Talanta 134 (2015) 16–23

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

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

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ARTICLE INFO

Article history:
Received 2 September 2014
Received in revised form
29 October 2014
Accepted 1 November 2014
Available online 8 November 2014

Keywords:
Carbon dots capped with polyethyleneimine
Slurry sampling
Chromium (VI)
Dispersed particle extraction

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 $\mu g\ L^{-1}$ 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 $\mu g\ L^{-1}$ 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.

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 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

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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; NRCCRM, 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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http://dx.doi.org/10.1016/j.talanta.2014.11.001

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 MΩ 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 PEI_{1800} (1 g) were added into 25 mL H_2O in a flask, heated to 90 °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 × 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 (MITORIKA 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 (4000–400 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 cm × 1 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 mm i. d. × 250 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/NH_4Ac and NH_3/NH_4Cl buffer solution containing 10 mg L^{-1} of Cr(VI) under different pH conditions. To measure the static adsorption capacity, 30 mg of CD-PEI was equilibrated with 25 mL of Cr(VI) solutions at pH 3.5 with various concentrations, respectively. In all the above batch experiments, the mixtures were mechanically shaken for 1 h at room temperature, and then centrifugally separated by ultrafiltration using Amicon Ultra-15 Centrifugal Filter Units at 6000 × *g*. The time-dependent uptake test was taken in a certain interval within 60 min. The filtrates were measured for uptakes of Cr(VI) by FAAS.

2.5. General analysis procedure

2.5.1. Slurry preparation of CD-PEI for extracting Cr(VI)

30 mg CD-PEI was dissolved with DDW and transferred into a 100-mL calibrated flask. After diluted with DDW, slurry solution of CD-PEI was formed. Various concentrations of Cr(VI) solution (14.0 mL) were mixed with 0.5 mL of 300 mg L^{-1} CD-PEI and the mixtures were transferred into a 15-mL calibrated Corning CentriStar centrifuge tubes, and then diluted to volume with pH 3.5 ammonium acetate/acetic acid buffer solution. Ultrasonic agitation is applied for 5 min in order to disperse the particles.

2.5.2. Separation and analysis procedure

We applied the slurry analysis for measurement of analytes including the sorbent particles to avoid the elution step required in conventional SPE. As mentioned above, the dispersed slurry solution were transferred into a Centrifugal Filter Unit (Millipore, 3 kDa, 15-mL), and centrifugally separated at 6000 × *g* by ultrafiltration. When the volume of analyte decreased to nearly 500 μL, the final slurry volume was diluted to 1.0 mL with DDW. The resultant slurry samples, loaded with the analytes, were directly aspirated into the flame atomic absorption spectrometer in the optimal conditions.

2.6. Sample preparation

The following certified reference material (NRCCRM, Beijing, China) was analyzed to evaluate the accuracy of the developed method: GBW08608 (trace elements in water). Some real samples (well water, spring water and river water) were also analyzed for determination of total Cr and Cr (VI). Environmental water samples: spring water, river water and well water were collected in polyethylene bottles and stored at 4 °C. The water samples were filtered through 0.22 μm mixed cellulose ester membrane filters. The procedure was performed according to the literature [24,43]. Because electrostatic interaction and anion exchange play important roles in allowing the approach of the ions to the sorbent surfaces, oxidation of Cr species with low valence state to Cr(VI) is necessary to ensure Cr to be absorbed on the positively charged layers of CD-PEI [44].

Both GBW08608 diluted with DDW and environmental water samples were adjusted to pH 3.5 before undergoing a separation and preconcentration process as detailed in the present study for further quantification analysis of Cr (VI).

3. Results and discussion

3.1. Characterization of the CD-PEI

TEM was used to obtain size information about CD-PEI. As shown in Fig. 1A, C, E, G the high-resolution transmission electron microscopy (HRTEM) image of CD-PEI showed that the prepared CDs were uniform sphere particles. The size distribution histogram in Fig. 1 was obtained by counting 100 particles randomly from various spots of the sample during TEM investigation. CD-PEI-a, CD-PEI-b, CD-PEI-c and CD-PEI-d in Fig. 1B, D, F, H showed an average diameter of about 2.2, 3.8, 5.7 and 8.1 nm, respectively.

