



Chitosan film loaded with silver nanoparticles—sorbent for solid phase extraction of Al(III), Cd(II), Cu(II), Co(II), Fe(III), Ni(II), Pb(II) and Zn(II)



Lubomir Djerahov^{a,b}, Penka Vasileva^a, Irina Karadjova^{b,*}, Rama Mohan Kurakalva^c, Keshav Krishna Aradhi^c

^a Department of General and Inorganic Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia “St. Kliment Ohridski”, 1 James Bourchier Blvd., Sofia, Bulgaria

^b Department of Analytical Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia “St. Kliment Ohridski”, 1 James Bourchier Blvd., Sofia, Bulgaria

^c Environmental Geochemistry, National Geophysical Research Institute (Council of Scientific & Industrial Research), Uppal Road, Hyderabad 500007, India

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ABSTRACT

The present study describes the ecofriendly method for the preparation of chitosan film loaded with silver nanoparticles (CS-AgNPs) and application of this film as efficient sorbent for separation and enrichment of Al(III), Cd(II), Cu(II), Co(II), Fe(III), Ni(II), Pb(II) and Zn(II). The stable CS-AgNPs colloid was prepared by dispersing the AgNPs sol in chitosan solution at appropriate ratio and further used to obtain a cast film with very good stability under storage and good mechanical strength for easy handling in aqueous medium. The incorporation of AgNPs in the structure of CS film and interaction between the polymer matrix and nanoparticles were confirmed by UV–vis and FTIR spectroscopy. The homogeneously embedded AgNPs (average diameter 29 nm, TEM analysis) were clearly observed throughout the film by SEM. The CS-AgNPs nanocomposite film shows high sorption activity toward trace metals under optimized chemical conditions. The results suggest that the CS-AgNPs nanocomposite film can be feasibly used as a novel sorbent material for solid-phase extraction of metal pollutants from surface waters.

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1. Introduction

The evaluation of chemical and ecological status of surface waters requires determination of background concentrations of chemical elements, naturally occurring in the aquatic environment. Reliable detection of such ultra-trace levels in highly mineralized waters or salted (sea, ocean) waters is difficult even with modern sensitive instrumental methods like ICP-OES or ICP-MS, due to spectral or isobaric matrix interferences. The separation of the analytes from the interfering matrix and their concentration by using solid-phase extraction (SPE) has become the most popular and greenest approach to solve the analytical problem. An ideal SPE procedure should be simple and easy to manipulate, should consume the least amounts of toxic reagents, should be performed in one reaction vessel and in the same time should ensure quantitative separation and concentration of all determined analytes.

Metal and metal oxide nanoparticles due to their unique optical, electrical, adsorptive, catalytic and magnetic properties as well as, high surface-to-volume ratio, have emerged as powerful adsorbents for environmental remediation's (Liu, Su, Zhang, Jiang, & Yan, 2011; Pradeep, 2009; Ray Phoebe, 2015) or as sorbents for environmental and biological sample preparation steps, for sensing, detection and speciation of toxic elements and organic contaminants (Dastafkan, Khajeh, Ghaffari-Moghaddam, & Bohlooli, 2015; Jiang et al., 2012; Liang & Guo, 2009; Ligler & White, 2013; Lucena, Simonet, Cárdenas, & Valcárcel, 2011; Pierce & Zhao, 2010; Valentini & Palleschi, 2008; Xu, Qi, Li, Bai, & Liu, 2015). However their low mechanical strength and low chemical resistance limit their practical application and complicate applied analytical procedures. In recent years, nanocomposites derived from inorganic nanoparticles incorporated in organic polymers are thoroughly studied because of their remarkably improved physical and chemical properties, achieved by combining the attractive functionalities of both components (Pan et al., 2010; Sarkar, Guibal, Quignard, & SenGupta, 2012; Wang, Xu, Chen, Huang, & Liu, 2014). Among the various biopolymers used, chitosan, a natural polysaccharide composed of poly(β-(1-4)-2-amino-2-deoxy-D-glucose), is considered as a potentially very good host material which has been reported for preparation and stabilization of metal nanopar-

* Corresponding author.

