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RESEARCH PAPER

Monomer-mediated growth of β-cyclodextrin-based microporous organic network as stationary phase for capillary electrochromatography

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Abstract

CD-MONs (β-cyclodextrin-based microporous organic networks), derived from β-cyclodextrin, possess notable hydrophobic characteristics, a considerable specific surface area, and remarkable stability, rendering them highly advantageous in separation science. This research aimed to investigate the utility of CD-MONs in chromatography separation. Through a monomer-mediated technique, we fabricated an innovative CD-MON modified capillary column for application in open-tubular capillary electrochromatography (OT-CEC). The CD-MON-based stationary phase on the capillary's inner surface was analyzed using Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). We assessed the performance of the CD-MON modified capillary column for separation purposes. The microstructure and pronounced hydrophobicity of CD-MON contributed to enhanced selectivity and resolution in separating diverse hydrophobic analytes, such as alkylbenzenes, halogenated benzenes, parabens, and polycyclic aromatic hydrocarbons (PAHs). The maximum column efficiency achieved was 1.5×10^5 N/m. Additionally, the CD-MON modified capillary column demonstrated notably high column capacity, with a methylbenzene mass loading capacity of up to 197.9 pmol, surpassing that of previously reported porous-material-based capillaries. Furthermore, this self-constructed column was effectively utilized for PAHs determination in actual environmental water samples, exhibiting spiked recoveries ranging from 93.2 to 107.9% in lake water samples. These findings underscore the potential of CD-MON as an effective stationary phase in separation science.

Keywords β-Cyclodextrin · Microporous organic networks · Capillary electrochromatography · Stationary phase · Monomer-mediated approach

Introduction

Chromatographic methods have attracted considerable interest in the food and biopharmaceutical sectors because of their exceptional separation capabilities, reproducibility, and precise qualitative and quantitative analysis capabilities [1–4]. Capillary electrochromatography (CEC) represents a cost-effective microcolumn separation technique that merges the high separation efficiency of capillary electrophoresis (CE) with the superior selectivity of high-performance liquid chromatography (HPLC) [5, 6]. Among the various CEC column formats, open-tubular CEC (OT-CEC) stands out for its advantageous features, including simple column preparation, surface modification ease, excellent permeability, and straightforward instrument operation [7]. Nevertheless, the limitations of relatively low phase ratio and column capacity impede the practical application of OT-CEC in real sample analysis [8]. Consequently, the continuous pursuit of developing new stationary phases to boost separation efficiency and capacity remains a critical area of interest in advancing OT-CEC. To address the evolving requirements of OT-CEC, a plethora of innovative stationary phases based on diverse materials have been suggested and synthesized, such as covalent organic frameworks (COFs) [9–13], metal–organic frameworks (MOFs) [14–18], materials derived from carbon dots [19], and porous organic cages (POCs) [20–22].

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Conjugated microporous polymers known as microporous organic networks (MONs) represent a distinctive category of polymers formed through the Sonogashira reaction, coupling rigid alkyne and arylhalide monomers [23–25]. With adjustable pore structures, high surface areas, and exceptional stability, MONs exhibit versatility for various applications such as adsorption, chromatographic separation, sample pretreatment, sensing, and catalysis [26–30]. β-Cyclodextrin (β-CD), a natural host molecule composed of seven D-glucopyranoside units, possesses a hydrophilic exterior and a hydrophobic inner cavity. β-CD could provide numerous recognition sites for host–guest interactions, which are particularly beneficial in separation science [31]. Leveraging its host–guest recognition capabilities, β-CD can selectively identify specific small molecules, enhancing its appeal in separation applications [32, 33]. In a recent study, a multifunctional microporous organic network of β-cyclodextrin (CD-MON) was synthesized and developed for wastewater treatment [34]. This CD-MON structure encompasses micro- and mesopores, facilitating diverse interactions like π-π interactions, hydrophobic bonding, hydrogen bonding, and inclusion mechanisms with target analytes, underscoring its significant potential in separation science. Hence, there is a pressing need to investigate the utilization of CD-MON-based stationary phases in chromatography to advance the field of CD-MON, an area that, to our knowledge, lacks prior exploration.

