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Hydrothermal carbon nanosphere-based agglomerated anion exchanger for ion chromatography

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ABSTRACT

This work reports the application of hydrothermal carbon nanospheres (HCNSs) as stationary phases in ion chromatography. HCNSs were facilely quaternized through polycondensation of methylamine and 1,4-butanediol diglycidyl ether. The quaternization was confirmed by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. Owing to the electrostatic interaction, quaternized HCNSs were equably attached onto the surface of sulfonated polystyrene-divinylbenzene (PS-DVB) beads to construct the anion exchangers. The aggregation was verified by scanning electron microscopy and elemental analysis. Common anions, aliphatic monocarboxylic acids, polarizable anions, and aromatic acids were well separated on the stationary phases with good stability and symmetry. The prepared column was further applied to detect phosphate content in Cola drink samples. The limit of detection ($S/N=3$) was 0.09 mg/L, and the relative standard deviation ($n=10$) of retention time was 0.31%. The average recovery was 99.58%.

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1. Introduction

Ion chromatography (IC) has become a popular chromatographic technique for the analysis of inorganic and organic ions [1,2] in water quality control procedures [3,4], food analysis [5], and pharmaceutical industry [6]. The key component of IC is the stationary phase; therefore, it has received much attention [7–9]. Silica is an attractive material for IC stationary phases because of its good mechanical strength, high purity, and convenience for covalent functionalization [10–12]. However, the silica-based anion exchangers could only be operated at pH 2.0–8.0, whereas the determination in IC was commonly carried out with the strongly acidic or basic mobile phases. Thus, owing to their high stability under extreme pH conditions, organic polymers, such as polystyrene-divinylbenzene (PS-DVB) [13,14] and polymethacrylate resins [15], were mostly applied in commercial ion chromatographic columns.

Latex-based agglomerated stationary phases comprise a sulfonated polymeric microspheres and a coated layer of quaternized polymer nanoparticles (latex) [1,16,17]. Such core/shell structure with a small thickness of the functional layer provides many

advantages, including high chemical stability under various pH levels (0–14) and the fast ion-exchange process [18,19]. Our group first introduced multiwalled carbon nanotubes as an agglomerated material for stationary phases of IC; the material showed good separation of inorganic anions with high column efficiency [20,21]. However, raw carbon nanotubes have strong chemical inertia because of their highly graphitized surfaces and excess strong oxidants such as concentrated nitric acid. In addition, sulfuric acid is always used to start the functionalization, which is tedious and harmful to the environment. Furthermore, the hydrophobicity of carbon nanotubes could also have an adverse effect on the chromatographic peak shapes of anions. Recently, the hydrothermal carbonization (HTC) of biomass to produce carbon materials (CMs) has received extensive attention because of its sustainability, convenience, and affordability [22,23]. The resulting CM surface possesses rich hydrophilic groups, such as hydroxyl and carboxyl [24,25], which greatly facilitate further functionalization [26]. The HTC-derived CMs have been widely applied in various fields such as catalysis [27], lithium-ion battery, [28,29] and adsorbents [30,31]. However, the potential of HTC-derived CMs in chromatographic stationary phases is rarely studied. Hydrothermal carbon-functionalized monolithic silica was prepared using silica monolith as framework in combination with HTC, and then applied as stationary phases in high-performance liquid chromatography

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[32]. To the best of our knowledge, the application of hydrothermal CMs into anion exchangers for IC has not been reported.

In this work, a novel anion exchanger agglomerated with quaternized hydrothermal carbon nanospheres (Q-HCNSs) was facilely produced for IC. Hydrothermal carbon nanospheres (HCNSs) were modified with polyelectrolytes that have quaternary ammonium groups in water under mild conditions. Owing to the electrostatic interaction, Q-HCNSs were stably attached onto the surface of sulfonated PS-DVB substrates to form the stationary phase. Thus, the Q-HCNSs were applied for detecting various anions.

2. Experimental

2.1. Instruments

Fourier transform infrared (FTIR) spectroscopy was performed with a Bruker Vector 22 spectrometer (Bruker, Germany). Elemental analysis was conducted on a Flash EA 1112 elemental analyzer (Thermo Fisher Scientific, USA). Scanning electron microscopy (SEM) images were obtained using a HITACHI S-4700 field-emission scanning electron microscope (Hitachi, Japan). X-ray photoelectron spectroscopy (XPS) was employed with an ESCALAB 250Xi instrument using a magnesium anode (Mg 1253.6 eV) X-ray source. The column was packed through a QP 6000 packing pump (Chuang Xin Tong Heng Science and Technology Co., Ltd., Beijing, China). A water purification system (Millipore, Milford, MA, USA) was used to collect deionized water for all eluents.

All chromatographic analysis were conducted by a Thermo Fisher Scientific analyzer (Waltham, MA, USA) ICS 2000, including a dual-piston serial pump, a DS6 conductivity detector, an ASRS-4 mm suppressor, a column heater, six-port valve fitted with a 25 μ L sampling loop, and an EGC-KOH eluent generator. Data were treated with Chromeleon 6.8 chromatogram workstation (Thermo Fisher Scientific). The column capacities were detected through ultimate UV340 detector (Thermo Fisher Scientific), with an eluent of 0.02 mol/L NO_3^- at 1.0 mL/min.