FT-IR spectra of the bare CDs are shown in Fig. 2A. The peak at 1690 cm^{-1} was ascribed to C=O stretching vibration. The peak at 1406 cm^{-1} was assigned to symmetric stretching vibration of carboxyl group. Compared with bare CDs, several characteristic peaks of PEI were observed from CD-PEI. Observation of six characteristic absorption bands of PEI (2930 and 2870 cm^{-1} for C–H stretch, NH_2 bending band at 1592 cm^{-1}, 1460 cm^{-1} for C–H bend, 1120 cm^{-1} for C–N stretch and CH_2 wagging motions at 1050 cm^{-1}) demonstrated that the PEI was successfully capped on CDs. No more new bands were found after the passivation process, therefore CD-PEI are probably prepared by coating the CDs with PEI via adsorption. The fluorescence spectra (Fig. S2) also confirmed that the as-prepared product was in accord with the general characteristics of CD-PEI.

Zeta potential was measured in order to verify the electrostatic attraction between CD-PEI and Cr(VI). As shown in Fig. 2B, the zeta potential of CD-PEI slurry showed pH-dependent feature in a pH range of 2.0–11.0. The changes of the slurry zeta potential showed an obvious impact on the dispersion state of particles in suspensions, which revealed the electrostatic interaction between particles in the dispersion. At isoelectric point, slurry may be unstable. Therefore, it is vital to determine the isoelectric point for the preparation of stable slurry [45]. Once the isoelectric point is measured, the appropriate pH, under which sufficient highly charged surface is obtained in solution, can be determined to stabilize slurry. The isoelectric points were found near pH 7.5 with no dispersant. Fig. 2B indicated that zeta potential was around 40 mV in the range of pH 2.0–4.0, which not only guided the appropriate pH range conditions for slurry preparation but also the adsorption of Cr (VI). The fine CD-PEI particles in slurry are highly charged.

As depicted in Fig. 3A, the elemental analysis results of CD-PEI-a, CD-PEI-b, CD-PEI-c and CD-PEI-d for nitrogen determination were 16.1%, 14.4%, 12.8% and 10.1%, respectively, which provided quantitative data for the loading of PEI. The average nitrogen content of PEI is 32.5%. C_{PEI}/C_{CD} means the mass ratio of PEI (C_{PEI}) and CD (C_{CD}). Therefore, the calculated ratio of C_{PEI}/C_{CD} was 0.98, 0.80, 0.65, 0.45 for CD-PEI-a, CD-PEI-b, CD-PEI-c, CD-PEI-d, respectively. Fig. 3B demonstrated that the ratio C_{PEI}/C_{CD} increased with the decrease of their diameter.

3.2. Kinetics and static investigations on adsorption

Kinetics and static investigations on adsorption showed the CD-PEI was an effective and favorable sorbent due to adsorb the Cr(VI) with high capacity and well efficiency. Its isothermal adsorption was studied and fitted in the Langmuir model (Table S1). The fast adsorption kinetics of CD-PEI showed advantage for its application in DPE (Fig. S3).

3.3. Influence factors of Cr(VI) determination by DPE slurry sampling coupled with FAAS

The feasibility of the CD-PEI for the DPE of Cr(VI) was evaluated by the slurry sampling technique, i.e. DPE preconcentration and separation slurry sampling with FAAS. Factors including sample's acidity, sample consumption, reaction time for analytes adsorption, final volume of slurry, CD-PEI addition and particle size, were optimized for the determination of Cr(VI) with good sensitivity and precision.

3.4. Effects of the CD-PEI addition and particle size

To evaluate the effect of the amount of CD-PEI addition on the quantitative retention of $Cr_2O_7^{2-}$ anions, the extraction was

