Silver nanoparticles embedded in biocompatible polymers: extraction efficiency toward metals

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The nanocomposite films of chitosan (CS) or polyvinyl alcohol (PVA) loaded down with pre-synthesized silver nanoparticles (AgNPs) were prepared by green chemical approach and studied as an efficient sorbents for solid phase extraction of various chemical elements. Film synthesis is simple and consists of two steps: preparation of AgNPs dispersion and solutions of biocompatible polymers, mixing under stirring of these solutions and final drying at controlled temperature. Nanocomposite films with very good chemical and mechanical properties were obtained; films are stable for at least 3 months and could be used in any time without further treatment. The optical properties, structure and morphology of AgNPs and nanocomposite films were characterized by UV-Vis, TEM and SEM. The extraction efficiency of nanocomposite films prepared toward the most of frequently determined chemical elements was studied. Results obtained showed that under optimal chemical parameters nanocomposite films CS-AgNPs ensured quantitative separation and concentration of Al, Cd, Ni and Pb. Solid phase extraction procedures were developed for the determination of priority pollutants Cd, Pb and Ni in surface waters and Al, Cd and Pb in hemodialysis solutions. Determination limits achieved satisfied accepted permissible limits which makes proposed analytical procedures and new nanocomposite sorbent suitable for routine laboratory practice.

Key words: silver nanoparticles, biocompatible polymers, nanocomposite films, extraction efficiency, toxic metal pollutants.

1. INTRODUCTION

Chemical elements are ubiquitous in the environment. They are derived from both natural and anthropogenic processes. Toxic elements have been recognized as harmful for human health when present above certain levels and could cause various diseases [1]. Reliable control of concentrations of these elements in the environment or human daily life is an important analytical task. Direct instrumental methods are preferable and have been conventionally used for the determination of low levels of chemical elements however matrix interferences observed in some cases still required application of separation and concentration procedures.

Nanomaterials and nanotechnology provide powerful capabilities for determination and treatment of trace pollutants in the environment. Macro-, micro-, and nanomaterial-based tools and strategies have been successfully used for detection of chemical elements and their species in the environment [2]. Substantial progress on detection and treatment of organic and toxic metal pollutants has been achieved by using nanomaterials and analytical nanotechnology [3]. The use of metallic nanoparticles and composite materials for fast and simple quantification of toxic elements has exponentially increased in the past decade due to their unique physical and chemical properties such as surface plasmon resonance (SPR) band, surface enhancement of Raman scattering, nonlinear optical properties, high thermal and electrical conductivity, chemical stability and catalytic activity [4, 5, 6]. Colorimetric sensors for determination of Hg(II), Pb(II), Cu(II) based on metal nanoparticles are very
attractive, because they are rapid, low-cost and can be easily read out with the naked eye [7, 8]. The activity of silver nanoparticles (AgNPs) has been utilized to remove a number of toxic contaminants found in drinking water including pesticides, heavy metals and micro-organisms. Noble metal nanoparticles have been used for ultra low concentration detection of toxic elements in drinking waters [8]. The use of nanoparticles in sample preparation step has noted as a topic of growing interest in analytical sciences [9]. Biocompatible polymers with embedded noble metal nanoparticles have been applied as effective new materials for removal of metals from aqueous solutions [10] or applied as antimicrobial packaging materials and wound dressings, or also grafted onto various implants [11].

The aims of this study were (i) synthesis and characterization of nanocomposite films which consists of AgNPs incorporated in biocompatible polymer (chitosan (CS) or polyvinyl alcohol (PVA)) (ii) investigations on the possibilities to apply them as sorbents in solid phase extraction procedures for the separation and concentration of trace elements and (iii) development of analytical procedure for the determination of priority pollutants Cd, Pb and Ni in surface waters and Al, Cd and Pb in solutions for hemodyalisis.