A novel microporous organic network (CD-MON) featuring a dual micro- and mesoporous structure, exceptional stability, and pronounced hydrophobicity was synthesized by combining 1,4-diethynylbenzene (DEB) and heptakis(6-iodo-6-deoxy)-cyclodextrin (I-β-CD). Subsequently, this CD-MON was employed as the stationary phase in capillary electrochromatography (CEC) separation using a straightforward monomer-mediated technique. The inclusion of β-CD in the structure of MONs significantly increases the number of interaction sites available (including host–guest interactions and hydrogen-bond interactions). In addition, the coupling units of alkynyl benzene rings offer favorable hydrophobic and π-π interactions. To demonstrate its efficacy, a capillary column coated with CD-MON was utilized as the separation medium for OT-CEC analysis of alkylbenzenes, halogenobenzenes, parabens, and polycyclic aromatic hydrocarbons (PAHs). The modified capillary column with CD-MON exhibited exceptional separation efficiency and selectivity for the target analytes. Additionally, this CD-MON modified capillary column was successfully utilized for the detection and separation of PAHs in authentic environmental water samples. This research not only introduces a novel method for preparing stationary phases based on CD-MON but also contributes significantly to the progress of CD-MON within the realm of chromatographic separation.

Experimental

Materials and reagents

Methanol (MeOH) and acetonitrile (ACN) for chromatography were procured from Merck in Germany. Various compounds such as methylbenzene, ethylbenzene, propylbenzene, butylbenzene, methylparaben, ethylparaben, propylparaben, chlorobenzene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, 3-aminopropyltriethoxysilane (APTES), copper(I) iodide (CuI), bis(triphenylphosphine) palladium dichloride ($Pd(PPh_3)_2Cl_2$), (3-iodopropyl)trimethoxysilane (IPTMS), 1,4-diethynylbenzene (DEB), and glutaraldehyde solution were sourced from Aladdin, a company based in Shanghai, China. Heptakis(6-iodo-6-deoxy)-β-cyclodextrin (I-β-CD) was obtained from Zhiyuan Biotechnology Co., Ltd. in Shandong, China. Naphthalene, fluoranthene, and phenanthrene were purchased from Sigma-Aldrich located in MO, USA. Essential chemicals like sodium hydroxide (NaOH), triethylamine, hydrochloric acid (HCl), thiourea, sodium phosphate dibasic dodecahydrate ($Na_2HPO_4{\cdot}12H_2O$), N,N-dimethyl-formamide (DMF), and phosphoric acid (H_3PO_4) were acquired from Sinopharm Group Chemical Reagent Co., Ltd. based in Shanghai, China. Fused-silica capillary columns (50 μm i.d. × 365 μm o.d.) without any treatment were supplied by Ruifeng Chromatographic Devices located in Hebei, China.

Instrumentation

The solutions were delivered into the capillary columns using a mechanical syringe pump sourced from Shenchen Precision Pump Company in Baoding, China. CEC experiments were conducted utilizing a Beckman Coulter CE system (P/ACE MDQ). The pH levels of the running buffer were monitored using a Mettler Toledo FE28-CN pH meter from Shanghai, China. SEM images of the capillary columns were captured using a Zeiss Sigma 300 microscope from Oberkochen, Germany. Pure water was obtained through a CANSHI CM-RO-C2 ultrapure water system located in Ningbo, China. Fourier transform infrared (FT-IR) spectra were recorded using a Thermo NICOLET iS 10 FT-IR spectrometer based in Waltham, MA, USA.

Fabrication of standard and sample solutions

All solutions containing alkylbenzenes, chlorobenzenes, parabens, and PAHs were prepared in methanol (MeOH) at a concentration of 3.0 mg/mL. Phosphate buffers at a concentration of 10 mM were prepared by dissolving $Na_2HPO_4{\cdot}12H_2O$ in ultrapure water. The pH values of the

phosphate buffer were adjusted within the range of 5.0 to 9.0 using either phosphoric acid or sodium hydroxide (NaOH). Mobile phases were created by mixing ACN with the phosphate buffer in specific proportions. The sample solutions for injection were prepared by combining standard solutions with running buffer. Both the prepared sample and standard solutions were refrigerated at 4 ℃ prior to usage.