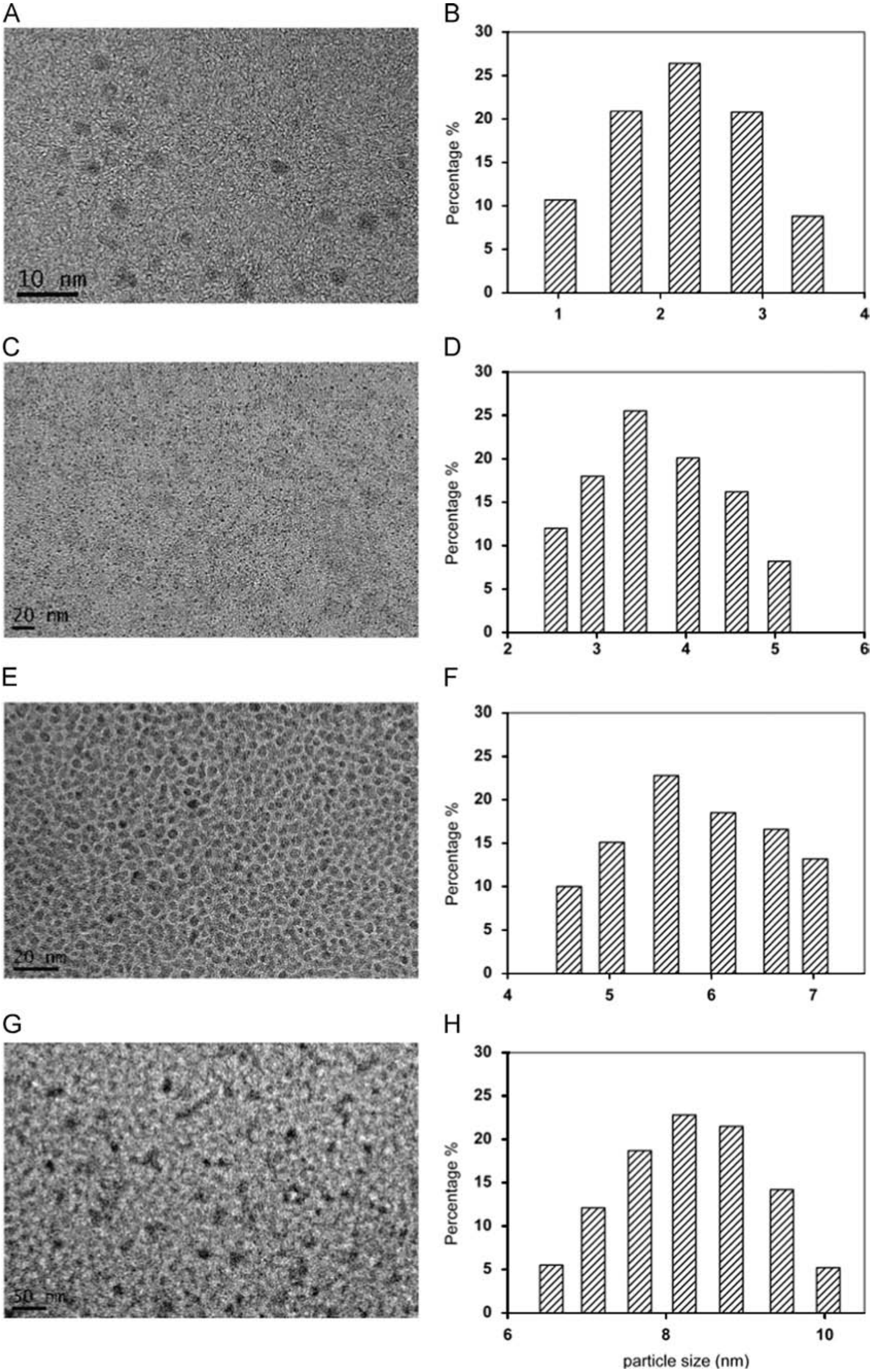

Fig. 1. (A) Representative HRTEM image of CD-PEI-a, (B) particle size distribution of CD-PEI-a, (C) representative HRTEM image of CD-PEI-b, (D) particle size distribution of CD-PEI-b, (E) representative HRTEM image of CD-PEI-c, (F) particle size distribution of CD-PEI-c, (G) representative HRTEM image of CD-PEI-d, and (H) particle size distribution of CD-PEI-d.

