 10.0) with either 1 mol L^{-1} NaOH or 1 mol L^{-1} HCl aqueous solution. As shown in Fig. 2c, the peak areas of the five carbamates varied little in the pH range from 4 to 6. However, the peak areas of the five carbamate pesticides was decreased in the pH range of 6–10, especially for metolcarb and carbaryl since they can be hydrolyzed in strong alkaline conditions [1,40,41]. Based on the above results, the sample pH should not be larger than 6 for the SPE. Since the pH values of the studied sample solutions fell in the range of 3–6, the sample solution pH was not adjusted.

3.2.4. Effect of the elution conditions

The elution conditions can influence the effective elution of the analytes from the cartridge and the sensitivity of the method. In

this work, the elution of the carbamate pesticides from the BD-THB-POP was tested by using the following three solvents, i.e., methanol (0.3 mL), acetonitrile (0.3 mL) and acetone (0.3 mL), with the other conditions being kept constant. As shown in Fig. 2d, methanol and acetonitrile have a similar elution power and they are better than acetone. Considering that acetonitrile was the component of the HPLC mobile phase, it was selected as the eluent. Then, to ensure a complete elution of the analytes from the BD-THB-POP, the volume of acetonitrile was optimized by changing it from 0.3 to 0.9 mL. The results showed that the extraction recoveries were almost unchanged in the range of 0.3–0.9 mL. Considering that a less volume of the eluent will produce a less dilution for the analytes, 0.3 mL acetonitrile was chosen for the elution in the following experiments.

3.3. Cartridge reusability

To investigate the reusability of the BD-THB-POP cartridge, it was reused after being washed with 1 mL acetonitrile and 3 mL water. The result showed that the extraction recoveries of the carbamates had no significant decrease after it was reused for 25 times.

3.4. Effect of the different batches of the BD-THB-POP

The BD-THB-POP materials were prepared in two different batches and then they were characterized by XRD, FT-IR and N_2 adsorption-desorption analysis, respectively. The results showed that their XRD and FT-IR patterns were consistent, and their BET specific surface areas were 436 and 458 $\text{m}^2 \text{g}^{-1}$, respectively. Then, the materials from the two batches were both used as the SPE sorbent for the extraction of the carbamates to compare their extraction performance. As a result, the extraction recoveries for the carbamates by the materials were almost the same, indicating that the preparation of the materials was reproducible.

Table 1
Linear range, limit of detections (LODs) and correlation coefficients (r) for the carbamate pesticides.

Samples	Carbamates	Linearity (ng mL ⁻¹)	r	RSDs (n=5) (%)	LODs (ng mL ⁻¹)	LOQs (ng mL ⁻¹)
Milk	Metolcarb	2.0–320.0	0.9991	6.3	0.30	0.90
	Carbaryl	1.0–320.0	0.9956	5.1	0.12	0.36
	Isoprocarb	2.0–320.0	0.9966	5.3	0.30	0.90
	Bassa	2.0–320.0	0.9998	4.9	0.40	1.20
	Diethofencarb	2.0–320.0	0.9966	5.4	0.40	1.20
White wine	Metolcarb	2.0–320.0	0.9993	5.4	0.30	0.90
	Carbaryl	1.0–320.0	0.9998	5.2	0.12	0.36
	Isoprocarb	2.0–320.0	0.9991	5.9	0.20	0.60
	Bassa	2.0–320.0	0.9998	5.4	0.40	1.20
	Diethofencarb	2.0–320.0	0.9966	4.9	0.40	1.20
Juice	Metolcarb	1.0–160.0	0.9990	5.8	0.10	0.30
	Carbaryl	0.5–160.0	0.9993	4.5	0.06	0.18
	Isoprocarb	1.0–160.0	0.9998	5.7	0.10	0.30
	Bassa	1.0–160.0	0.9987	5.2	0.20	0.60
	Diethofencarb	1.0–160.0	0.9966	5.6	0.20	0.60