Fabrication of CD-MON modified capillary column

The process of fabricating the CD-MON modified capillary column is depicted in Fig. 1. Initially, the untreated fused-silica capillary columns underwent a series of rinsing steps: exposure to 1.0 M NaOH for 1 h, followed by rinsing with ultrapure water for 30 min, treatment with 1.0 M HCl for 1 h, another rinse with ultrapure water for 30 min, and finally a rinse with MeOH for 30 min, in sequence. Subsequently, the capillary column was dried using a nitrogen stream for 1 h. Next, the pretreated capillary column was filled with a solution of IPTMS/DMF (1%, v/v). The column ends were sealed, and it was immersed in a water bath at 60 ℃ for 12 h. After this, the capillary column underwent thorough flushing with methanol for 1 h followed by drying with a nitrogen stream for another hour. The column was then modified using (3-iodopropyl)trimethoxysilane to introduce iodine sites for the coupling with alkynyl monomers. The CD-MON synthesis solution was prepared based on a previous study with modifications [34]. Specifically, I-β-CD (9.52 mg), DEB (3.31 mg), $Pd(PPh_3)_2Cl_2$ (1.05 mg), and CuI (0.32 mg) were combined in 1 mL of triethylamine/DMF (1/1, v/v) solution. The mixture was sonicated and subsequently injected into the iodine-modified capillary column as described above. After sealing both ends of the capillary, it was placed in an 80 °C water bath for 24 h. Following the reaction, the capillary column was flushed with MeOH for 1 h. Finally, the prepared column was dried using a nitrogen stream to obtain the CD-MON modified capillary column.

Formulas

The calculated formulas are shown in Supporting information.

Sample preparation

Individual PAHs, namely naphthalene, fluoranthene, and phenanthrene, were dissolved in methanol to prepare the sample solutions. Prior to usage, the samples were further diluted to a specific concentration using a 10 mM phosphate buffer solution. The actual sample used in the study was collected from Qingshan Lake in Nanchang, China. To eliminate larger particulate impurities, the lake water sample underwent three rounds of centrifugation at 10,000 r/min, and the resulting supernatant was retained. Subsequently, the supernatant was subjected to filtration using a 0.22-μm nylon membrane, repeated three times. Finally, the prepared PAH sample solutions were added to the treated lake water sample for subsequent analysis.

Results and discussion

Characterization of the CD-MON modified capillary column

To confirm the successful modification of CD-MON within the capillary's inner surface, a scanning electron microscopy (SEM) experiment was conducted. The SEM image of

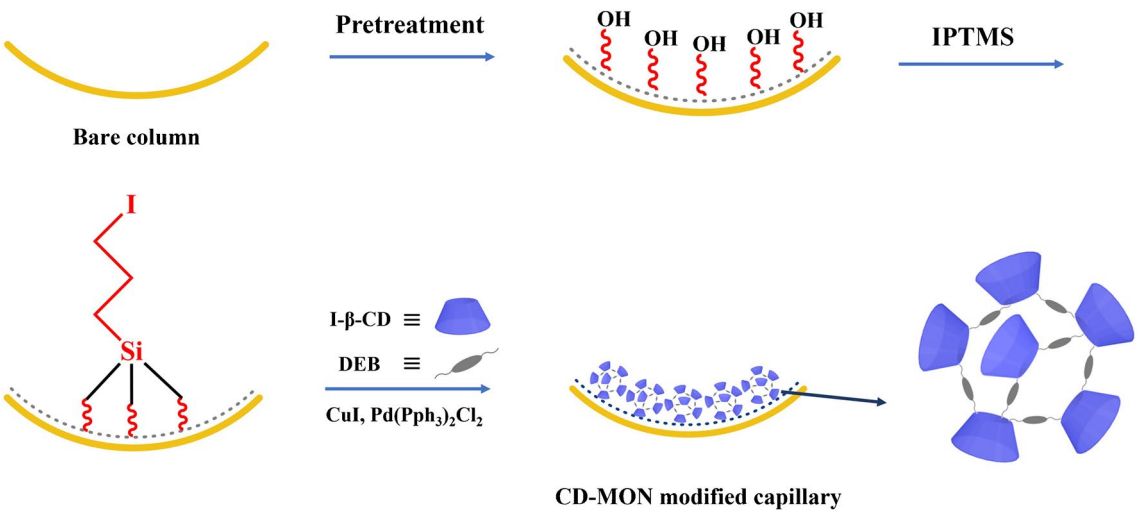

Fig. 1 Schematic procedure for the preparation of the CD-MON modified capillary column via the monomer-mediated method

