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Synthesis of polyethyleneimine capped carbon dots for preconcentration and slurry sampling analysis of trace chromium in environmental water samples

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ABSTRACT

Carbon dots capped with polyethyleneimine (CD-PEI) were synthesized and applied in selective separation and preconcentration of trace Cr(VI). Dispersed particle extraction (DPE) slurry sampling with flame atomic absorption spectrometry (FAAS) was used to selectively and sensitively determine Cr(VI) in water samples. The as-synthesized CD-PEI was confirmed by Fourier transform infrared spectroscopy, high-resolution transmission electron microscopy, elemental analysis, fluorescence and zeta potential measurement. The adsorption of Cr(VI) on CD-PEI was evaluated. Its isothermal adsorption was studied and fitted in the Langmuir model. Nearly 85% of Cr(VI) was adsorbed within 10 min showed that the CD-PEI exhibited fairly fast kinetics for the sorption of Cr(VI). Experimental conditions, including the content and size of CD-PEI, sample pH, adsorption time, sample volume, slurry volume and interfering ions, were further optimized to obtain efficient preconcentration and high-precision determination of Cr(VI). CD-PEI with small size turned to be a good candidate for the preparation of slurry. CD-PEI served not only as a promising adsorbent for separation and preconcentration of Cr, but also a signal-enhancing agent in FAAS. The method achieved an enhancement factor of 30 and a detection limit ($S/N=3$) of $0.21 \mu\text{g L}^{-1}$ Cr(VI) with a consumption of 14.0 mL sample and an adsorption time of 5 min, which provided two times of signal enhancement. The RSD for 11 replicate measurements of $5.0 \mu\text{g L}^{-1}$ Cr(VI) was 2.8%. The possible signal enhancement mechanism was proposed. The developed method has been applied to determine trace Cr(VI) in a variety of water samples.

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1. Introduction

Carbon dots (CDs) have attracted an extensive interest in the field of carbon materials, due to their unique physical and chemical properties. In the past few years, much progress has been made in the synthesis, functionalization and application of CDs [1]. Compared to conventional metal quantum dots and

Abbreviations: CD-PEI, carbon dots capped with polyethyleneimine; DPE, dispersed particle extraction; CDs, carbon dots; SPE, solid-phase extraction; PEI, polyethyleneimine; RSD, relative standard deviation; FAAS, flame atomic absorption spectrometry; NRC CRM, national research center for certified reference materials; DDW, doubly de-ionized water; HRTEM, high-resolution transmission electron microscopy; FL, fluorescence; M, metal

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organic dyes, photoluminescent CDs preserve the characteristics of carbon materials. Moreover, they possess a wide variety of novel properties such as high aqueous solubility, robust chemical inertness, ease of functionalization, high resistance to photobleaching, low toxicity and good biocompatibility [2]. These excellent properties make CDs promising in numerous applications [3], such as bioimaging [4,5,6], optoelectronics [7,8], sensor [9,10], surface-enhanced Raman scattering [11], and photocatalysis [12]. CDs have shown remarkably high binding affinity for various substances, such as proteins [13], DNA [14], metal and non-metal ions [15–18], and dopamine [16]. Similar to other well-known members in carbon family, (e.g., active carbon, carbon nanotubes, carbon nanofibers, graphite), functionalized CDs can facilitate the adsorption of analytes in consequence of electrostatic interaction, anion exchange, chelate interaction or nano/meso/macro-porous physical structure [19–26]. Like most carbon materials, CDs can be

employed in SPE as separation and preconcentration materials in either online or off-line modes, especially for the determination of trace metal analytes [27,28].

Cr(VI) is highly toxic and can cause multiple carcinogenic effects in human bodies even at low abundance [29,30]. The World Health Organization proposes a guideline limit of 0.05 mg L^{-1} for Cr in drinking water [31]. It is vital to develop sufficiently selective and highly sensitive method to separate and determine Cr in various human-related samples [31,32].

Therefore, novel water-soluble CDs capped with branched polyethyleneimine (PEI) which served as “proton sponge” polymer to introduce tunable positive charges to CDs were designed and synthesized. Dispersed particle extraction (DPE) strategy coupled with slurry sampling technique were employed on Cr(VI) containing analytes while CD-PEI acted as selective sorbent for separation and preconcentration of Cr(VI). Further the flame atomic absorption spectrometric (FAAS) method was adopted to determine Cr (VI). It was found that CD-PEI can also enhance the sensitivity of Cr (VI) determination when using aqueous atomic absorption spectrometry. The possible reason of sensitivity enhancement involved the cationic surfactant PEI promoting small droplets generation during the aspiration and nebulization processes, which resulted in greater efficiency in the flame processes. Also, CD-PEI improved atomization efficiency by decreasing lateral diffusion and reduction in the flame atmosphere, which also lead to the signal enhancement.

Here we first reported the application of CD-PEI on Cr(VI) determination from a variety of environmental water samples based on DPE slurry sampling with FAAS strategy. Compared with the conventional SPE method, DPE strategy coupled with the slurry technique achieves eliminating the elution steps thus simplifying the operation, reducing the time, minimizing the risk of contamination and improving accuracy [31,33–37]. By using DPE strategy, we jettison expensive automatic flow injection equipment and complicated pipeline design for on-line SPE. Combination of slurry sampling with FAAS offers significant benefits for sample introduction, including low sample and reagent consumption, better precision and enhanced selectivity.