3.5. Evaluation of the method

The calibration curves, linear range (LR), correlation coefficients (r), limits of detection (LODs) and limits of quantification (LOQs) were evaluated under the optimal conditions. To establish the calibration curves for the analytes, a series of carbamates-free milk, white wine and juice samples spiked with each of the analytes at different concentrations (1.0, 2.0, 4.0, 8.0, 20.0, 40.0, 80.0, 120.0, 320.0 ng mL⁻¹ for milk and white wine samples, and 0.5, 1.0, 2.0, 4.0, 10.0, 20.0, 40.0, 80.0, 160.0 ng mL⁻¹ for juice sample) were prepared, respectively. As shown in Table 1, a good linearity for the five carbamates was achieved with r ranging from 0.9956 to 0.9998 for milk, white wine and juice samples. The LODs estimated at a signal-to-noise ratio of 3 (S/N = 3) were 0.12–0.40 ng mL⁻¹ for milk and white wine samples and 0.06–0.20 ng mL⁻¹ for juice sample, depending on the compounds. The repeatability of the method was determined by performing five parallel analyses of the samples spiked with each of the carbamates at 2.0, 12.0 and 60.0 ng mL⁻¹ for milk and white wine samples, and 1.0, 6.0 and 30.0 ng mL⁻¹ for juice sample, respectively. The relative standard deviations (RSDs)

were in the range of 4.5–6.3%, indicating a good repeatability of the method.

3.6. Analysis of real samples

To evaluate the applicability of the method, the developed SPE method with BD–THB–POP -packed cartridge was used for the extraction of carbamates from milk, white wine and juice samples. As shown in Table 2, metolcarb was found at a concentration lower than its LOQ in the white wine sample; none of the carbamate pesticides was found in milk and juice samples. The method recoveries for the analytes were then investigated by using the spiked samples with the carbamates. As a result, the method recoveries of the five carbamates were in the range from 86.0 to 110.0% for milk sample with the RSDs of 3.2–6.3%, from 86.5 to 109.0% for white wine sample with the RSDs of 2.1–6.5%, and from 82.0 to 105.3% for juice samples with the RSDs of 2.8–6.3%, respectively. The typical chromatograms of the white wine sample before and after being spiked with the analytes at 12.0 ng mL⁻¹ are displayed in Fig. 3.

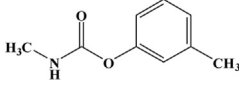
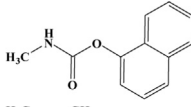
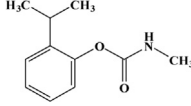
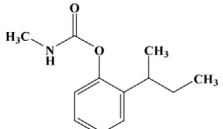
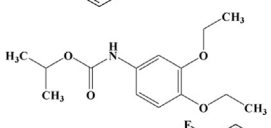
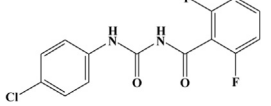
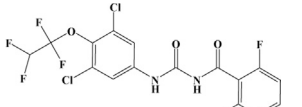
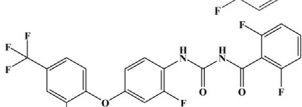
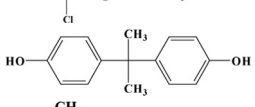
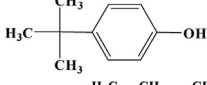
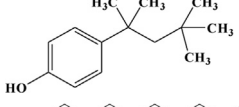
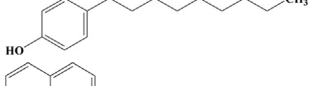
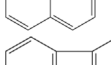
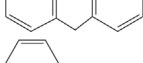
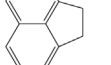
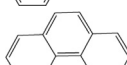
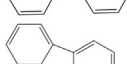
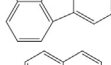
Table 2
Determinations of carbamate pesticides in milk, white wine, juice samples and method recoveries for the samples.

