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Carbon Dot-Decorated Graphite Carbon Nitride Composites for Enhanced Solid-Phase Microextraction of Chlorobenzenes from Water

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Abstract: In this work, carbon dot-decorated graphite carbon nitride composites (CDs/g-C₃N₄) were synthesized and innovatively used as a SPME coating for the sensitive determination of chlorobenzenes (CBs) from water samples, coupled with gas chromatography–mass spectrometry. The CDs/g-C₃N₄ coating presented superior extraction performance in comparison to pristine g-C₃N₄, owing to the enhancement of active groups by CDs. The extraction capacities of as-prepared SPME coatings are higher than those of commercial coatings due to the functions of nitrogen-containing and oxygen-containing group binding, π–π stacking, and hydrophobic interactions. Under optimized conditions, the proposed method exhibits a wide linearity range (0.25–2500 ng L⁻¹), extremely low detection limits (0.002–0.086 ng L⁻¹), and excellent precision, with relative standard deviations of 5.3–9.7% for a single fiber and 7.5–12.6% for five fibers. Finally, the proposed method was successfully applied for the analysis of CBs from real river water samples, with spiked recoveries ranging from 73.4 to 109.1%. This study developed a novel and efficient SPME coating material for extracting organic pollutants from environmental samples.

Keywords: carbon dots; graphite carbon nitride; sorbent; solid-phase microextraction; chlorobenzenes

1. Introduction

Chlorobenzenes (CBs) are a kind of raw materials for the synthesis of pesticides, dyes, chemical agents, polymers, and other fine chemicals, and have been widely used in modern industries. However, CBs would also endanger human health due to their refractory degradation, high toxicity, fat solubility, and bioaccumulation. CBs are very irritating to the eyes and skin, and can even inhibit the human nerve center and damage the liver and kidneys if water contaminated with CBs is ingested [1,2]. Therefore, CBs have been listed as priority pollutants by many governments all over the world. In view of this, it is essential to develop a simple and sensitive analytical method for monitoring the contamination of CBs in water.

Generally, traditional approaches for the determination of CBs in water have been established by using gas chromatography (GC) or gas chromatography–mass spectrometry (GC-MS) after pretreatment procedures such as liquid extraction and solid-phase extraction [3]. It is well known that the sample pretreatment consumes most of the time and labor during an analytical process. In comparison to traditional pretreatment techniques,
solid-phase microextraction (SPME) presented outstanding performances for the extraction of organic compounds from water, owing to its advantages of solvent-free sampling, straightforward operation, and the integration of sampling, extraction, and injection into a single step [4,5]. The extraction capacity for analytes depends on the adsorption performance of coating materials; therefore, SPME coatings play an important role in the sensitive extraction of targeted analytes [6,7]. Although various commercial SPME coatings have been developed, a great effort should be made to further improve the extraction capacity for determining trace analytes.

Up to now, a variety of materials have been investigated as SPME coatings, such as carbon-based materials, metal oxides, metal–organic frameworks, covalent organic frameworks, and polymers, etc. [8–10], wherein carbon-based materials displayed glorious extraction performance towards non-polar and slightly polar compounds because of their hydrophobicity and ease of functionalization [11–13]. As a type of zero-dimensional carbon-based material, carbon dots (CDs) have been widely used in various fields, such as chemical sensing, biosensing, drug delivery, catalysis, etc. [14–17], given that CDs possess abundant oxygen-containing groups on the surface, e.g., hydroxyl and carbonyl groups, which provide plentiful active sites for adsorbing targeted compounds through electrostatic attraction, hydrogen bonding, and π–π interactions [18]. However, the application of CDs for extracting targeted compounds from aqueous samples was limited by the isolating difficulty of CDs after adsorption due to their strong hydrophilicity. Therefore, a supported material can be used for the immobilization of CDs to overcome this drawback [19]. Li et al. [20] synthesized carbon dot@poly(glycidyl methacrylate) (PGMA)@Fe₃O₄ nanoparticles as an adsorbent for the solid-phase extraction of polycyclic aromatic hydrocarbons from water samples. The extraction performance was tunable through controlling the doped amounts of CDs and changing the polymer length. Qiu’s group prepared CDs and polyethyleneimine-functionalized CD-decorated silica microparticles as a stationary phase of liquid chromatography [21,22]. Results showed that the decorated CDs enhanced the separation capacities for nucleosides and sulfonamides effectively. Although the adsorption performance of CDs has been investigated by modifications to support materials, alternative supports should be explored for expanding the application of CDs. Furthermore, there are few reports on the research of CDs in SPME.