E-mail addresses: lubomirdjerahov@abv.bg (L. Djerahov), nhpv@wmail.chem.uni-sofia.bg (P. Vasileva), karadjova@chem.uni-sofia.bg (I. Karadjova), krngri@rediffmail.com (R.M. Kurakalva), keshav.aradhi@rediffmail.com (K.K. Aradhi).

ticles (Zain, Stapley, & Shama, 2014). Chitosan and its derivatives combine properties like biocompatibility, biodegradability and nontoxicity with a high capacity for metal complexation (Guibal, Vincent, & Roussy, 2009; Varma, Deshpande, & Kennedy, 2004; Vold, Vårum, Guibal, & Smidsrød, 2003) and have been used as efficient materials for the adsorptive removal of toxic elements (Kandile & Nasr, 2009; Liu & Bai, 2014; Wan Ngah, Teong, & Hanafiah, 2011; Wu, Tseng, & Juang, 2010; Yong, Shrivastava, Srivastava, Kunhikrishnan, & Bolan, 2015). Nanocomposites and hybrid nanomaterials based on chitosan matrix loaded with metal nanoparticles showed synergistically enhanced properties and high efficiency for sorption of metal and organic pollutants (Kyzas & Bikiaris, 2015; Shukla, Mishra, Arotiba, & Mamba, 2013). Chitosan composites with different shapes (particles, membranes, fibers), containing magnetic nanoparticles demonstrate high sorption activity toward toxic elements and rare earth elements (Abdollahi, Zeinali, Nasirimoghaddam, & Sabbaghi, 2014; Galhoum et al., 2015; Wang et al., 2014). A goethite/chitosan nanocomposite sorbents and chitosan coated magnetic nanoparticles have been used for removal of Pb and Cu from contaminated water (Rahimi, Moattari, Rajabi, & Derakhshan, 2015; Neeraj, Krishnan, Senthil Kumar, Shriaiashvarya, & Vinoth Kumar, 2016). For instance incorporation of Cu nanoparticles into chitosan matrix ensures sorption of toxic As, chromate and vanadate anions (de Godoi et al., 2014; de Godoi, Rodriguez-Castellon, Guibal, & Beppu, 2013). Nanosorbents based on nano sized zero valent Fe entrapped in chitosan matrix have been used for environmental remediation (Guo, Zhao, Qiu, & Shi, 2015; Horzum, Demir, Nairat, & Shahwan, 2013). A multi-functional nanocomposite of chitosan, silver nanoparticles, copper nanoparticles and carbon nanotubes has been used for Cd (II), Cu (II) and Pb(II) removal (Alsabagh, Fathy, & Morsi, 2015).

The incorporation of highly reactive Ag nanoparticles in chitosan with chelate forming capabilities, good mechanical strength and an excellent film-forming ability could be an efficient approach to prepare a sorbent film for quantitative retention of chemical elements and further development of simple analytical procedure for their determination. Chitosan film loaded with silver nanoparticles has not been used for SPE of trace metals however such approach avoids additional processes of centrifugation/filtration for sorbent removal and ensures very simple and easy handling. The present study is focused as a first step on the green synthesis of chitosan film loaded with raffinose capped Ag nanoparticles and its characterization, and as a second step on the examination of its sorption activity and capacity for application as a new synergistically improved nanocomposite sorbent for separation, enrichment and sensitive determination of trace metals in surface waters. To the best of our knowledge, this is the first time that nanocomposite film comprised of three components, *viz.*, AgNPs, raffinose and chitosan, has been applied as a sorbent material for solid phase extraction of trace elements from surface waters prior to their determination by inductively coupled plasma massspectrometry (ICP MS).