Carbamates	Milk (n = 5)				White wine (n = 5)				Juice (n = 5)			
	Spiked (ng mL ⁻¹)	Found (ng mL ⁻¹)	MR ^a (%)	RSDs	Spiked (ng mL ⁻¹)	Found (ng mL ⁻¹)	MR (%)	RSDs	Spiked (ng mL ⁻¹)	Found (ng mL ⁻¹)	MR (%)	RSDs
Metolcarb	0.0	nd ^b			0.0	<LOQ			0.0	nd		
	2.0	1.72	86.2	6.3	2.0	2.18	109.0	5.4	1.0	0.95	95.0	5.8
	12.0	11.52	96.0	5.1	12.0	11.79	98.3	5.3	6.0	5.93	98.9	5.8
	60.0	61.14	101.9	4.7	60.0	56.28	93.8	5.7	30.0	31.28	104.3	4.1
Carbaryl	0.0	nd			0.0	nd			0.0	nd		
	2.0	1.95	97.5	5.1	2.0	1.73	86.5	5.4	1.0	0.82	82.0	4.5
	12.0	11.02	91.8	3.8	12.0	11.91	99.2	4.5	6.0	6.02	100.4	3.4
	60.0	54.12	90.2	3.2	60.0	54.14	90.2	5.7	30.0	31.40	104.7	2.8
Isoprocarb	0.0	nd			0.0	nd			0.0	nd		
	2.0	1.72	86.0	5.3	2.0	1.80	90.0	5.9	1.0	0.87	87.0	5.7
	12.0	11.44	95.3	6.1	12.0	10.96	91.3	6.5	6.0	5.99	99.8	4.9
	60.0	54.84	91.4	5.2	60.0	53.96	89.9	2.1	30.0	27.12	90.4	5.0
Bassa	0.0	nd			0.0	nd			0.0	nd		
	2.0	2.13	106.5	4.9	2.0	2.01	100.5	5.4	1.0	1.10	110.0	5.2
	12.0	13.49	110.0	5.9	12.0	11.13	92.8	6.1	6.0	5.76	96.0	4.1
	60.0	61.14	101.9	3.9	60.0	53.61	89.4	3.2	30.0	31.59	105.3	3.4
Diethofencarb	0.0	nd			0.0	nd			0.0	nd		
	2.0	1.72	86.0	5.4	2.0	1.98	99.0	4.9	1.0	1.00	100	5.6
	12.0	12.14	101.2	5.0	12.0	11.39	94.9	3.2	6.0	5.62	93.6	6.3
	60.0	61.14	101.9	3.2	60.0	60.20	100.3	2.7	30.0	30.16	100.5	4.5

^a MR, recovery of the method.

^b nd, not detected.

Table 3
Extraction recoveries of the different compounds.

Compound	Structure	Molecular	H bond acceptors	H bond donors	^a LogK _{ow}	^b ER(%)
Metolcarb		165.2	3	1	1.72	100.0
Carbaryl		200.2	3	1	2.35	99.5
Isoprocarb		193.2	3	1	2.37	102.2
Bassa		207.3	3	1	2.86	103.4
Diethofencarb		267.3	5	1	3.29	102.9
Diflubenzuron		310.7	4	2	3.59	98.0
Hexaflumuron		461.1	5	2	5.64	72.0
Flufenoxuron		488.2	5	2	5.97	53.8
BPA		228.3	2	2	3.64	98.1
4-t-BP		150.2	1	1	3.42	92.2
4-t-OP		206.3	1	1	5.28	85.1
NP		220.4	1	1	5.99	46.0
Naphthalene		128.2	0	0	3.17	54.8
Fluorene		166.2	0	0	4.02	40.3
Acenaphthene		154.2	0	0	4.15	43.2
Phenanthrene		178.2	0	0	4.35	42.6
Fluoranthene		202.3	0	0	4.93	44.7
Pyrene		202.3	0	0	4.93	47.7

^a K_{ow}, octanol/water partition coefficient.