Graphite carbon nitride (g-C₃N₄) has attracted wide attention as an effective adsorbent for sample pretreatment due to its simple preparation, abundant π-electron structure, hydrophobicity, and excellent thermal and chemical stability [23–26]. In view of its excellent properties, g-C₃N₄ provided great potential as an ideal support for anchoring CDs. In this work, the CD-decorated g-C₃N₄ (CDs/g-C₃N₄) was synthesized by precipitating CDs into g-C₃N₄ sheets in aqueous solution, and was used as a SPME coating for the sensitive determination of CBs in water. The decoration of CDs onto g-C₃N₄ exhibited more abundant oxygen- and nitrogen-containing groups and enlarged the surface area, resulting in the improvement of extraction efficiencies for CBs from water. Furthermore, the CDs/g-C₃N₄ composites took full advantage of the abundant chemical groups of CDs and the hydrophobicity of g-C₃N₄, and overcame the drawbacks of CDs in pollutant-extraction from water due to its strong hydrophilicity. After optimizing the extraction conditions, the proposed method was finally applied for the analysis of CBs in real river water. To the best of our knowledge, the CDs/g-C₃N₄ composites were, for the first time, used for the SPME of pollutants from water. This study not only provided a novel material for SPME coating, but also extended the application field of CDs in SPME techniques.

2. Experimental

2.1. Reagents and Materials

The CBs standards, including 1,3,5-trichloro-benzene (1,3,5-TCB), 1,2,4-trichloro-benzene (1,2,4-TCB), 1,2,3-trichloro-benzene (1,2,3-TCB), 1,2,3,5-tetrachloro-benzene (1,2,3,5-TCB), 1,2,4,5-tetrachloro-benzene (1,2,4,5-TCB), pentachloro-benzene (PCB), hexachloro-benzene (HCB), and pentachloronitro-benzene (PCNB) were purchased from AccuStandard (New York, USA). The reagents, such as methanol and acetonitrile, were obtained from Merck (Darmstadt, Germany) and used as received.

The CDs were prepared according to the literature [14]. In a typical procedure, 100 mg of LAH was added to 10 mL of ethyl alcohol, and the mixture was refluxed for 5 h. After cooling to room temperature, 10 mL of water and 10 mL of ethyl alcohol were added, and the mixture was stirred for 30 min. The precipitate was filtered and washed with ethyl alcohol and water, and then dried in a vacuum oven at 80°C for 12 h. The g-C₃N₄ was prepared according to the literature [23]. In a typical procedure, 100 mg of melamine and 100 mg of urea were dissolved in 10 mL of water, and the mixture was refluxed for 5 h. After cooling to room temperature, the precipitate was filtered, washed with water and ethanol, and then dried in a vacuum oven at 80°C for 12 h.

The CDs/g-C₃N₄ composites were synthesized by precipitating CDs into g-C₃N₄ sheets in aqueous solution. In a typical procedure, 10 mg of CDs was dissolved in 10 mL of aqueous solution, and then 10 mL of g-C₃N₄ suspension was added. The mixture was stirred for 30 min, and then the precipitate was filtered, washed with water and ethanol, and then dried in a vacuum oven at 80°C for 12 h.

2.2. Methods

The extraction of CBs from water samples was performed according to the literature [24]. In a typical procedure, 50 mg of CDs/g-C₃N₄ composite was added to 10 mL of water sample, and the mixture was stirred for 30 min. Then, the composite was removed by filtration, and the concentration of CBs in the filtrate was determined by liquid chromatography-mass spectrometry (LC-MS). The chromatographic separation was performed on a C₁₈ column (250 mm x 4.6 mm, 5 μm) at a flow rate of 1.0 mL/min. The mobile phase consisted of methanol and water (80:20) and was monitored by an UV detector at 254 nm. The mass spectrometer was operated in the negative ionization mode, and the mass range was set from 50 to 1000 m/z.