the synthesized CD-MON exhibited a sheet-like structure, consistent with previous findings (Fig. S1) [34]. Figure 2A displays the SEM images of the inner wall of both the fabricated capillary column and the bare column. The bare column's inner surface was observed to be remarkably smooth. Conversely, the CD-MON modified capillary column exhibited a noticeable morphological change, as evidenced by the presence of a dense and uniform CD-MON coating layer. Further characterization was carried out using Fourier transform infrared (FT-IR) spectroscopy on the as-synthesized CD-MON, CD-MON modified capillary column, and bare column. The FT-IR spectrum of the as-synthesized CD-MON (Fig. S2) demonstrated absorption peaks consistent with previous reports [34]. Notably, the CD-MON modified column displayed a distinctive peak at 826 cm^{-1}, attributed to the bending vibration of =C-H in the CD-MON (Fig. S3). These characterization outcomes provide substantial evidence supporting the successful modification of CD-MON within the capillary column's inner wall.

Electroosmotic flow test experiment

In capillary electrochromatography (CEC) experiments, electroosmotic flow (EOF) plays a vital role in driving analytes and the mobile phase through the column. Figure S4 illustrates the experimental outcomes. On the CD-MON modified column, an anodic EOF mobility was observed, which increased gradually as the pH value ranged from 5 to 9. This occurrence was primarily due to the improved dissociation exposed silanol groups on the capillary's inner wall.

Retention behavior

Prior research has established that CD-MON has strong hydrophobic interactions and π-π interactions with target analytes [34]. Therefore, it is probable that the CD-MON stationary phase will exhibit conventional reversed-phase retention behavior. To verify this, the retention behavior of the CD-MON modified column was evaluated. The elution order of the alkylbenzenes examined corresponded to their *log P* values for oil–water partitioning. Additionally, the retention factors (*k*) of the four analytes increased as the acetonitrile concentration decreased from 50 to 30% (Fig. S5). Elution capacity was observed to improve as the acetonitrile ratio increased, thus supporting the conventional reversed-phase retention behavior of the CD-MON modified column.

Mass loading ability

The adoption of OT-CEC may be limited by a relatively low phase ratio and column capacity, as mentioned earlier. Hence, the column loading capacity is a critical parameter for evaluating the newly prepared OT-CEC capillary column. The capacity is determined by analyzing the impact of sample loading on the column efficiency. To verify the loading capacity of the CD-MON modified capillary column, methylbenzene was injected sequentially into the prepared capillary at varying concentrations (0.15 to 0.90 mg/mL). The half-height peak widths ($W_{1/2}$) of the analytes are plotted in Fig. S6. Employing the method detailed in previous studies [9], the maximum column capacity of the CD-MON modified capillary column was calculated to be 197.9 pmol.

OT-CEC separation performance

The CD-MON modified column's OT-CEC separation capacity was assessed. Initially, four alkylbenzenes (methylbenzene, ethylbenzene, n-propylbenzene, n-butylbenzene) and three halo-benzenes (chlorobenzene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene) were employed to validate the separation efficiency. The results are shown in Fig. 3A and B. Optimal CEC separation conditions resulted in baseline separation of the tested compounds on the CD-MON modified capillary, with excellent column efficiency and peak

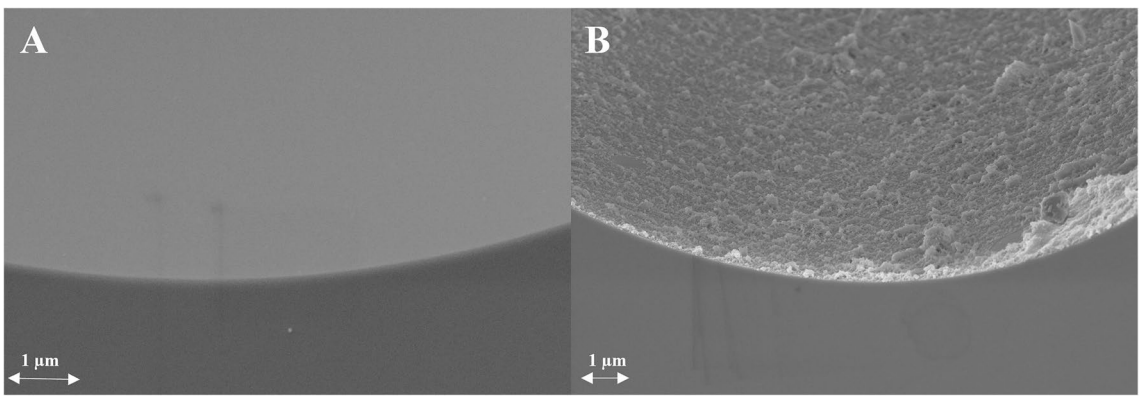

Fig. 2 SEM images of inner surfaces of bare capillary (**A**, 10,000×) and CD-MON modified column (**B**, 5000×)