2. EXPERIMENTAL

2.1. Materials

Silver nitrate (AgNO₃, 99.8%, Merck, Germany), D-(+) raffinose pentahydrate (Alfa Aesar, Germany), and sodium hydroxide (NaOH, 99%, Merck, Germany) were used to prepare aqueous dispersions of silver nanoparticles. Chitosan (low molecular weight, 75–85% deacetylated), polyvinyl alcohol (molecular weight 72000) and acetic acid (CH₃COOH) were purchased from Sigma–Aldrich, Germany. The stock standard solutions for Al(III), Cd(II), Ni(II) and Pb(II)) (1,000 μg/ml) were Titrisol, Merck (Germany) in 2% HNO₃. Working standard solutions were prepared daily by appropriate dilution. Doubly distilled water was used in all experiments.

2.2. Methods and apparatus

Ultraviolet-visible (UV–Vis) absorption spectra were recorded on an Evolution 300 spectrometer (Thermo Scientific, USA). The optical spectra of the solutions were recorded using doubly distilled water as a reference. The morphology and particle sizes of silver nanoparticles in colloidal solutions and in nanocomposite films were examined using a transmission electron microscope (TEM, JEM-2100) operating at accelerating voltage of 200 kV. The pure polymer films (without AgNPs) and nanocomposite films with incorporated AgNPs were studied for surface morphological variations using a scanning electron microscope (SEM, JEOL JSM 5510). Zeta (ζ) potential of silver nanoparticles was measured with a Zetasizer Nano ZS (Malvern) instrument. Ultrasonic bath UST2.4-150 (Siel, Bulgaria) was used.

2.3. Synthesis

2.3.1. Synthesis of AgNPs

Raffinose-stabilized AgNPs were prepared according to method previously described [12]. The one-step, one-phase “green” synthesis of silver nanoparticles in aqueous solution is based on chemical reduction of Ag⁺ (AgNO₃, 0.1 M) using D-(+) raffinose (0.1 M) as both reducing and stabilizing agent, and sodium hydroxide (0.1 M) as a reaction catalyst. The as-synthesized dispersion of AgNPs (with Ag concentration of 1.0×10⁻³ mol/L) were kept in closed container at room temperature and were stable for at least 2 months. They were used in any further experiments after homogenization by an ultrasonic bath for 30 min.

2.3.2. Preparation CS-AgNPs and PVA-AgNPs films

Transparent nanocomposite films were prepared by: mixing under stirring (15 min at room temperature) of 1% (w/V), chitosan solution in 1% (V/V) CH₃COOH or 4% (w/V) PVA solution in distilled water with AgNPs aqueous dispersion in a different volume ratios. 7.5 ml of mixtures obtained were transferred in 25 ml glass beaker and dried in a controlled environment at 50 °C. Depending on the polymer/AgNPs ratios nanocomposite films with different amounts of AgNPs were obtained. The formed CS-AgNPs films were then immersed for 1 h in 1 mol/L NaOH at room temperature in order to neutralize the excess of acid and finally were washed twice with doubly distilled water. For comparison, pure polymer films of CS or PVA were also prepared by drying the respective aqueous solutions of pure polymers. The thickness of the nanocomposite films was optimized taking into account their mechanical stability during process of sorption – the aim was to keep the integrity of the film.

2.4. General procedure

A model solution of 20 ml with pH adjusted in the range from 7–9 containing 500 μg/L Al(III),
Cd(II), Ni(II) and Pb(II) was placed in a beaker with nanocomposite film. After sorption time of 24 h, the supernatant was carefully decanted; the film was washed twice with doubly distilled water and eluted with 2 ml 1–4 mol/L HNO₃ or dissolved in 0.4 ml of conc. HNO₃ at 80 °C and diluted to 2 ml with doubly distilled water. Metal content in the supernatant and in the eluate solutions was measured by Electrothermal Atomic Absorption Spectrometry (ETAAS). Matrix matched standards were used for calibration of ETAAS measurements. They were obtained by additions of known amounts of analytes to the blank composite film, dissolved according to the same dissolution procedure.