The calibration curve was obtained by spiking different concentrations of CBs into the organic solvent and measuring the peak area of CBs. The linear regression equation was calculated by the least squares method. The extraction performance was evaluated by the extraction efficiency and the enrichment factor. The extraction efficiency was calculated as the ratio of the peak area of CBs in the sample solution to the peak area of CBs in the standard solution. The enrichment factor was calculated as the ratio of the peak area of CBs in the sample solution to the peak area of CBs in the standard solution, multiplied by the dilution factor.

The repeatability of the method was evaluated by analyzing the same water sample three times under the same experimental conditions. The relative standard deviation (RSD) was calculated as the ratio of the standard deviation to the mean value. The detection limit was calculated as the concentration corresponding to the signal-to-noise ratio of 3:1.
Haven, CT, USA). Melamine was purchased from Damao Chemical Reagent Factory (Tianjin, China). Ethanol, ethylenediamine, and citric acid were obtained from China National Pharmaceutical Group Co., Ltd. (Beijing, China). Stainless steel wire (O.D. 100 µm) was produced by Hubei Baofeng Industrial Co., Ltd. (Shenzhen, China). Sylgard184 silicone elastomer was purchased from Dow Silicons Corporation (Seneffe, Belgium). Commercial SPME coatings, including PA, DVB, and PDMS were provided by ANPEL Laboratory Technologies Inc. (Shanghai, China).

2.2. Apparatus

The microstructures of the CDs/g-C$_3$N$_4$ composites were characterized by a scanning electron microscope (SEM, SU8010, Hitachi, Tokyo, Japan) and a high-resolution transmission electron microscope (HRTEM, JEM-2100, JEOL, Tokyo, Japan). X-ray diffraction spectra (XRD, X’Pert3 Powder, PANalytical B.V., Almelo, Holland) was used to characterize the compositions of as-prepared materials. Fourier-transform infrared (FTIR) spectra were recorded by a Thermo Nicolet NEXUS spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) in the range of 4000–400 cm$^{-1}$. The surface chemical groups were detected by X-ray photoelectron spectroscopy (XPS, VG Multilab 2000 X spectrometer, Thermo Fisher Scientific, Waltham, MA, USA). The BET surface area and pore size distribution of CDs/g-C$_3$N$_4$ composites were obtained by a nitrogen adsorption/desorption apparatus (Micromeritics ASAP 2020 M, Atlanta, GA, USA). Thermogravimetric analysis was carried out on a comprehensive thermal analyzer (TG, STA449C, Netzsch, Selb, Germany). CBs were determined using a 7890B–7000D GC-MS instrument (Agilent, Santa Clara, CA, USA) equipped with a HP-5 MS fused quartz capillary column (30 m × 0.25 mm × 0.25 µm).

2.3. Synthesis of CDs/g-C$_3$N$_4$ Composites

The preparation of the CDs/g-C$_3$N$_4$ composites was carried out by simple precipitation of CDs on g-C$_3$N$_4$ in aqueous solution. The CDs were synthesized using a hydrothermal process, according to the literature, with modifications [27]. Typically, 5 g citric acid and 1.5 mL ethylenediamine were dissolved in deionized water (50 mL). Then, the solution was placed into a 100-mL Teflon-lined autoclave and heated at 180 $^\circ$C for 5 h. After cooling to room temperature, the CDs were obtained, followed by dialysis for 2 days using a dialysis membrane with a molecular weight cut-off of 3500 daltons (Viskase, Lombard, IL, USA).

The g-C$_3$N$_4$ was prepared through a facile calcination procedure in a muffle furnace according to previous reports [28]. A total of 10 g melamine powder was placed into a crucible with a cover, and then transferred to a muffle furnace for annealing for 4 h at 550 $^\circ$C with ramp rate of 5 $^\circ$C min$^{-1}$. The g-C$_3$N$_4$ was obtained after cooling down to room temperature. For the preparation of CDs/g-C$_3$N$_4$ composites, 500 mg g-C$_3$N$_4$ powder was added into a CD aqueous solution, followed by stirring thoroughly for 4 h at room temperature. Then, the CDs/g-C$_3$N$_4$ composites were observed after centrifugation, washing, and drying in a vacuum oven. The doping amounts of CDs on g-C$_3$N$_4$ were controlled by changing the CDs concentration in solution (1, 5, 10, and 20 mg mL$^{-1}$), which were denoted as CDs/g-C$_3$N$_4$-1, CDs/g-C$_3$N$_4$-2, CDs/g-C$_3$N$_4$-3, and CDs/g-C$_3$N$_4$-4, respectively.

