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Visible-light photoreduction, adsorption, matrix conversion and membrane separation for ultrasensitive chromium determination in natural water by X-ray fluorescence

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ABSTRACT

Nano-TiO_2 was immobilized onto cellulose filter paper, surface self-assembled with acid violet 43, denoted as TCP-AV, and used as a photocatalyst, solid phase adsorbent, filter membrane, and chemical sensor. Because the UV–vis wavelength response range of TCP-AV was expanded to 750 nm, 96.0% of Cr(VI) could be photoreduced to nontoxic and immobile Cr(III) under visible-light irradiation. After phototransformation of Cr(VI), both Cr(VI) and Cr(III) in natural water could be enriched onto TCP-AV with an adsorption ratio of 92.7%, which was due to the high adsorption capacity of TCP-AV (more than 4.66 mg) and the strong electric attraction between acid violet 43 (an anionic dye) and cationic Cr(III). After matrix conversion and matrix effects elimination, total chromium was determined directly by X-ray fluorescence, which detection limit (3σ, $n = 11$) was improved from about 2 mg L^{-1} to 0.59 $\mu g\,L^{-1}$. This proposed method with linear range of 2–100 $\mu g\,L^{-1}$ was successfully applied for total chromium determination in real water samples.

1. Introduction

Chromium (Cr) pollution in aquatic systems and drinking water sources is a serious threat to the environment and human health. According to the United States Environmental Protection Agency, the maximum acceptable concentration for total chromium in drinking water is 100 $\mu g\,L^{-1}$ and a more strict threshold (50 $\mu g\,L^{-1}$) is set by the World Health Organization and China [1]. Chromium in aqueous media occurs predominantly in its Cr(VI) and Cr(III) [2]. Cr(VI) is considered a priority pollutant by many countries, including the USA, UK, Canada, and China. Toxic and mobile Cr(VI) can be reduced into Cr(III), which will not only reduce the toxicity of chromium on living organisms, but also help in chromium preconcentration [2]. However, Cr(III) is a potential hazard, especially in the aquatic environment. Cr(III) is a competitive inhibitor of many cellular processes [3]. Furthermore, Cr(III) can be transformed into toxic Cr(VI) by the pathway of photo-oxidation in natural environments [4] and accumulated by aquatic organisms [5]. To avoid the toxicity of chromium in drinking waters, both Cr(III) and Cr(VI) should be monitored strictly.

The techniques for removing Cr from wastewater and drinking water are chemical reduction and precipitation, electrocatalytic reduction, coagulation, ions exchange, membrane separation, oxidation–reduction, and adsorption by several types of adsorbents, such as activated carbon, *Pinus sylvestris* bark, sphagnum moss peat, bone charcoal, clino-pyrrhotite, and humic acid coated magnetite [1,4,6–8]. Most of these methods focus on Cr(VI) removal, i.e., the methods for effective and simultaneous removal of Cr(VI) and Cr(III) are limited. They are often inefficient at low concentrations and limited by some drawbacks, such as sludge generation, exhausted materials disposal, and high operational costs [4,6].

Chromium in solid and liquid samples can be detected directly by X-ray fluorescence (XRF) for avoiding or at least reducing sample pretreatment to a minimum [9,10]. However, when XRF is used for aqueous samples, it suffers a number of limitations, including short linear range, matrix effects, and poor sensitivity (about 2 mg L^{-1}) [9]. Furthermore, both the chromium concentration in natural waters and the drinking water criterion of chromium (0.05 mg L^{-1}) are low, the preconcentration and matrix conversion are often necessary prior to determination by XRF.

Although the reduction from Cr(VI) to Cr(III) can be easily done by the other chemical treatment, photochemistry-based sample

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treatment has been used as greener approaches for the removal of Cr(VI) [6,11–13] and determination of Cr(III) and Cr(VI) [14], owing to its subsequent achievements in analytical characteristics (e.g., improved detection limits, low blanks, fewer matrix effects and simpler procedures) and greenness-related issues (environmentally friendly, safe procedures, cost-effective methods, and minimum use of chemicals) [15]. However, its application on total chromium determination by XRF has never been explored, to the best of our knowledge. Our analysis method involves on-line visible-light driven photoreduction of Cr(VI) into Cr(III), adsorption enrichment of Cr(III), membrane separation, matrix conversion, and determination by XRF without elution or digestion.

Nanosized TiO_2 is an ideal adsorbent and photocatalyst because of its excellent adsorptive and photocatalytic properties [16]. But the disadvantages of nano-TiO_2 on sample pretreatment for total chromium detection should be overcome, including UV irradiation, low reduction percentage, aggregation, removing and recycling. The immobilization of TiO_2 can offer stability, feasible continuous operation, easy separation and recycle, and significant decrease of operation costs [16]. As a cheap and abundant porous material, cellulose filter paper is used to immobilize nano-TiO_2 and denoted as TiO_2/cellulose paper (TCP). TCP can be easily prepared. Furthermore, TCP is sensitized by anionic dye (e.g., acid violet 43) to expand its UV–vis wavelength response range into visible-light region, improve adsorption affinity between it and Cr(III), and enhance its photoreduction activity on Cr(VI).