2. Materials and methods

2.1. Reagents and materials

Polyethylenimine(PEI) (branched, M.W. 1800, 99%) was from Alfa Aesar (Tianjin, China). Candles were purchased from local super market. Amicon Ultra-15 Centrifugal Filter Units[®] (3 kDa, 15-mL) (Millipore, Billerica, MA, USA) and Corning CentriStar[™] Centrifuge Tubes (15-mL) (Corning, USA) were used for slurry sample preparation in this study. All other reagents used were of the highest purity available but at least of analytical grade. All metal stock solutions (1000 mg L^{-1}) were purchased from the National Research Center for Certified Reference Materials (NRCCRM, Beijing, China). Standard Cr(VI) solutions were prepared by stepwise dilution of the stock 1000 mg L^{-1} Cr(VI) solution just before use, respectively. Doubly deionized water (DDW, $18.2 \text{ M}\Omega \text{ cm}$) was obtained from WaterPro water system (Labconco Corporation, Kansas City, MO, USA) and was used throughout the experiments.

2.2. Synthesis of CD-PEI

Functionalized carbon quantum dots were synthesized according to published method with some modifications [38,39]. Candle soot was collected by putting a piece of glass plate on top of burning unscented candles [40]. The resultant solid was purified with acetone. The purified carbon soot was refluxed in aqueous

nitric acid solution (2.6 M) for 12 h, dialyzed against fresh water, and then centrifuged at 1000 g to retain the supernatant. The treated carbon particle sample (100 mg) and PEI₁₈₀₀ (1 g) were added into 25 mL H₂O in a flask, heated to $90 \text{ }^\circ\text{C}$, and vigorously stirred under nitrogen for 3 h. The reaction mixture was cooled to room temperature and dispersed in water. Larger particles were removed by centrifugation at $11,000 \times \text{g}$ for 15 min three times. The supernatant was collected and dialyzed using the dialysis bag with a molecular weight cutoff of 3000 against DDW for 12 h six times to remove free PEI (M.W. 1800). After lyophilization, dry CD-PEI was obtained. In order to render carbon dots a more narrow defined size distribution, they were separated by high performance liquid chromatography according to published method [41,42]. After enriching fractions 3, 14, 5, 12, four resultants were collected by separating from semipreparative anion-exchange HPLC column, respectively (Fig. S1). At last, CD-PEI-a, CD-PEI-b, CD-PEI-c and CD-PEI-d were collected and denoted according to former depicted.

2.3. Instrumentation and characterization

A model Shimadzu AA6300 atomic absorption spectrometer equipped with quadline deuterium arc background correction, a universal air-cooled titanium burner, and a PTFE spray chamber with impact bead and baffle Pt/Ir PTFE nebulizer was used to detect Cr. The instrument was controlled by the Shimadzu AA6300 instrumental operation software. Hollow cathode lamps (MITOR-IKA Co. under the license of Hitachi Ltd., Japan) were used as the radiation sources at 357.9 nm with a current of 6.0 mA , a slit width 0.7 nm for Cr and a burner height of 10 mm . The recommended acetylene flow rate of 3.4 L min^{-1} for Cr was employed. The air flow rate of 15.0 L min^{-1} was automatically adjusted to meet the air-acetylene flame conditions.

The morphologies of the CD-PEI were characterized by high-resolution transmission electron microscopy (HRTEM) at 200 kV Tecnai G2 F20 (Philips, Holland). FT-IR spectra ($4000\text{--}400 \text{ cm}^{-1}$) were recorded with a Magna-560 spectrometer (Nicolet, USA). Fluorescence measurements were performed on a RF-5301 spectrofluorometer (Hitachi, Japan) equipped with a plotter unit and a quartz cell ($1 \text{ cm} \times 1 \text{ cm}$). Zeta potentials of the CD-PEI were measured on a Zetasizer Nano ZS analyzer (Malvern, UK). Elemental analyses were performed on an Elementar Vario EL analyzer (Elementar, Germany). The carbon dots samples were analyzed by HPLC with an Agilent 1100 system from Agilent Technologies equipped with a diode array detector. Data collection and system operation were controlled via the ChemStation for LC software from Agilent Technologies. All separations were carried out at a flow rate of 1 mL min^{-1} with ultraviolet (UV) detection at 250 nm . The chromatographic column consisted of a strong anion-exchange column ($4.0 \text{ mm i. d.} \times 250 \text{ mm}$ length, IonPac AS14, Dionex). Elution was accomplished by a gradient elution from 100 to 140 mM ammonium acetate over 5 min , hold until 10 min , gradient elution from 140 to 300 mM ammonium acetate over 25 min , gradient elution from 300 to 600 mM ammonium acetate over 10 min and hold until 50 min . The column was flushed with 600 mM ammonium acetate for at least 30 min in between runs. A model PHS-3 C Potentiometer (Lei Ci, China) was employed to monitor the pH of the solution. At least 6 samples can be concentrated at the same time by a typical lab-use centrifuge (Xiang Yi, China). All optical measurements were performed at room temperature under ambient conditions.

2.4. Static and uptake kinetics adsorption test

The effect of pH on the static adsorption of Cr(VI) was studied by equilibrating 30 mg of CD-PEI with 25 mL of HAc/NH₄Ac and NH₃/NH₄Cl buffer solution containing 10 mg L^{-1} of Cr(VI) under

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