2.4. Fabrication of SPME Fiber Based on CDs/g-C$_3$N$_4$ Composites

The fabrication of the SPME coating based on the CDs/g-C$_3$N$_4$ composites was carried out by physical adhesion with silicone glue, according to reported literatures [29–31]. In a typical procedure, a stainless-steel wire with a length of 3–4 cm was washed thoroughly by acetone, hydrochloric acid (3 mol L$^{-1}$), and deionized water, respectively. The cleaned stainless-steel wire was immersed into silicone sealant solution, which consisted of PDMS pre-polymer and a curing agent with mass ratio of 10:1. Then, the stainless-steel wire was dipped into CDs/g-C$_3$N$_4$ composites powder to form a uniform coating after curing at 120 $^\circ$C in an oven. Finally, the SPME fiber based on CDs/g-C$_3$N$_4$ composites was fabricated
by assembling stainless-steel wire with an empty SPME needle, and was aged for 20 min at 250 °C in a GC injector before the extraction procedures.

2.5. SPME Procedure and Real Samples Analysis

The SPME processes were carried out in 20-mL commercial vials containing 10 mL aqueous solution with an immersion mode. In detail, the SPME fiber was immersed into aqueous solution for extraction for 10–50 min at temperatures of 30–70 °C. After extraction, the SPME fiber was inserted into the GC-MS inlet for desorption. The operating parameters of the GC-MS are shown in Section S1 and Table S1. The real water samples, numbered 1#, 2#, and 3#, were collected from the river located in Puding County, Guizhou Province. After collection, the samples were stored in a refrigerator at 4 °C before analysis by the proposed method.

3. Results and Discussion

3.1. Characterizations of CDs/g-C3N4 Composites

The microtopography, structural compositions, chemical groups, specific surface area, and pore size distribution of materials can reveal the formation of microstructures and the active adsorption sites of composites. Therefore, various characterizations were carried out to investigate the properties of CDs/g-C3N4 composites, including SEM, TEM analysis for microtopography, XRD, FTIR, and XPS analysis for crystal structures and chemical group compositions, and N2 adsorption–desorption and pore size distribution isotherms for surface area and porosity.

The SEM and TEM were used for investigating the microtopographies of CDs/g-C3N4 composites (Figure 1). As shown in Figure 1a, as-prepared CDs/g-C3N4 composites present the irregular stacked structure composed of lamellae. TEM images (Figure 1b, c) show that as-prepared CDs display a circular structure with diameters of approximately 2 nm (Figure 1c (inset)), and the CDs are uniformly distributed on the surface of the g-C3N4 sheets without visible aggregation. The interactions of CDs and g-C3N4 can be ascribed to π-π stacking [32]. The optical microscope image (Figure 1d) shows that the uniform coating is formed on the surface of the stainless-steel wire, and the coating thickness is calculated to be approximately 35 μm.

![Figure 1](image_url)

Figure 1. SEM (a) and TEM (b, c) images of CDs/g-C3N4 composites, magnified TEM image (c (inset)) of CDs anchored on composites, and optical microscope image of as-prepared SPME fiber (d).

To investigate the crystal structures of CDs/g-C3N4 composites, XRD patterns were recorded for pristine g-C3N4 and CDs/g-C3N4-3 (Figure 2a). It can be seen that the XRD patterns display two peaks at 13.1° and 27.6°, which can be ascribed to the planes of (002) and (001), respectively, referring to g-C3N4 (JCPDS 87-1526) [33]. The stronger peak, at 27.6°, is derived from inter-planar stacking of the aromatic system, and the diffraction peak at 13.1° describes the formation of in-plane repeated tri-s-triazine units [34,35]. There is no diffraction peak recorded that corresponds to CDs, due to their low contents on the composites, and the doping of CDs does not change the crystal structure of g-C3N4.
To investigate the crystal structures of CDs/g-C_3N_4 composites, XRD patterns were recorded for pristine g-C_3N_4 and CDs/g-C_3N_4-3 (Figure 2a). It can be seen that the XRD patterns display two peaks at 13.1° and 27.6°, which can be ascribed to the planes of (100) and (002), respectively, referring to g-C_3N_4 (JCPDS 87-1526) [33]. The stronger peak, at 27.6°, is derived from inter-planar stacking of the aromatic system, and the diffraction peak at 13.1° describes the formation of in-plane repeated tri-s-triazine units [34,35].