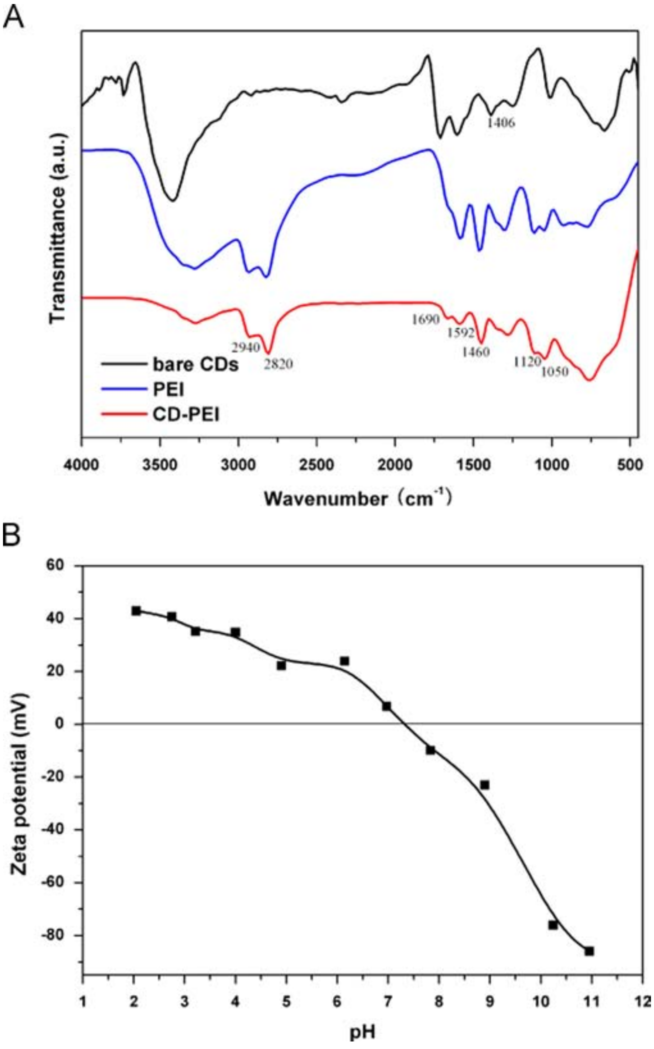

Fig. 2. (A) FT-IR spectra of bared CDs and CD-PEI and (B) zeta potential of the CD-PEI within a range of pH 2–11.

conducted by varied the amounts of the CD-PEI from 3 to 50 mg L^{-1}. The absorbance of Cr by AAS was recorded to evaluate the influence of CD-PEI with various concentrations. Two times of signal enhancement for Cr ($Cr_2O_7^{2-}$) was achieved when *c* (CD-PEI) was 10.0 mg L^{-1}. It kept relatively stable with the increase of CD-PEI concentration (Fig. 4A). The fact that no more obvious improvement was observed with the increased concentration of CD-PEI, was mainly restricted to nebulization efficiency. Therefore, 10 mg L^{-1} of nano-sorbent was employed in this work.

The particle size of CD-PEI, involved in the determination of Cr (VI), was also investigated. 4.0 μM of CD-PEI-a, CD-PEI-b, CD-PEI-c, CD-PEI-d was employed in the slurry, respectively. The absorbance was decreased as the particle size gradually increased. Meanwhile, the RSD% turned large significantly (Fig. 4B). The atomization efficiency of the particles in the formation of slurry would be improved as the particle size decreased. Therefore, CD-PEI with smaller size was a better candidate for the preparation of slurry, leading to higher sensitivity and precision.

3.5. Possible signal enhancement mechanism

The mechanism of the two times of signal increasement for Cr(VI) was further discussed. The positive surfaces formed by hydrophilic chain of the CD-PEI had strong electrostatic interaction with analyte anions during the nebulization process. Such interaction might lead to the formation of smaller dispersed aerosol particles which can cause redistribution of aerosol particles and thus lead to better atomization efficiency than larger particles. Also the atomization efficiency was proposed to be enhanced by reduced decomposition of the surfactant around the analytes. Higher atomization efficiency contributed to the formation of aerosol particles with enriched surface, which was much heavier than free Cr(VI) in weight and showed increased resistance to motion simultaneously [46,47]. Therefore, the speed of lateral diffusion turned slow down. The concomitant delayed the atomization of spray droplets or solid particles, thus shortening the time available for lateral diffusion in the flame by Cr atoms before they reached the optical path. Therefore, Cr free atoms were concentrated at the center of the flame and decreased at the edges [48,49]. As shown in Fig. 4B, the bigger particles lead to worse sensitivity and lower precision than smaller particles. According to what we have observed so far, bigger particles were restricted by nebulization efficiency while smaller particles showed benefit for controlling lateral diffusion, which was proposed to be the main reason for atom yield improvement. Besides, reduction of oxides, which was achieved by carbon-containing radicals in the interconal zone of the flame, might be another minor possible reason of generating analyte atoms in flames with production of carbon monoxide. CD-PEI contains sufficient *C*, *N* element sources including primary amine, secondary amine and tertiary amine groups. The addition of CD-PEI may provide an enhanced reductive chemical micro-environment in the flame.