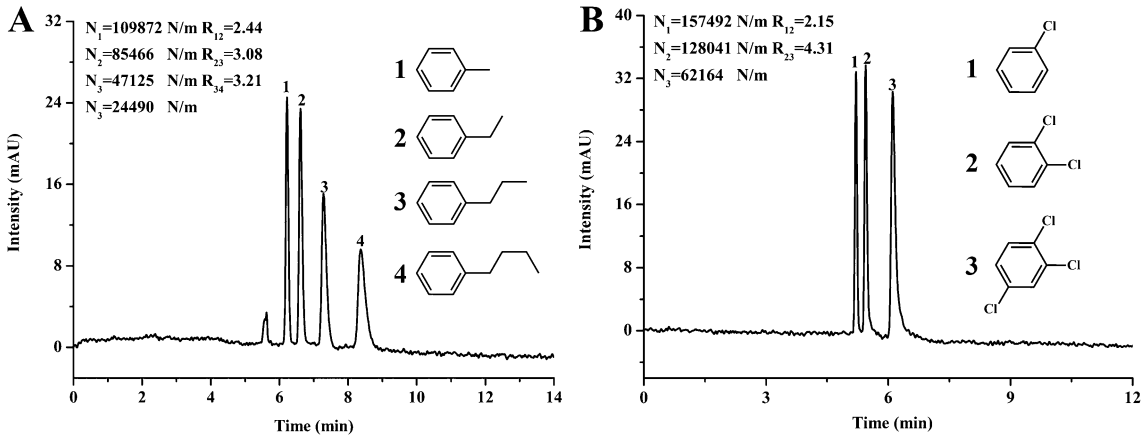

Fig. 3 **A** Separation behavior of alkylbenzenes on the CD-MON modified column. Experimental conditions: mobile phase, 50% ACN in pH 9.0 10 mM phosphate buffer; applied voltage, 20 kV; injection, 15 mbar×5 s; detection wavelength, 214 nm. Peaks: 1, methylbenzene; 2, ethylbenzene; 3, n-propylbenzene; 4, n-butylbenzene. **B** Separation behavior of chlorobenzenes on the CD-MON modified column. Experimental conditions: mobile phase, 50% ACN in pH 9.0 10 mM phosphate buffer; applied voltage, 20 kV; injection, 10 mbar×5 s; detection wavelength, 214 nm. Peaks: 1, chlorobenzene; 2, 1,2-dichlorobenzene; 3, 1,2,4-trichlorobenzene

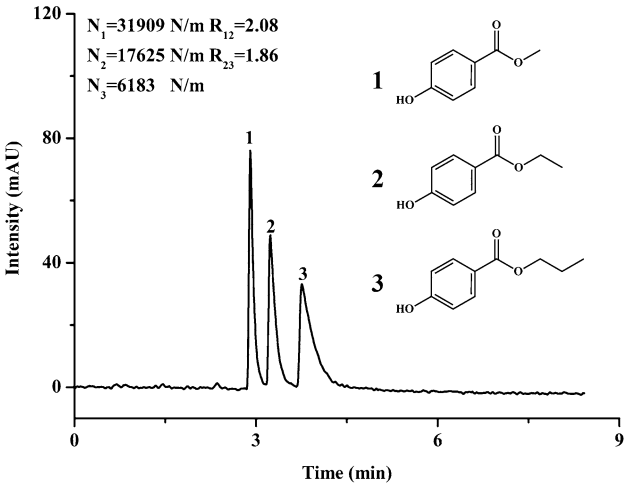

Fig. 4 Separation behavior of parabens on the CD-MON modified column. Experimental conditions: mobile phase, 30% ACN in pH 8.0 10 mM phosphate buffer; applied voltage, 21 kV; injection, 10 mbar×5 s; detection wavelength, 210 nm. Peaks: 1, methylparaben; 2, ethylparaben; 3, propylparaben