2.5. Sorption characteristics

The degree of sorption of the investigated pollutants is presented as

\[
Ds (%) = \left( \frac{A_i - A_{eff}}{A_i} \right) \times 100,
\]

where \(A_{eff}(\mu g)\) is the mass of metal in the supernatant after sorption from a solution with a total metal mass \(A_i(\mu g)\).

The kinetics of the analytes sorption was investigated in a batch system for 0.5–24 hours. Sample aliquots were analyzed by ETAAS (to maintain constant sample volume) and it was established that the saturation values (i.e., equilibrium extraction efficiency) were gradually reached within 24 hours.

2.6. Analytical procedures

2.6.1. Analysis of surface waters: 30 ml water sample with pH (8–8.5) was placed in a beaker with a nanocomposite film. After 24 h sample solution is decanted, film washed twice, dissolved with 0.4 ml of conc. HNO₃ and diluted to 2 ml with doubly distilled water. Priority pollutants Cd(II), Pb(II) and Ni(II) content was quantified in this solution by ETAAS.

2.6.2. Analysis of solutions for hemodialysis: 20 ml 15% (w/w) saline hemodialysis solution was placed in a beaker with a nanocomposite film. After 24 h sample solution is decanted, film washed twice, dissolved with 0.4 ml of conc. HNO₃ at 80 °C and diluted to 2 ml with doubly distilled water. The content of trace elements Al, Cd and Pb was quantified in this solution by ETAAS.

3. RESULTS AND DISCUSSION

3.1. Characterization of silver nanoparticles and nanocomposite CS-AgNPs and PVA-AgNPs films

UV-Vis absorption measurements of the primary yellow orange solution of raffinose-stabilized AgNPs showed UV-Vis spectrum with SPR band at \(\lambda_{\text{max}}\) 412 nm (Fig. 1a). The shape of the plasmon band is symmetrical and quite narrow, suggesting
that AgNPs are mainly spherical with narrow size distribution [13]. The raffinose-stabilized AgNPs were observed to be stable in solution even 2 months after their preparation. The high colloidal stability of raffinose-stabilized AgNPs was confirmed by the ζ potential value of $-47.2 \pm 1.1$ mV measured in 1 mmol/L KCl at pH 6.8. The CS-AgNPs mixed solution exhibits slightly broadened main SPR band peaking at the same wavelength as AgNPs colloidal solution. The asymmetric broadening toward long wavelengths in the spectrum is a sign for some degree of agglomeration in CS-AgNPs solution. It is worth noting that the intensity of this broad band increases with the increase of storage time, most probably due to the attraction forces between the nanoparticles inside the chitosan matrix, making them to move, agglomerate, and form the crystal structures. The TEM observation of CS-AgNPs film (Fig. 1b) indicates that some agglomeration of part of AgNPs takes place during their incorporation into the chitosan matrix and reveals the presence of quasi-spherical silver nanoparticles with an average diameter of about 25 nm. Despite the observed partially agglomeration of nanoparticles, CS-AgNPs films maintain optical clarity. An even distribution of the agglomerates and individual silver nanoparticles into the CS-AgNPs film was clearly observed in SEM image shown on Fig. 1c.

The absorption spectra of the colloidal solution containing Ag nanoparticles and the corresponding PVA-AgNPs film matrix solution are shown in Figure 2a. It can be seen that the PVA-AgNPs solution exhibits the same symmetrical and narrow surface plasmon absorption band as colloidal solution of AgNPs, however, located at 420 nm. The shift to the longer wavelengths upon incorporation of Ag nanoparticles into PVA can be explained by the change of the dielectric properties of the surrounding environment [14]. The absence of any band broadening clearly indicates that the Ag nanoparticles are not agglomerated and are well distributed within the polymer matrix. TEM measurement showed that the resulting film mainly contains individual quasi-spherical silver nanoparticles with average diameter of 25 nm (Fig 2b). In addition to the nanospheres, some typical polyhedral nanoparticles (multiple twined nanocrystals) can be easily observed (Fig. 2b: inset).