2.2. Reagents

Glucose, acetic acid, and dichloromethane were of analytical reagent grade and purchased at Huipu Chemical Reagent Co., Ltd. (Hangzhou, China). PS-DVB microspheres were produced according to our previous work [14]. Methylamine (MA, 40% in H_2O , v/v) and 1,4-butanediol diglycidyl ether (BDDE, 60% in H_2O , v/v) were obtained from Aladdin Chemical Co., Ltd. (Shanghai, China). Concentrated sulfuric acids were provided by Huipu Chemical Reagent Co., Ltd. (Hangzhou, China). The Cola drink sample was brought from a Wal-Mart store.

2.3. Synthesis of Q-HCNSs

2.3.1. The production of HCNSs

Monodisperse carbon nanospheres (CNSs) were produced according to previous literatures [33]. In a typical procedure, 4 g of glucose was dissolved in 50 mL of deionized water through a magnetic stirrer. Then, the solution was transferred into a Teflon-lined autoclave, sealed, and treated at 190 °C for 2 h. The obtained carbonaceous materials were washed with water and ethanol and dried in the oven.

2.3.2. The quaternization of HCNSs

The HCNSs were functionalized with quaternary ammonium groups inspired by previous report [13]. A total of 60 mL solution of MA (5%, v/v) and BDDE (7.5%, v/v) was added to 0.6 g of HCNSs with magnetic stirring and heated at 60 °C for 1 h. Then, the obtained solid was added into 60 mL of MA (4%, v/v) and heated at 60 °C for

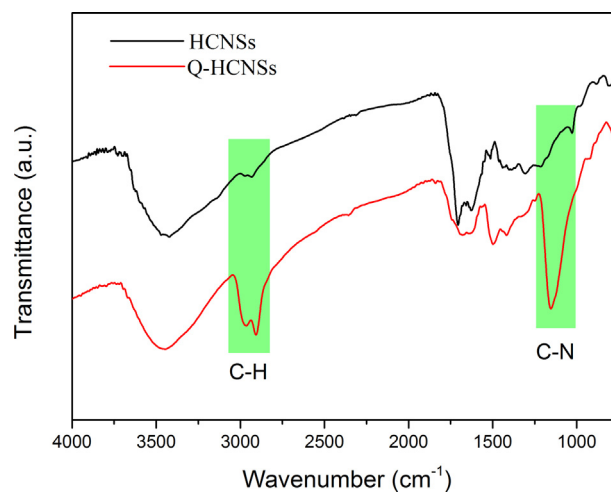


Fig. 1. The FTIR spectrum of HCNSs and Q-HCNSs.

1 h. Subsequently, another 60 mL of BDDE (10%, v/v) was added to the obtained products and heated at 60 °C for 1 h. In every procedure, the solid was filtered and washed with deionized water. The last two procedures were repeated six times to build six layers of polyelectrolytes on HCNSs. Thus, Q-HCNSs were prepared.

2.4. Preparation of PS-DVB/Q-HCNS anion-exchange stationary phases

PS-DVB microspheres (2.6 g) were dispersed into 12 mL glacial acetic acid under magnetic stirring for 15 min. Then, 2 mL dichloromethane was added and left for 1 h at room temperature. PS-DVB microspheres were swelling after above two steps. Finally, PS-DVB microspheres were sulfonated by 85% sulfuric acid for 4 min; subsequently, the reaction was halted through 1.0 mol/L cold sulfuric acid. After washing and filtration, the PS-DVB microspheres bearing sulfonic acid groups were obtained. The water suspension of Q-HCNSs was mixed with the sulfonated PS-DVB microspheres and stirred for 6 h. Q-HCNSs were electrostatically absorbed onto the surface of PS-DVB substrates. The flavescent solid was precipitated at the bottom of the flask after agglomeration. The PS-DVB substrates agglomerated with a Q-HCNSs layer (PS-DVB/Q-HCNS composite) were used as anion-exchange stationary phases.

2.5. Column packing procedure

Slurry of 2.6 g of PS-DVB/Q-HCNS composite in 50 mL of deionized water was sonicated for 6 min and packed into the column (stainless steel, 150 mm \times 4.6 mm i.d.). A total of 400 mL of deionized water was utilized as filling liquid and pressed above slurry into the column at 40 MPa. Then, the column was flushed with 10 mM KOH at 0.2 mL/min for at least 24 h before tested on the ion chromatography.

3. Result and discussion

3.1. Characterization of Q-HCNSs and PS-DVB/Q-HCNS anion exchangers

The prepared Q-HCNSs were characterized by FTIR and XPS spectrum. Fig. 1 shows the FTIR spectrum of HCNSs and Q-HCNSs samples. The band at 2900–3600 cm^{-1} corresponded with the stretching vibration of O–H; the bands in the region between 2940 cm^{-1} and 2860 cm^{-1} could be attributed to the stretching vibration of the aliphatic C–H. The two peaks at 1700 cm^{-1} and

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