2. Experimental

2.1. Reagents and stock solutions

The ultrapure water (>18 MΩ cm) used throughout this study was prepared using a deionized water system (Milli-Q, Millipore). Stock solutions (1000 mg L^{-1}) of Cr(III) and Cr(VI) were purchased from Merck. Cellulose filter paper (qualitative, Φ7 cm) was purchased from Xinhua Paper Industry (Hangzhou, China). Tetrabutyl titanate (TBOT), ethanol, acetic acid (HAc), and NaOH were analytical grade (Sigma, USA). River-derived humic acid (HA) was purchased from International Humic Substances Society (USA) and dissolved in 0.1 mol L^{-1} of NaOH. The desired pH was adjusted by 0.1 mol L^{-1} of NaOH or HCl. All containers were soaked in 10% HCl solution at least 24 h before use.

2.2. Surface modification of TCP

TCP was prepared according to our literature procedure [16]. TCP was immersed, respectively, in acid violet 43 solution (4.0, 8.0, 12.0, 16.0, or 20.0 mg L^{-1}, pH 6.5, 50 mL). After ultrasound for 30 min, TCP was taken out from the solution, washed by water, dried at 60 °C till constant weight, and denoted as TCP-AV.

2.3. On-line visible-light driven photoreduction, adsorption, and filtration

The photoreduction and enrichment performances of TCP-AV were evaluated in a circulating filtration system shown in Fig. S1. After on-line adsorption of Cr(III) in dark (or on-line photoreduction of Cr(VI) and adsorption of Cr(III) under irradiation using a 160-W high pressure mercury lamp) from a given volume of water samples for selected time intervals, TCP-AV was taken out and dried at 60 °C. The concentration of Cr(III) on TCP-AV, Cr(VI) in water sample, or Cr(III) in water sample was determined by XRF (JSX-3400R, JEOL, Japan, with Rh-tube, operating at 50 kV, 1 mA, and 50 W), spectrophotometer (an UV-1200 PC spectrophotometer Beijing Rayleigh Analytical Instrument Co., Ltd, using diphenylcarbazide as chromogenic reagent), and ICP-MS (Agilent 7500cx, Agilent Technologies Co., USA), respectively. The mass of chromium adsorbed on the adsorbent (TCP-AV or TCP) was calculated according to the difference between the initial and final concentration in the solution. The adsorption (or removal) ratio was calculated based on the mass ratio between the adsorbed chromium on the adsorbent and the total chromium in the initial water sample.

2.4. Real samples analysis

The water samples, including drinking water and Jiulongjiang water, were collected from Zhangzhou, Fujian Province, China. These samples were filtered on a 0.22 μm pore cellulose acetate membrane (Millipore) to exclude insoluble particles. Without adjusting the solution pH, the filtrates were used for the further procedures, including photoreduction, adsorption, filtration, and determination by XRF.

3. Results and discussion

3.1. Characteristics of TCP-AV

Under the same preparation conditions of TCP, anatase TiO_2 with an average crystal size of 6.1 nm was obtained using hydrothermal method. Then, the light adsorption performance of nano-TiO_2 and TCP-AV was characterized in the range of 300–900 nm by solid ultraviolet spectrometry as shown in Fig. 1.

TCP only absorbed UV light ($\lambda < 387$ nm). After surface self-assembly, a stable, purple-blue complex was formed quickly on TCP, the UV–vis wavelength response range of TCP-AV was expanded to 750 nm, i.e., the visible-light region, and the band gap of the photocatalyst was reduced from 3.10 to 2.95 eV. Dye firmly adhered to the surface of TiO_2 because of the reaction between phenol hydroxyl (—OH) and hydroxyl (—OH) from acid violet 43 and nano-TiO_2 surface, respectively. Each of the cellulose filter paper was weighed before and after successive loading with TiO_2 and acid violet 43. The weight of filter, TiO_2, and acid violet 43 on the TCP-AV was 320.2, 40.8, and 7.7 mg.

3.2. Effect of surface self assembly on adsorptive and photocatalytic performance

Nano-TiO_2 surface self-assembled with the optimal concentration of acid violet 43 was necessary to improve its adsorptive and photocatalytic performance, at the same time to avoid the waste

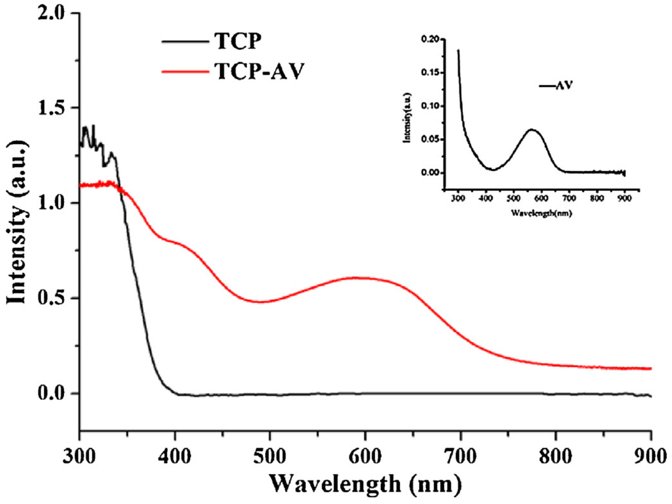

Fig. 1. Ultraviolet spectra of TCP and TCP-AV.