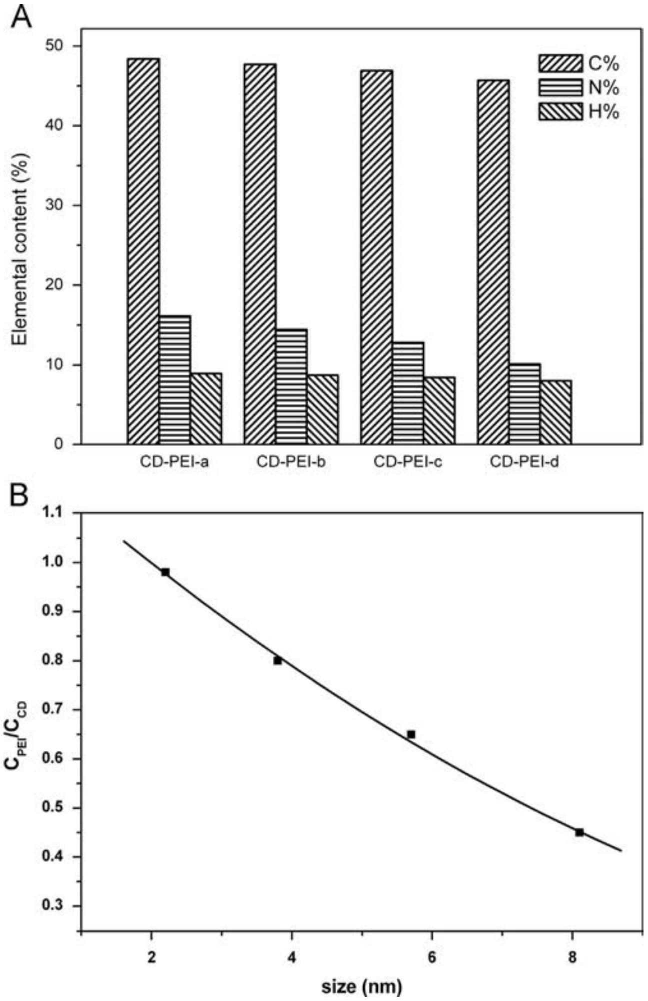

Fig. 3. (A) Elemental analysis of CD-PEI-a, CD-PEI-b, CD-PEI-c, CD-PEI-d, and (B) Dependence of the ratio C_{PEI}/C_{CD} from the mean size of CD-PEI.

