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A bipotentiostat based separation-free method for simultaneous flow injection analysis of chromium (III) and (VI) species

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ABSTRACT

Chromium(III) species is an essential micronutrient, whereas, its hexavalent form, Cr(VI) is considered to be a carcinogen. For the selective detection of Cr(III) in presence of Cr(VI), separation coupled spectroscopic techniques have been often used. For the first time in this work, we report a flow injection analysis coupled dual electrochemical detector (FIA-DECD) for separation-free detection of Chromium (III) and (VI) species. A gold nanoparticles decorated carbon nanofibres-chitosan modified electrode has been prepared by a quick and in-situ electrochemical deposition of Au^{3+} ion in pH 7 phosphate buffer solution (PBS) and has been used as a dual electrochemical detector for Cr(VI)-reduction and Cr(III)-oxidation reactions in pH 2 PBS. Under an optimal hydrodynamic FIA-DECD condition, i.e., at applied potentials 0.1 V (for Cr(VI)-reduction) and 1 V vs Ag/AgCl (for Cr(III)-oxidation) and at a flow rate = 0.8 mL min^{-1}, calculated linear range and detection limit values are; 0.1–100 ppm and 0.69 ppb (0.72 ppt for 20 µL sample loop volume) for Cr(III) and 0.1–100 ppm with detection limit, 0.32 ppb (0.33 ppt for 20 µL) for Cr(VI). No marked interference from other cations and anions like Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+}, Ca^{2+}, Fe^{2+}, Mg^{2+}, NO_3^-, NO_2^-, SO_3^{2-} and SO_4^{2-} were noticed. Selective detection of Cr species (Cr(III) and Cr(VI)) in industrial waste water samples with data comparable to ICP-OES was demonstrated.

1. Introduction

Chromium (Cr) is an essential biological and engineering metal has been used for wide variety of applications [1–5]. It exists in variable oxidation states from −2 to +6. Amongst them, trivalent, Cr(III) and hexavalent, Cr(VI) are found to be stable species and are accountable for the bioavailability and toxicological activity [6,7]. Trivalent Cr species is an important nutrient for the biological activities in human and animal because of its involvement in several biochemical processes such as the metabolism of carbohydrates, fats, proteins, and nucleic acids [7–13]. For example, in human, Cr(III) affects the glucose-lipid and glucose-insulin metabolisms by increasing the pro-activities of enzymes, proteins and nucleic acids [7,8]. In contrast, hexavalent chromium which exists as a $Cr_2O_7^{2-}$ (dichromate) in strong acidic and as a chromate, CrO_4^- in alkaline solution induces carcinogenic activity because of its DNA oxidative character [10,11]. Meanwhile, both Cr(III) and (VI) species adversely contaminate the underground and drinking water. As per World Health Organization (WHO) [14], International Agency for Research (ICAR) [15] and United States Environmental Protection Agency (USEPA) [16] regulations, the allowable limits of Cr species in the environment should be < 50 ppb. Thus, development of a rapid and reliable detection method for the speciation and quantification of inorganic chromium in biological and environmental processes is a demanding one in analytical chemistry.

Several analytical methods based on spectrophotometry [17,18], spectrofluorimetry [19], electro-thermal atomic absorption spectroscopy (ETAAS) [20,21], ion-chromatography (IC) [22] and high performance liquid chromatography coupled inductively coupled plasma mass spectroscopy (HPLC-ICP-MS) [23], and energy dispersive X-ray fluorescence spectrometry (EDXRF) [24] have been reported for the speciation and detection of the Cr species. However, the above mentioned methods have inadequate sensitivity and selectivity for direct determination of Cr at ultra-race levels. In

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addition, most of these techniques are associated with expensive instrumentation, tedious sample preparation, pre-concentration and derivatization based indirect detection procedures [17–24]. For example, in case of spectrophotometric technique, gold nanoparticles or silver nanoparticles capped citrate was used as a colorimetric probe for the determination of total chromium by distinct color change from pink red to blue, due to the interaction of Cr(III) or Cr(VI) species (total chromium) [17,18]. In the hyphenated inductively coupled plasma mass spectroscopy with ion-chromatography or high performance liquid chromatography approach, a series of anion/cation-exchanging columns were used to discriminate the chromium ions (on basis of complexation and trapping techniques) [22,23]. Note that in the ICP-MS technique, the isotopes such as $^{35}Cl^{16}OH^{+}$ or $^{40}Ar^{12}C^{+}$ generated during the high plasma process, is found to interfere with the Cr species [22]. On the other hand, electrochemical techniques can provide derivatization-less, separation-less, selective and sensitive response with user-friendly instrumentation like flow injection analysis (FIA) coupled dual electrochemical detectors (DECD) system [25,26]. Herein, for the first time, we report a FIA for single-run detection of both Cr(III) and Cr(VI) species without any separation technique using a bifunctional gold nano particles decorated carbon nanofibres-chitosan (GCE/CNF-CHIT@Au_{nano}) as a dual electrochemical detector (DECD) using pH 2 phosphate buffer solution as a carrier solution.

In the literature, several electrochemical methods have been reported for the detection of chromium ions [27–38] utilizing the electrochemical techniques like stripping voltammetric [28–36], cyclic voltammetric (CV) [37] and differential pulse voltammetric techniques (DPV) [38]. In particular, adsorption stripping voltammetric method, the pre-concentration of Cr species followed by stripping by voltammetric technique, has been frequently used [28–36]. Note that co-immobilization of other trace metal ions during pre-concentration is a major concern in the stripping voltammetric technique. To the best of our knowledge, a FIA-DECD based analytical technique is never reported for the chromium speciation. In this work, a FIA-DECD method was introduced for the speciation and determination of chromium ions, Cr(III) and Cr(VI) without any separation technique and validated by testing industrial effluent wastewater samples.