^b ER, extraction recovery.

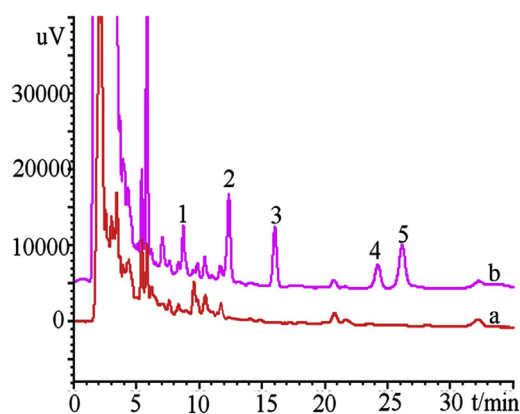


Fig. 3. The typical chromatograms of (a) white wine sample, (b) the white wine sample spiked with the carbamate pesticides at each concentration of 12.0 ng mL^{-1} . The common UV detection wavelength: 208 nm. Peak identification: (1) Metolcarb, (2) Carbaryl, (3) Isoproc carb, (4) Bassa, (5) Diethofencarb.

3.7. Adsorption mechanism of the BD-THB-POP

In addition to the carbamate pesticides, other three different types of compounds (benzoylurea insecticides, EDCs and PAHs) were also studied to elucidate the possible adsorption mechanism of the BD-THB-POP. All the experiments were tested under their respective optimal conditions: sample volume: 100 mL; spiked analyte concentration: 80.0 ng mL^{-1} ; desorption solvent: 1.2 mL acetonitrile for benzoylurea insecticides, 1.2 mL methanol for EDCs and 1.2 mL acetone for PAHs. The H bond acceptors and H bond donors are the indicators for hydrogen bonding preferences, and the octanol/water partition coefficient ($\log K_{ow}$) is an indicator for hydrophobicity.

As shown in Table 3, the extraction recoveries with the BD-THB-POP for the PAHs (40.3%–54.8%) were lower than those for either the carbamates (99.5%–103.4%), the EDCs (46.0%–98.1%) or the benzoylurea insecticides (53.8%–98.0%). Since the BD-THB-POP contains large conjugated system and abundant H-bond acceptors and donors, it is expected that both π - π stacking and hydrogen-bonding interactions are favorable for the adsorption. It can be seen from the molecular structures of the analytes that H-bond acceptors and donors of the carbamates, benzoylurea insecticides, EDCs and PAHs are 4–6, 6–7, 2–4, and 0, respectively. Since the PAHs contain the largest conjugated systems and the lowest H-bond acceptors and donors (0) among them, the lowest extraction recoveries for the PAHs suggest that the hydrogen-bonding interactions between the analytes and the BD-THB-POP played a greater role than the π - π stacking interactions. For the benzoylurea insecticides, the extraction recoveries (53.8%–73%) for hexaflumuron and flufenoxuron with the $\log K_{ow}$ values of 5.64 and 5.97 are lower than that (98%) for diflubenxuron with a lower $\log K_{ow}$ value of 3.59, and the similar result was also observed for the four EDCs, indicating that a strong hydrophobicity is unfavorable for the adsorption.

4. Conclusions

In summary, a BD-THB-POP with large conjugated system and abundant H-bonding sites was synthesized by diazo coupling reaction. It showed excellent adsorption performance for carbamate pesticides. An effective SPE method with the BD-THB-POP as the adsorbent was established for the extraction of five carbamate pesticides from milk, white wine and juice samples. The adsorption of the BD-THB-POP for the analytes was mainly attributed to hydrogen bonding, and strong hydrophobicity has adverse effect on the adsorption. Therefore, BD-THB-POP is expected to be an effective adsorbent for the compounds with weak hydrophobicity and more

hydrogen-bonding sites. However, further study needs to be done to elucidate its adsorption mechanism more clearly and to enlarge its applications.

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