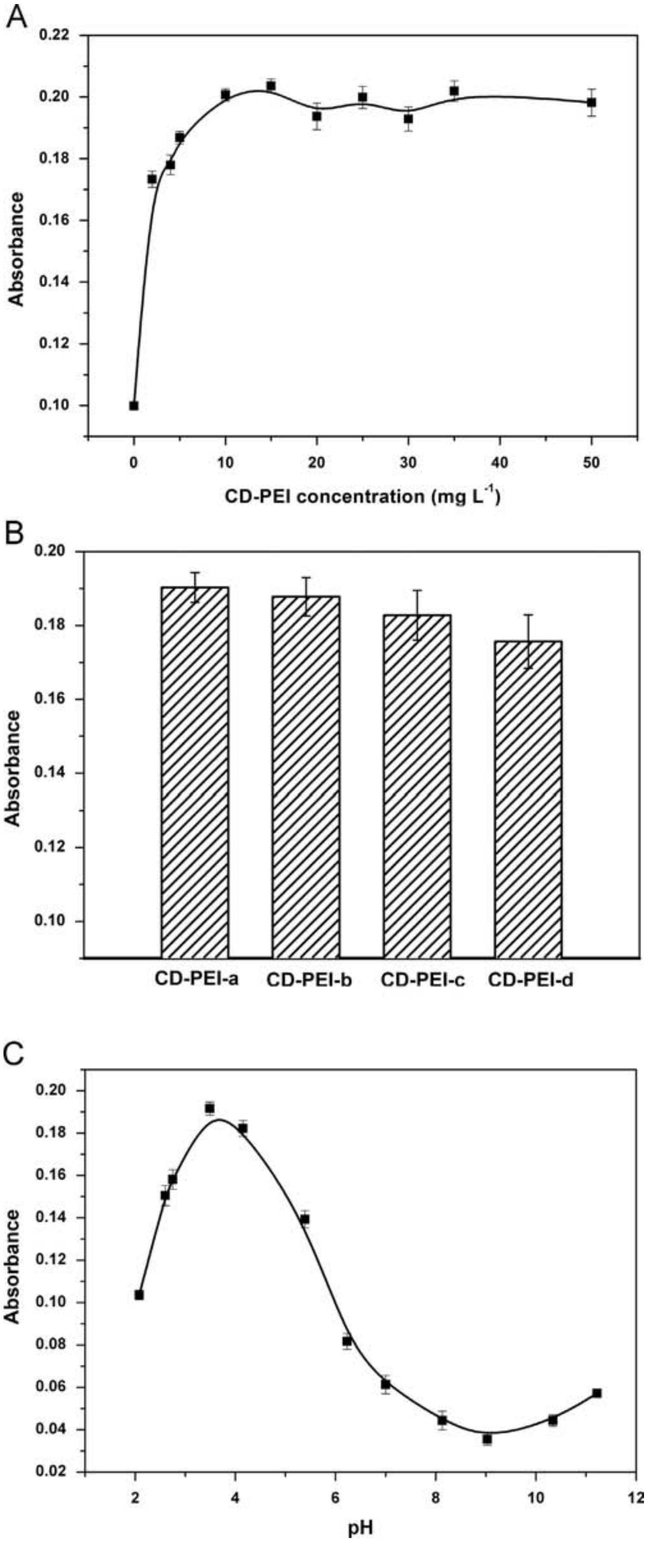

Fig. 4. (A) Effect of concentration of CD-PEI addition within a range of 3–50 mg L^{-1}. Sample: 15.0 mL, 40 μg L^{-1} Cr(VI). (B) Effect of sensitivity and precision dependent on the different sizes of CD-PEI fractions. (C) Effect of pH on the preconcentration of Cr(VI) by CD-PEI in aqueous solution. Sample: 15.0 mL, 40 μg L^{-1} Cr(VI).

These factors ensured the formation of free atom in a reducing atmosphere. Furthermore, the flame temperature could be increased by exothermic reactions and the elevated combustion in the presence of CD-PEI. The organic species were burnt exothermically in the flame and metal atoms were liberated more easily from the refractory oxides. Therefore, CD-PEI could enhance atomizing efficiency owing to the free atom much more stablely formed. In a word, the signal enhancement was a combined result of a variety of effects. The process could be concluded using the following equilibrium: [50] (*M* represents Metal)

$$MxOy(s,l)+yC\rightarrow xM(s,l)+yCO$$

$$MxOy(s,l)+yCO\rightarrow xM(s,l)+yCO_2$$

$$MxOy(s,l)+yNH\rightarrow xM(s,l)+yN+yOH$$

$$MxOy(s,l)+yCN\rightarrow xM(s,l)+yCO+yN$$

$$xM(s,l)\leftrightarrow \frac{x}{2}M_2(g)\rightarrow xM(g)$$

3.6. *Effects of sample acidity*

CD-PEI consisted of positively charged layers with charge balancing anions between the layers. Due to its permanent positive charges on the surface, CD-PEI was considered as a new class of green nano-sorbents for DPE with good stability, well water dispersed structure and rapid adsorption with high adsorption capacity characteristics. According to the adsorption mechanism of Cr(VI) on CD-PEI, pH value played an important role in the preconcentration procedure by influencing both the dominated form of Cr(VI) (in solution) and the PEI protonation status. When $pH < 1.0$, H_2CrO_4 was the main species. The main forms were $HCrO_4^-$ and $Cr_2O_7^{2-}$ in the pH range from 2.0 to 6.0. Under basic solution, CrO_4^{2-} was the main species [51]. The functional NH_2 groups in PEI were considered to be active sites for the adsorption of Cr(VI). PEI protonated mainly in two steps: the primary groups on the side chains protonated first at pH around 9.5 and the second protonation occurred at pH near 4.5 [52].