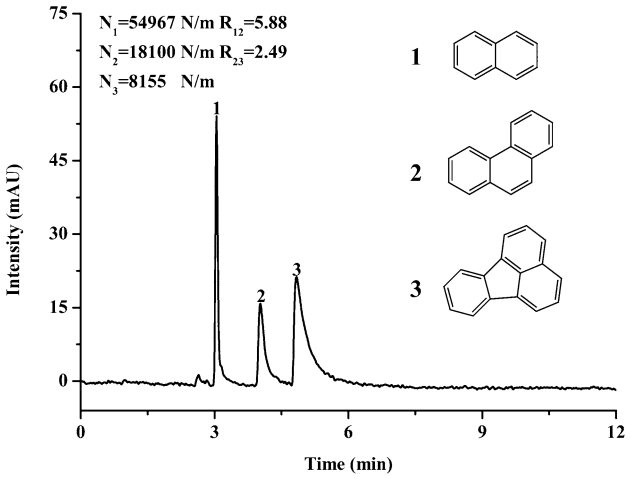

Fig. 5 Separation behavior of PAHs on the CD-MON modified column. Experimental conditions: mobile phase, 50% ACN in pH 9.0 10 mM phosphate buffer; applied voltage, 21 kV; injection, 50 mbar×5 s; detection wavelength, 210 nm. Peaks: 1, naphthalene; 2, phenanthrene; 3, fluoranthene

shape. Chlorobenzene and methylbenzene exhibited column efficiencies greater than 150,000 plates/m and 100,000 plates/m, respectively. The elution order corresponded to *log P* values, with the separation of these neutral analytes by the CD-MON modified column primarily relying on hydrophobic interaction with the CD-MON stationary phase. Furthermore, the CEC separation of three parabens (methylparaben, ethylparaben, and propylparaben) was conducted, yielding an excellent resolution of the three analytes on the CD-MON modified column (Fig. 4). Additionally, the self-made CEC column was utilized to separate three polycyclic aromatic hydrocarbons, including naphthalene, phenanthrene, and fluoranthene, resulting in good separation performance (Fig. 5). The elution order was related to the PAH molecular structures. The peak sequences of three PAHs were consistent with the increase of the number of aromatic benzene rings. Namely, the hydrophobic interactions and π-π interactions possessed a significant role in the separation selectivity for PAHs.

The outstanding separation capability of the CD-MON modified column for the compounds under investigation can be attributed to the following factors. First is the stationary phase of CD-MON with abundant micro- and mesoporous

structures, which offer a multitude of interaction sites that enhance the mass transfer of analytes and improve resolution. Secondly, the CD-MON-based stationary phase, rich in benzene rings, facilitates robust hydrophobic interactions and π-π interactions with the analytes being tested. Additionally, β-CD could form stable inclusion complex with analyte molecules, and confirmed the host–guest inclusion mechanism might be the other main driving force for analyte separation. The obtained separation outcomes affirm the CD-MON modified column's prospective utility in chromatographic separation of hydrophobic analytes.

Reproducibility and stability

Table 1 presents the RSD values for the retention times of methylbenzene, ethylbenzene, n-propylbenzene, and n-butylbenzene, which were used to assess the reproducibility and stability of the custom-made OT-CEC column. The RSD values for intra-day ($n=3$), inter-day ($n=3$), and across three parallel columns exhibited a range of 0.94 to 4.99%. Additionally, the prepared CD-MON modified capillary exhibited remarkable resolution for methylbenzene, ethylbenzene, n-propylbenzene, and n-butylbenzene even after 90 consecutive injections. Figure S7 visually demonstrates the consistent retention time peak shapes of the four alkylbenzenes. These results affirm the high stability and reproducibility of the custom-made OT-CEC column when operated under CEC conditions.