2. Experimental

2.1. Reagents and materials

Carbon nanofibres (CNF), ~99.9% purity on carbon basis, size 100 nm × 2–200 μm (Aldrich, USA), gold atomic absorption solution (Au-AAS), 1000 mg/l (SRL, India), chromium (III) chloride (Sigma Aldrich, USA) and potassium dichromate (Sigma Aldrich, USA) and all other chemicals (ACS certified analytical grade) were used as received without further purification. Aqueous solutions were prepared using deionized and alkaline $KMnO_4$ distilled (DD) water. A supporting electrolyte pH 7 phosphate buffer solution (PBS) for electrode preparation and pH 2 PBS (pH adjusted with phosphoric acid) for electrocatalysis of ionic strength 0.1 M was used throughout this work. ***Caution!*** Since the dichromate ion is hazardous in nature proper care must be taken while handling.

2.2. Apparatus

Electrochemical and hydrodynamic amperometric measurements (DECD system) were performed using a CHI 760D electrochemical workstation (Bipotentiostat, Austin, TX, USA). The three electrode system consisted of GCE of 0.0707 cm^2 geometrical surface area and its chemically modified form as an ECD, Ag/AgCl with 3 M KCl as a reference electrode and platinum wire as a counter electrode. Rotating ring disc-electrode (RRDE) experiment was carried out using a glassy carbon disc/gold-ring based electrode with RDE-2 Rotating Disk Electrode instrument (BASi, USA). The FIA system consisted of Hitachi L-2130 pump delivery (Japan), a Rehodyne model 7125 sample injection valve (20 μL loop) interconnected with Teflon tubes and a conventional electrode with two GCE working surfaces (BAS, USA) [25]. For the inductive coupled plasma analysis (ICP-OES), Perkin Elmer Optima 5300 DV (USA) instrument was used.

2.3. Preparation of the chemically modified electrode

The modified GCE/CNF-CHIT@Au_{nano} electrode was prepared similar to our previous reported procedure [39]. Shortly, a chitosan (CHIT) solution, 0.1 wt %, was first prepared by mixing 10 mg CHIT flakes with 10 mL of 1% glacial acetic acid and stirring it 3 h at room temperature (25±2 °C) followed by adjusting the solution pH as 4–5by dilute 1 M NaOH solution. The GCE/CNF-CHIT@Au_{nano} modified electrode was prepared by successive drop coating of 5 μL of CNF-CHIT and Au^{3+} atomic absorption solution on a clean GCE surface (i.e., GCE/CNF-CHIT@$Au^{3+}{}_{ads}$; ads = adsorbed) and kept for drying (5 ± 2 min) at room temperature respectively. A well dispersed Au^{o}-nanoparticles-immobilized GCE/CNF-CHIT, i. e, GCE/CNF-CHIT@Au_{nano} was then prepared by continuous CV cycling (n = 10) of the GCE/CNF-CHIT@$Au^{3+}{}_{ads}$ in a potential window −0.6–1.0 V in pH 7 PBS at a $v = 50$ mVs^{-1}. It is likely that carboxyl and amide functional groups of the CNF@CHIT electrostatically interact with the Au^{3+} ion and stabilize its species. When potential cycling experiment was performed, the stabilized Au^{3+}-ions get reduced to Au^{o}-nanoparticles within the surface of the composite modified electrode. For FIA-DECD, CNF-CHIT@Au_{nano} modified system prepared on a FIA-GCE base was used. For real sample analysis (standard addition approach), two chromium-polluted industrial effluent waste water samples (#1 and #2) collected from industrial areas nearby VIT were used. Prior to the analysis, the real samples were filtered by normal filter paper and the filtrate was diluted with 10 mL of pH 2 PBS.

3. Result and discussion

3.1. Electrochemical behaviour of chromium on CNF-CHIT@Au_{nano} modified electrode

Initial studies with unmodified GCE, Au, carbon nanomaterials (carbon nanotubes and carbon nanofiber)-Nafion modified electrodes have failed to show any marked and stable voltammetric signals for the Cr(III) and Cr(VI) species (data not included). Since, Cr(VI) has high oxidation potential ($E^{o'}$~1 V vs Ag/AgCl in pH 2), for studying simultaneous FIA of the Cr species (Cr(VI) and Cr(III)), structurally stable and electro-catalytically active chemically modified electrode is highly required. On the basics of trial and error, it has been found that CNF-CHIT@Au_{nano} modified electrode system, which was used previously for a simple FIA of a pharmaceutical compound (isoniazid) [39], is highly suitable for a bifunctional electrochemical oxidation and reduction reactions of the Cr species in mild acid condition, pH 2 phosphate buffer solution adjusted with phosphoric acid in this work. Novelty of the present work is a first separation-free electrochemical method for simultaneous FIA of chromium species (Cr(III) and Cr(VI)) species.

Fig. 1A curve a is a continuous CV response of GCE/CNF-CHIT@$Au^{3+}{}_{ads}$ in 0.1 M pH 7 PBS at $v = 50$ mV s^{-1}. As can be seen, two electron-transfer responses, wherein, a quasi-reversible pair of peaks (A2/C2) with a half-wave potential, $E_{1/2}$ = 0.6 V vs Ag/AgCl, and an irreversible reduction peak (C1) at cathodic potential