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Full Papers
doi.org/10.1002/slct.202001338

Chemistry Europe
European Chemical Societies Publishing

Materials Science inc. Nanomaterials & Polymers

Comparative Insight into the Performance of Two Different Amine-Functionalized CNTs** for the Chemical Speciation of Chromium

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Persistent industrial activities have led to an increase in the chromium content in environmental water bodies. The accurate quantification of trace chromium species such as Cr(III) and Cr (VI) is crucial as Cr(VI) can exhibit toxicity even at sub-ppb levels. We report herein a comparative chromium speciation study using two chemically functionalized nanoadsorbents and determination with hyphenated flow injection-flame atomic absorption spectrometry (FI-FAAS). The most efficient preconcentration performance was obtained by optimizing the chemical and hydrodynamic parameters. Cr(VI) concentration was ascertained by the reduction to Cr(III) as the nanoadsorbents were selective for Cr(III) adsorption only; thus, speciation was achieved. The method was selective for Cr(III) in the presence of interfering matrix components. Preconcentration factor >90 and detection limit $<0.11\ \mu g\,L^{-1}$ were obtained for both the nanoadsorbents (%RSD ~ 1.0%). The adsorption capacity of CNT-TYR and CNT-ASA was found to be 42.0 and 43.2 $mg\,g^{-1}$, respectively. The application of the proposed method to contaminated water samples gave recoveries $>95\%$. The accuracy of the method was verified using NIST SRM 1640a.

1. Introduction

The vast application of chromium in industrial activities, involving leather tanning, metal electroplating, paint manufacturing, and color additives, coupled with negligent waste disposal has led to the contamination of the environment. Water is the most severely affected realm of the biosphere due to chromium contamination as industrial and agricultural runoffs from contaminated sites and waste treatment plants are eventually disposed into various water bodies. Therefore, the level of chromium in potable water may surpass the permissible value (0.05 $mg\,L^{-1}$) provided by the World Health Organization.[1] Cr(III) is an essential trace element for normal metabolism in humans. However, Cr(VI) is a certified carcinogen that causes inflammatory responses, cell transformation, and respiratory cancers.[2] High concentrations of chromium compounds in water can have deleterious effects on human, animal, and plant health. Thus, the simultaneous detection and removal of both these species from water is essential.

The detection techniques based on flame, electrothermal, and plasma atomic spectrometry can directly detect total chromium concentration in various matrices. Amongst these, flame atomic absorption spectrometry (FAAS) is one of the most widely used due to its good analytical performance and low cost.[3] However, most direct techniques suffer from interferences present in the matrix and low sensitivity. Therefore, speciation analysis requires a step for chromium preconcentration such as co-precipitation,[4] dispersive liquid-liquid microextraction,[5] syringe-tip preconcentration system,[6] ultrasound assisted methods,[7] cloud point extraction (CPE), and solid phase extraction (SPE).[8] SPE is an advantageous preconcentration technique as the solid sorbent can be easily regenerated without extra cost or effort. The off-line mode of SPE along with FAAS has been widely used with different sorbent materials for chromium preconcentration such as ion-imprinted polymers,[9] carbon nanotubes,[10] nanoparticles,[11] biosorbents,[12] silica,[13] chitosan,[14] and chelating resins.[15] However, the off-line mode is time-consuming, employs large volumes of reagents, and is prone to external contamination and analyte loss. The hyphenated flow injection-FAAS (FI-FAAS) system is advantageous over the conventional off-line methods as it rectifies the above shortcomings and automates the system.[16]

Carbon nanotubes (CNTs) are tubular carbon nanostructures comprising rolled up graphene sheets with diameter ~1 nm and large lengths, which provides them a high aspect ratio (length:diameter).[17] The CNTs can be classified as single-walled or multi-walled, depending on the number of sheets of graphene that constitute the walls of the CNTs. The aspect ratio for nanomaterials is several times higher than traditional adsorbents (chitosan,[18] silica,[19] polymeric adsorbents,[20] biosorbents,[21] etc.), thus enhancing some physical and chemical properties, the most important of which is the adsorption capacity. Thus, multiwalled carbon nanotubes (MWCNTs) have excellent surface areas and can serve as adsorbents for the remediation of metal contaminated systems.[22] In the past,

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.202001338