Here the effect of the pH of the sample solution was evaluated using 40 μg L^{-1} Cr(VI) in a pH range of 2.0–11.0 (Fig. 4C). It was found that extremely high or low pH resulted in sharp decrease in absorbance. The low absorbance of the analytes at low pH (<2.0) was resulted from the low retention efficiency of the dispersed material, which was possibly due to the occupation of the $Cr_2O_7^{2-}$ ions by proton. At higher pH (>6.0), the decrease of the analytes absorbance might be caused by the positive charges diminution of CD-PEI [53]. It was demonstrated that the optimal pH of the sample solution was in the range of 2.5–4.5 (Fig. 4C). In this range, the retention was more than 85%. As depicted in Fig. 2B, the zeta potential was around 40 mV in the pH range of 2.0–4.0. However, the zeta potential was only around 20 mV at pH 4.5. With the pH increased, the positive charge decreased quickly. Therefore, the best retention of Cr(VI) was obtained when sample pH was in the range of 3.5–4.0. All working standard and sample solutions were procedured at this optimal pH range in further studies.

3.7. *Effects of sample volume, adsorption time and final volume of slurry*

The effect of sample volume was investigated in the range of 1.0–14.0 mL. Studies on the effect of sample volume on the preconcentration of 40 μg L^{-1} Cr(VI) for 5 min. It was shown that the absorbance of the analyte increased linearly to up to at least 14.0 mL. The results also indicated that the kinetics for the adsorption of Cr(VI) by the CD-PEI was fairly fast. The final condensed slurry volume of 1.0 mL was chosen with satisfying precision ($<5\%$ RSD). The wide range of linearity for absorbance against sample volume in the presented DPE preconcentration system offered potential for achieving higher preconcentration factors by increasing sample volume without losing retention efficiency.

3.8. Selectivity of the developed DPE slurry sampling with FAAS using CD-PEI as sorbent for the determination of Cr(VI)

To further demonstrate the selectivity of CD-PEI for Cr(VI) in DPE, interferences from representative foreign ions were examined. The interferences investigated in this study included alkali metal ions K^+, Na^+, alkaline metal ions Mg^{2+}, Ca^{2+}, Sr^{2+}, typical transition metal ions of Ag^+, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, other metal ions Al^{3+} and some common anions SO_4^{2-}, NO_3^-, CO_3^{2-}, PO_4^{3-}, ClO_4^-, Cl^-, Br^-, I^- on the DPE preconcentration of 40 μg L^{-1} Cr(VI) using CD-PEI as sorbent were examined. The effect was expressed as the recoveries of target ions in the presence of interfering ions relative to the interference free response. The tolerance limit was defined as the amount of ions causing recoveries of examined ions to be less than 90%. As shown in Table S2, up to 100 mg L^{-1} of K^+, 150 mg L^{-1} of Na^+, 50 mg L^{-1} of Mg^{2+}, 60 mg L^{-1} of Ca^{2+}, 80 mg L^{-1} of Sr^{2+}, 50 mg L^{-1} of Ag^+, 80 mg L^{-1} of Al^{3+}, 50 mg L^{-1} of Cd^{2+}, 40 mg L^{-1} of Pb^{2+}, 60 mg L^{-1} of Zn^{2+}, 25 mg L^{-1} of Cu^{2+}, 40 mg L^{-1} of SO_4^{2-}, 100 mg L^{-1} of NO_3^-, 40 mg L^{-1} of CO_3^{2-}, 30 mg L^{-1} of PO_4^{3-}, 35 mg L^{-1} of ClO_4^-, 80 mg L^{-1} of Cl^-, 75 mg L^{-1} of Br^-, 90 mg L^{-1} of I^- showed no significant interference in the determination of 40 μg L^{-1} Cr(VI). No interference was observed from most of the common matrix constituents of alkali and alkaline metals.

Table 1
Analytical performance of the CD-PEI preconcentration and separation slurry sampling FAAS for determination of trace Cr.