The N 1 s spectrum (Figure 2e) is deconvoluted into four peaks at 398.6, 399.1, 400.9, and 401.4 eV, which correspond to the stretching vibration of heptazine-derived repeating units and C–N or C–NH–C groups. The peaks at 806.1 cm⁻¹, 1389.4 cm⁻¹, and 1437.1 cm⁻¹ in the FTIR spectra are similar in shape, which indicates that the decoration of CDs does not change the chemical structures of g-C_3N_4. It should be noted that the adsorption peaks are enhanced after the CD-decoration, with the result that more abundant chemical groups are formed.

XPS analysis was performed to determine the chemical composition and surface groups of CDs/g-C_3N_4 composites. As shown in the survey scan spectrum (Figure 2c), three peaks are observed at 288.3, 398.8, and 532.2 eV for CDs/g-C_3N_4, which are attributed to C 1 s, N 1 s, and O 1 s, with atom contents of 47.17%, 46.62%, and 6.21%, respectively. The high-resolution spectra of C 1 s (Figure 2d) can be deconvoluted into three peaks at 284.9, 288.1, and 288.6 eV, which are attributed to C-C, C-(NHX), and C-(N3), respectively [37]. The N 1 s spectrum (Figure 2e) is deconvoluted into four peaks at 398.6, 399.1, 400.9, and 404.8 eV corresponding to the triazine ring of nitrogen (N-(C2)), tertiary nitrogen atoms (N-(C3)), N-HX, and π-π* stacking [38]. The O 1 s spectrum (Figure 2f) can be divided into two peaks at 531.7 and 532.6 eV, which can be ascribed to the C-OH group and adsorbed O on the surface [39]. The abundant chemical groups formed on CDs/g-C_3N_4 composites can provide huge active adsorption sites for analytes.

Figure 2b exhibits the FTIR spectra of pristine g-C_3N_4 and CDs/g-C_3N_4 composites. Multiple peaks from 1200 to 1700 cm⁻¹, which formed both on g-C_3N_4 and CDs/g-C_3N_4 composites, correspond to the stretching vibration of heptazine-derived repeating units and C–N or C–NH–C groups. The peaks at 806.1 cm⁻¹ reflect the flexural vibrations of triazine units, and the wide peak that emerges at 3000–3500 cm⁻¹ is ascribed to NH2 or NH groups [33,36]. In comparison with g-C_3N_4 and CDs/g-C_3N_4 composites, the obtained FTIR spectra are similar in shape, which indicates that the decoration of CDs does not change the chemical structures of g-C_3N_4. It should be noted that the adsorption peaks are enhanced after the CD-decoration, with the result that more abundant chemical groups are formed.

The TG curve (Figure 3c) of pristine g-C_3N_4 and CDs/g-C_3N_4 composites has two steps. The first step is the release of absorbed water on the surface at temperatures below 100 °C. The second step is associated with the degradation and subsequent pyrolysis of the polymer networks, which leads to the formation of a carbonaceous residue [40].
demonstrates that as-prepared CDs/g-C$_3$N$_4$ composites have no obvious weight loss within 500 °C, indicating that the composites possess excellent thermal stability.

Figure 3. N$_2$ adsorption–desorption isotherms (a) and pore diameter distributions (b) of g-C$_3$N$_4$ and CDs/g-C$_3$N$_4$ composites, and TG curve of CDs/g-C$_3$N$_4$ (c).