2. Experimental

2.1. Materials

Chitosan (CS, 82% deacetylated, low molecular weight, average weight 168 ± 14 kD (determined by intrinsic viscosity measurements, (Rinaudo, Milas, & Dung, 1993)) and acetic acid (CH_3COOH) were purchased from Sigma–Aldrich, Germany. Analytical grade silver nitrate (AgNO_3 , 99.8%, Merck, Germany), D-(+) raffinose pentahydrate (Alfa Aesar, Germany), and sodium hydroxide (NaOH, 99%, Merck, Germany) were used to prepare aqueous dispersion of silver nanoparticles. The stock standard solution for Al, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn was Multielement standard 5 for ICP

TraceCERT® Fluka in 10% HNO_3 . Working standard solutions were prepared daily by appropriate dilution. Certified Reference Material SLRS-5 (River Water Reference Material for Trace metals), National Research Council Canada was used for the validation of developed analytical procedure. Doubly distilled water was used in all experiments.

2.2. Preparation of chitosan film loaded with AgNPs (CS-AgNPs films)

Raffinose stabilized AgNPs were obtained by reduction of Ag^+ ions (AgNO_3 , 1.2×10^{-3} mol/L) with D-(+) raffinose (0.1 mol/L) used as both reducing and stabilizing agent, and NaOH (0.1 mol/L) as a reaction catalyst (Supplementary material, Scheme 1S). The CS-AgNPs matrix dispersion was obtained by mixing the as prepared AgNPs sol with chitosan solution (1 g chitosan dissolved in 100 mL 0.17 mol/L CH_3COOH) at a volume ratio 2:1, while stirring for 15 min, at room temperature. Transparent nanocomposite films were prepared by casting 7.5 mL of CS-AgNPs matrix dispersion on the bottom of 25 mL glass beakers and allowing the solvent to evaporate for 24 h, at a controlled environment of 50°C (Supplementary material, Scheme 2S). Nanocomposite films with total area of 15 cm^2 good mechanical strength during operation in aqueous medium were fabricated, most probably due to the cross-linking action of the AgNPs ($540\text{ }\mu\text{g Ag per film}$, determined by ICP-OES) embedded in the chitosan film. The formed films were immersed in 1 mol/L NaOH at room temperature for 1 h in order to neutralize the excess of acetic acid and finally washed with doubly distilled water until neutral pH. For comparison, pure chitosan films were also prepared by casting 2.5 mL CS solution following the same drying procedure.

2.3. Characterization of AgNPs and chitosan film loaded with AgNPs

The optical properties of chitosan solution, AgNPs aqueous suspension and CS-AgNPs nanocomposite film were characterized by UV–vis spectroscopy.

The crystal structure of AgNPs in nanocomposite CS-AgNPs film prepared was confirmed by X-ray diffraction (XRD) analysis. The XRD patterns were registered using an X-ray powder diffractometer (Siemens D500) equipped with $\text{CuK}\alpha$ radiation ($\lambda = 1.54\text{ \AA}$) in 2θ ranging from 10° to 80° .

Fourier transform infrared (FTIR) spectra were recorded in the spectral region of $4000\text{--}400\text{ cm}^{-1}$ using Thermo Scientific Nicolet 6700 FT-IR spectrometer. Dried CS-AgNPs nanocomposite film and native chitosan powder were pelletized with KBr for FTIR studies.

The morphology and particle sizes of AgNPs in the CS-AgNPs nanocomposite film were examined using a transmission electron microscope (TEM, JEM-2100) operating at accelerating voltage of 200 kV. Volume of $5\text{ }\mu\text{L}$ CS-AgNPs matrix dispersion were placed on a carbon-covered copper grid for TEM and then air-dried.

The CS-AgNPs nanocomposite film was studied using a scanning electron microscope (SEM, Hitachi S3400N) equipped with energy dispersive X-ray (EDX) spectroscope (Horiba EMAX7021H). EDX was used to address the composition of the nanocomposite film.

Zeta (ζ) potential of AgNPs was measured with a Zetasizer Nano ZS (Malvern) instrument after appropriate dilution of studied dispersion in 1 mmol/L KCl solution.

2.4. Sorption procedure

The pH of a 20 mL test solution, containing $100\text{ }\mu\text{g/L}$ (C_{initial}) of Al(III), Cd(II), Co(II), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II) and Zn(II) was adjusted to desired value (examined range 7–9), reached by addi-

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