Real sample analysis

PAHs, which primarily result from incomplete combustion of anthropogenic or natural energy sources, are recognized as global priority pollutants due to their mutagenic and carcinogenic properties, posing significant public health concerns. Therefore, it is crucial to develop a cost-effective and straightforward analytical method to quantify PAH concentrations in environmental samples. In this investigation, we successfully employed a custom-made CD-MON modified column for the determination of PAH concentrations in lake water samples. The detailed sample preparation procedure can be found in the "Sample preparation" Section, while the corresponding results are presented in Table 2. The linear ranges for naphthalene, phenanthrene, and fluoranthene were 5–125 μg/mL. The limits of detection (LODs) for naphthalene, phenanthrene, and fluoranthene were 0.250 μg/mL, 0.290 μg/mL, and 0.058 μg/mL, respectively. The limits of quantification (LOQs) for naphthalene, phenanthrene, and fluoranthene were 0.862 μg/mL, 0.967 μg/mL, and 0.200 μg/mL, respectively. To validate the accuracy of the proposed method, lake water samples were spiked with low, medium, and high concentrations of the three PAHs and analyzed using the developed approach. The corresponding spiked recoveries are provided in Table S1, demonstrating recoveries ranging from 99.7 to 103.6% for naphthalene, 99.5 to 107.9% for phenanthrene, and 93.2 to 104.3% for fluoranthene. The relative standard deviations (RSDs) of the recovery ranged from 0.63 to 6.24%. These findings confirm the applicability of the suggested approach to effectively separate and quantify PAHs in complex water environments.

Table 1 Repeatability of the CD-MON modified capillary column

Analytes	Retention time (RSDs%)		
	Intra-day ($n=3$)	Inter-day ($n=3$)	Column-to-column ($n=3$)
Methylbenzene	1.05	4.87	4.99
Ethylbenzene	1.02	4.69	4.86
n-Propylbenzene	1.05	4.44	4.42
n-Butylbenzene	0.94	4.11	4.18

Comparison with other material-based OT-CEC columns

To date, extensive research has been conducted on porous polymers, COFs, and MOFs-based stationary phases for OT-CEC separations. In order to evaluate the performance of the CD-MON modified column, a comparison was made with previously proposed OT-CEC columns in terms of analytes, column efficiency, loading capacity, and LODs. The corresponding results can be found in Table S2. The CD-MON modified column exhibited a column efficiency that was comparable to that of the previously reported columns. However, in terms of loading capacity, the prepared column surpassed all other materials-based OT-CEC columns. In addition, the analytical advantages for PAHs using this novel column were compared with other columns. As shown in Table S3, compared with other reported columns, the CD-MON modified column offered better column efficiency for retained PAHs. Moreover, the prepared column was successfully used for the

Table 2 The linear equation, correlation coefficient (R^2), limit of detection, and limit of quantitation of naphthalene, phenanthrene, and fluoranthene

Analytes	Linearity (μg/mL)	Linear equation	R^2	LODs (μg/mL)	LOQs (μg/mL)
Naphthalene	5–125	Y = 2.6219X-0.1531	0.9985	0.259	0.862
Phenanthrene	5–125	Y = 4.8397X + 353.06	0.9903	0.290	0.967
Fluoranthene	5–125	Y = 27.862X + 57.582	0.9921	0.058	0.200

determination of PAH concentrations in actual samples. Wide linear range, low LODs, and good repeatability were obtained according to this method. The monomer-mediated method proposed in this study simplified the preparation processes of CD-MON-based stationary phases while maintaining their effectiveness. These unique properties indicate the reliable applicability of the self-made CD-MON modified column in chromatography separation, thus advancing the field.

Conclusion

In this investigation, we proposed a novel stationary phase utilizing CD-MON for OT-CEC separation, prepared through a monomer-mediated method. The successful growth of CD-MON on the inner capillary wall was confirmed by SEM and FT-IR characterization results. This uniform CD-MON stationary phase demonstrated exceptional super hydrophobicity, a large specific surface area, and high stability, leading to a significantly increased loading capacity compared to other materials-based OT-CEC columns. Furthermore, the developed column was capable of effectively detecting and separating PAHs in water environments. The self-prepared OT column displayed satisfactory repeatability and stability, and low LODs. These results highlight the substantial potential of CD-MON-based stationary phases in the realm of chromatography separation science.

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Author contribution Zhengzheng Liao: investigation, methodology, funding acquisition, writing—original draft. Jinfang Hu: supervision, validation, writing—review and editing. Zhentao Li: conceptualization, methodology, funding acquisition, project administration, data curation, writing—review and editing.

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Declarations

Conflict of interest The authors declare no competing interests.

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