3.2. SPME Performance of CDs/g-C$_3$N$_4$ Composites

The extraction performances of pristine g-C$_3$N$_4$ and CDs/g-C$_3$N$_4$ coatings with various doped-CD amounts were investigated. As shown in Figure 4a, the extraction efficiencies of CDs/g-C$_3$N$_4$ display a distinct improvement towards eight CBs, in comparison to pristine g-C$_3$N$_4$. The extraction efficiencies increase gradually with the enlarged amounts of CD-doping, and the maximum extraction capacity are achieved with CDs/g-C$_3$N$_4$-3. The further enlargement of CD amounts lead to a diminishment in extraction efficiencies, especially for 135-TCB, 124-TCB, and 123-TCB. Furthermore, the comparisons of extraction capacities for CBs with commercial SPME coatings were also studied to verify the advantages of the CDs/g-C$_3$N$_4$ coating (Figure 4b). Results show that the CDs/g-C$_3$N$_4$ coating presents superior performance, compared to the PA, PDMS, and PDMS/CAR/DVB coating. The enhancement in extraction capacities for CDs/g-C$_3$N$_4$ coating can be ascribed to the following reasons. Firstly, the adsorption of CBs on CDs/g-C$_3$N$_4$ composites mainly depends on the chemical group binding, π–π stacking, and hydrophobic interactions. Secondly, abundant nitrogen-containing and oxygen-containing groups on CDs/g-C$_3$N$_4$ are beneficial for bonding with compounds containing polar groups. The addition of CDs introduced more polar groups for composites. However, excessive CD amounts also decrease the hydrophobic interactions between analytes and materials, especially for trichlorobenzenes.

Figure 4. Extraction efficiencies of pristine g-C$_3$N$_4$ and CDs/g-C$_3$N$_4$ composites with different doping amounts of CDs (a); GC-MS chromatograms of CBs by CDs/g-C$_3$N$_4$-3 and commercial SPME coatings (b). Error bars represent the standard deviation of the mean (n = 3).

3.3. Optimization of SPME Conditions

To further improve the extraction efficiencies towards CBs, the SPME conditions, including extraction temperature, extraction time, salt contents, and pH, were optimized with spiked aqueous solutions with a concentration of 5 ng mL$^{-1}$. 

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Extraction temperature plays an important role on the extraction efficiency for SPME. In general, increased temperature can facilitate the diffusion rate of analytes, and thus, enables the extraction process to reach equilibrium in a short time. However, excessive temperature will decrease the distribution coefficient between the sample matrix and the fiber coating for analytes, which lead to a severe diminishment of the extraction. Therefore, the extraction efficiencies towards CBs for the CDs/g-C\textsubscript{3}N\textsubscript{4} coating were evaluated in the temperature range of 30–70 °C. It can be seen from Figure 5a that the extraction efficiencies towards eight CBs exhibit a trend of increasing before decreasing with elevating temperature. The maximum extraction efficiencies are observed at an extraction temperature of 50 °C.

![Figure 5](image_url)

**Figure 5.** Effect of extraction temperature (a), extraction time (b), salt concentration (c), and pH (d) on the extraction efficiencies of the CDs/g-C\textsubscript{3}N\textsubscript{4} SPME coating for CBs. Error bars represent the standard deviation of the mean (n = 3).

Enough extraction time is indispensable to achieve the optimum extraction efficiency, due to the fact that SPME is an equilibrium-based process. Herein, the effect of extraction times ranging from 10 to 50 min on the extraction efficiencies for eight CBs was investigated. As shown in Figure 5b, the extraction efficiencies towards CBs increase, following the increase of extraction time from 10 to 30 min. With further prolonged extraction time, the extraction efficiencies maintain a constant value, which indicates that the SPME process reaches equilibrium.

A certain salt concentration in aqueous solution can effectively decrease the analyte solubility, which leads to an increase of extraction efficiency for non-polar and weak polar compounds [41]. In this work, NaCl was used for adjusting the salt concentration in aqueous solution. The extraction efficiencies of as-prepared SPME coating towards eight CBs were studied in aqueous solution with NaCl contents varying from 0 to 30% (Figure 5c). Results show that the extraction efficiencies display a distinct increase with an increase of NaCl content from 0 to 20%. However, further increased NaCl content leads to a certain reduction in extraction efficiencies, which can be ascribed to excessive NaCl adhesion on the surface of the coating during the extraction process, resulting in the inhibition of active adsorption sites [29,42].