	Cr
Enhancement factor	30
Sample consumption (mL)	14.0
300 mg L^{-1} CD-PEI addition (mL)	0.5
Buffer solution (mL)	0.5
Final volume of slurry (mL)	1.0
Reaction time for analyte adsorption ($_{\text{min}}$)	5
Precision (RSD, $n=11$)%	2.8 (5 μg L^{-1} Cr)
Detection limit (3 s) (μg L^{-1})	0.21
Range of calibration graph (μg L^{-1})	1–120
Calibration function ($n=5$) (A, absorbance, C in μg L^{-1})	$A=0.0048\ C–0.0028$
Correlation coefficient	0.9964

3.9. Analytical performance

The analytically characteristic data for the developed DPE slurry sampling with FAAS for the determination of trace Cr(VI) under the optimized conditions were given in Table 1. With a sample consumption of 14.0 mL, CD-PEI addition of 0.5 mL, buffer solution of 0.5 mL, final volume of slurry of 1.0 mL, an enhancement factor of 30 and a detection limit (3 s) of 0.21 μg L^{-1} were achieved at a reaction time of 5 min for analytes adsorption. The precision (RSD) for 11 replicate measurements of 5 μg L^{-1} Cr(VI) was 2.8%. Table 2 compare the figures of merit of some recent published SPE FAAS methods for the determination of chromium [54–61]. According to what we had assessed, it was concluded that the developed method described above could offer a sensitive and accurate determination of Cr (VI).

3.10. Sample analysis

Both certified reference materials and real environmental water samples, i.e. GBW08608 (trace elements in water), well water, spring water and river water were analyzed. The calibration curve was also processed by DPE in the process of detecting certified reference materials and real samples. As shown in Table 3, the determined concentrations of chromium in certified reference materials or real samples by the present method were in good agreement with the certified values as using a simple aqueous standard calibration protocol. The analytical results for the spiked samples were achieved with good recovery ranged from 96% to 104%. These results demonstrated the applicability of the developed CD-PEI for DPE slurry sampling of Cr (VI) and total Cr in a variety of environmental water samples.

4. Conclusions

In this study, a new application of CDs was introduced. CDs modified with the PEI were synthesized and successfully applied for DPE slurry sampling with FAAS for the determination of Cr. Without any automation on-line sampling equipment, complicated pipeline design or procedure control, limit detection (LOD) of 0.21 μg L^{-1} for Cr was achieved. Owing to the merits of

Table 2
Comparison of the developed method with some recent reported solid-phase extraction preconcentration FAAS methods for the determination of Cr.

Analytes	Sorbent	Sample consumed (mL)	Enhancement factor	Detection limit (μg L^{-1})	RSD (%)	Refs.
Cr	CD-PEI	14	30	0.21	2.8%	This work
Cr	HBIG loaded groundnut shells	200	200	3.64	1.2%	[54]
Cr	Amberlite XAD-1180 resin	150	75	8.6	–	[55]
Cr	NH_2-SBA-15	–	44	0.2	2.1%	[56]
Cr	poly(DPMAAm-co-DVB-co-AMPS) resin	1500	150	1.11	2.0%	[57]
Cr	AXAD-4-HBAM resin	100	380	0.49	–	[58]
Cr	Polystyrene	10	30	2.5	2.2%	[59]
Cr	Ni^{2+}/2-Nitroso-1-naphthol-4-sulfonic acid	100	50	1.33	< 7%	[60]
Cr	BrPMAAm/AMPS/DVB resin	1000	100	1.58	3.0%	[61]

Table 3
Analytical results (mean ± σ, $n=3$) for the determination of trace Cr in the certified reference materials and real samples.

Samples	Certified	Found (μg L^{-1})		spiking(μg L^{-1})	Recovery(%)
		total Cr	Cr(VI)	Cr(VI)	
GBW08608 (trace elements in water)	31.4 ± 2.0	30.8 ± 1.7	not detected	–	–
GBW08608 (after oxidation)			30.1 ± 1.5	25.0	104.3
River water	–	2.63 ± 0.34	1.15 ± 0.48	1.0	97.7
Well water	–	7.67 ± 0.38	4.02 ± 0.29	5.0	96.2
Spring water	–	2.18 ± 0.26	1.83 ± 0.35	1.0	103.1

simplicity, selectivity and sensitivity, CD-PEI could be used as a promising sorbent for separation and preconcentration of Cr in water samples.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant 21245001), and the Tianjin Natural Science Foundation (Grant 13JCQNJC06200). We also appreciate the kindly help from Dr. Ting Zhang.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.11.001.

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