The extraction efficiencies can also be affected by solution pH due to changes in the surface charge of coating materials and analytes [43,44]. The effect of solution pH ranging from 3 to 11 on the extraction efficiencies of as-prepared SPME coatings are evaluated
herein (Figure 5d). It can be observed that the highest extraction efficiencies were obtained with solution pH of 7. Therefore, the solution pH was set to 7 for further experiments.

3.4. Method Performance

Under the optimized conditions, the parameters for method-performance evaluation, such as linearity, relative standard deviations (RSDs), limits of detection (LODs), and limits of quantitation (LOQs), are summarized in Table 1. Results show that the proposed method exhibits excellent linearity for analyzing eight CBs in a concentration range of 0.25–2500 ng L$^{-1}$, with a linear coefficient ($R^2$) of 0.9822–0.9996. The LODs and LOQs were calculated to be 0.002–0.086 ng L$^{-1}$ and 0.007–0.288 ng L$^{-1}$, according to three and ten times of signal-to-noise, respectively. Method precision was evaluated by the values of RSD. As can be seen from Table 1, the obtained RSDs for one single fiber range from 5.3 to 9.7%, and the RSDs among five SPME fibers are in the range of 7.5–12.6% towards eight CBs. Furthermore, comparisons with other methods that have been reported in the literature for the determination of CBs from water were investigated to verify the advantages of the proposed method. As shown in Table 2, the proposed method presents a higher sensitivity for the determination of CBs in water by comparing with other reported methods in terms of LODs and LOQs. Excellent linearity, high sensitivity, and good reproducibility enable the proposed method to be of great potential in real water analysis. Furthermore, the lifetime of as-prepared SPME fiber based on CDs/g-C$_3$N$_4$ composites was also evaluated in this study. It can be seen from Figure S1 that no significant loss occurred in the extraction efficiency of as-prepared SPME fiber for eight CBs after 120 repeated uses.

Table 1. Analytical performance of the CDs/g-C$_3$N$_4$ SPME coating towards CBs.

| Analytes   | Linear Ranges (ng L$^{-1}$) | $R^2$    | LODs (ng L$^{-1}$) | LOQs (ng L$^{-1}$) | One Fiber (n = 7) | Fiber-to-Fiber (n = 5) |
|------------|----------------------------|----------|--------------------|--------------------|-------------------|-----------------------|
| 135-TCB    | 0.25–2500                  | 0.9989   | 0.003              | 0.010              | 8.0               | 9.1                   |
| 124-TCB    | 0.25–2500                  | 0.9974   | 0.086              | 0.288              | 9.7               | 12.6                  |
| 123-TCB    | 0.25–2500                  | 0.9948   | 0.033              | 0.108              | 9.4               | 10.3                  |
| 1245-TeCB  | 0.25–2500                  | 0.9865   | 0.007              | 0.024              | 5.3               | 7.5                   |
| 1234-TeCB  | 0.25–2500                  | 0.9822   | 0.016              | 0.053              | 7.7               | 9.5                   |
| PeCB       | 0.25–2500                  | 0.9933   | 0.005              | 0.016              | 8.5               | 8.9                   |
| HeCB       | 0.25–2500                  | 0.9996   | 0.002              | 0.007              | 6.1               | 8.2                   |
| PeCNB      | 0.25–2500                  | 0.9945   | 0.024              | 0.083              | 7.2               | 9.8                   |

Table 2. Comparisons with other analytical methods for the determination of CBs in water.

| Methods      | Sorbents                                      | Linear Range (ng L$^{-1}$) | LODs (ng L$^{-1}$) | LOQs (ng L$^{-1}$) | References  |
|--------------|-----------------------------------------------|-----------------------------|--------------------|--------------------|-------------|
| SDME/GC-FID  | 1-Octyl-3-Methylimidazolium hexafluorophosphate | $1000–1 \times 10^7$        | 100–500            | –                  | [45]        |
| SDME/GC-MS   | Toluene                                       | 500–50,000                  | 10–50              | 40–440             | [46]        |
| HSSE/GC-MS   | PDMS coated stir bar                          | 10–200                      | 0.4–1.4            | 1.4–4.7            | [47]        |
| SPME/GC-ECD  | Nanoporous carbon                             | 2.5–100                     | 0.10–1.03          | –                  | [48]        |
| HS-SPME/GC-MS| Nano-structured ZnO                           | 0.05–1000                   | 0.01–0.1           | –                  | [49]        |
| SPME/GC-ECD  | Nitrogen/Porous biochar                       | 1–1000                      | 0.007–0.079        | 0.023–0.261        | [50]        |
| SPME/GC-MS   | CDs/g-C$_3$N$_4$                              | 0.25–2500                   | 0.002–0.086        | 0.007–0.288        | This work   |

3.5. Real Water Samples Analysis

The proposed method was finally used to determine CBs from real water samples (1#, 2#, 3#), which were collected from the river located in Puding County, Guizhou Province.
The analysis results for the three collected water samples are listed in Table 3. It was found that no CBs were detected in the sample 1#, however, 135-TCB and 123-TCB were detected in samples 2# and 3#, which were collected from a location that is near to a port. Recoveries were obtained, ranging from 73.4 to 109.1%, for eight CBs from water samples with spiked concentrations of 10 ng L\(^{-1}\). Satisfactory recoveries illustrate the applicability of the proposed method for the analysis of trace CBs in real water samples.

### Table 3. Analytical results and recoveries for the determination of CBs in real water samples.

| Analytes       | 135-TCB | 124-TCB | 123-TCB | 1245-TeCB | 1234-TeCB | PeCB   | HeCB   | PeCNB  |
|----------------|---------|---------|---------|-----------|-----------|--------|--------|--------|
| Found (ng L\(^{-1}\)) | ND      | ND      | 1.7     | ND        | ND        | ND     | ND     | ND     |
| RSDs (%, \(n = 3\)) | -       | -       | 0.8     | -         | -         | -      | -      | -      |
| Recoveries (% spiked with 1 ng L\(^{-1}\)) | 105.1   | 75.5    | 88.8    | 94.5      | 93.8      | 80.3   | 101.1  | 83.4   |
| Found (ng L\(^{-1}\)) | 154.0   | ND      | 11.7    | ND        | ND        | ND     | 57.6   | ND     |
| RSDs (%, \(n = 3\)) | 11.4    | -       | 13.9    | -         | -         | -      | 20.6   | -      |
| Recoveries (% spiked with 10 ng L\(^{-1}\)) | 108.5   | 105.5   | 109.1   | 84.4      | 84.2      | 122.3  | 93.5   | 75.5   |
| Found (ng L\(^{-1}\)) | 60.4    | ND      | 6.4     | ND        | ND        | ND     | ND     | ND     |
| RSDs (%, \(n = 3\)) | 9.9     | -       | 24.6    | -         | -         | -      | -      | -      |
| Recoveries (% spiked with 10 ng L\(^{-1}\)) | 90.8    | 81.9    | 83.4    | 83.1      | 73.4      | 76.8   | 81.2   | 81.8   |

### 4. Conclusions

In conclusion, CDs/g-C\(_3\)N\(_4\) composites were synthesized and innovatively applied as SPME coatings for the sensitive determination of eight CBs from water coupled to GC-MS. The doping of CDs improved the extraction efficiency, owing to their abundant chemical groups, and enabled CDs/g-C\(_3\)N\(_4\) composites exhibit superior extraction efficiency in comparison to commercial coatings. The proposed method presented extremely low LODs, ranging from 0.002 to 0.086 ng L\(^{-1}\) for CBs, which is better than the methods reported in the literature. Finally, the proposed method was used for the analysis of real river waters successfully. Outstanding properties, such as high sensitivity and excellent reproducibility, gives the proposed method great potential for the analysis of trace pollutants from aqueous samples.

### Supplementary Materials

The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12030335/s1, Section S1: Operating parameters of GC-MS; Table S1: Retention time and characteristic ions of eight CBs; Table S2: BET and BJH results of as-prepared materials; Figure S1: Reusability of as-prepared SPME fiber.

### Author Contributions

S.X.: conceptualization, methodology, and writing—original draft preparation; H.L. (Hailin Liu): investigation and validation; A.L.: resources; H.L. (Huilmin Li): formal analysis; C.C.: writing—review and editing; S.F.: supervision; J.F.: project administration. All authors have read and agreed to the published version of the manuscript.

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### Institutional Review Board Statement

Not applicable.

### Informed Consent Statement

Not applicable.

### Data Availability Statement

This study presents novel concepts and did not report any data.
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