The CS film (Fig. 3b) exhibited a dense and uniform plain microstructure. As far as AgNPs are anchored by chitosan functional groups, the homogeneity of surface morphology is maintained in CS-AgNPs film (Fig. 3d) [15]. CS-AgNPs film showed the presence of nanoparticles in the entire film (white dots in Fig. 1c), confirming the good dispersion of AgNPs within the polymer matrix. In the case of PVA based films, inhomogeneous rough surface with aggregates of polymer submicroparticles was observed for PVA film (Fig. 3a), whereas PVA-Ag NPs film showed homogeneous surface morphology (Fig. 3c).

### 3.2. Effect of chemical parameters on the extraction efficiency of CS-AgNPs and PVA-AgNPs composite films toward Al(III), Cd(II), Ni(II) and Pb(II)

The effect of various parameters such as pH, sorption medium and sorbent amount (Ag content

Fig. 2. UV–vis absorption spectra of PVA – AgNPs matrix solutions (a), Transmission electron microscopy image of PVA – AgNPs nanocomposite film (b)
in nanocomposite film) on the extraction efficiency of nanocomposite films toward Al(III), Cd(II), Ni(II) and Pb(II) was studied.

3.2.1. Effect of pH and sorption medium on the degree of sorption of Al(III), Cd(II), Ni(II) and Pb(II). Sorption behaviour of elements depends on a number of experimental parameters and sorbent properties and are related mainly to (i) presence of a large number of functional groups (acetamido, primary amino and hydroxyl groups) in the chitosan and degree of their protonation/deprotonation (pKa varies between 6.3 and 6.8 [17]); (ii) surface properties of AgNPs (negatively charged particle surface confirmed by highly negative ζ-potential measured) and (iii) metal speciation in solution. The results obtained for the influence of pH which was varied in the range 7–9 and achieved by using NH₄OH or NaOH on the degree of sorption of elements studied are presented in Figure 4.

The trend observed is an increased sorption for each metal ion with increasing pH of the solution. Quantitative sorption for Al(III), Cd(II), Ni(II) and Pb(II) is achieved at pH 8–9 in the presence of NH₄OH (Fig. 4a). This is due to a favorable combination of several factors resulting in high values of the extraction efficiency. First, amino groups of chitosan are in the non-protonated form, and become available for interaction with metal cations through the pair of electrons disposed by nitrogen, leading to an increase on the degree of adsorption. Second, hydroxyl groups of chitosan are partially deprotonated, as well and available for complex formation. Third, the negatively charged surface of AgNPs attracts positively charged metal species (free metal ions or metal complexes with NH₃). When the pH of the solution was adjusted with NaOH, maximum extraction efficiencies varied between 50% (for Al(III) and Pb(II)) and 80% (for Cd(II) and Ni(II)) at pH 9 (Fig. 5b). This could be related to the ability of Al(III) and Pb(II) to form stable negatively charged hydroxocomplexes. Finally, pH 8–8.5 adjusted with NH₄OH could be accepted as an optimal for simultaneous quantitative sorption of Al(III), Cd(II), Ni(II) and Pb(II) on CS-AgNPs nanocomposite films. Analogous experiments carried out with PVA-AgNPs showed much lower degree of sorption especially for Cd(II) and Pb(II), most probably due to the much lower sorption activity of PVA film itself and absence of N-containing functional groups.

In order to prove hypothesis that the sorption efficiency of nanocomposite film CS-AgNPs is due to the combined chemical activities of CS film and incorporated AgNPs, experiments were performed...
for degree of sorption (at optimal sorption conditions pH 8–8.5, NH$_4$OH) achieved with each one of CS/PVA films and AgNPs. Results presented in Table 1 undoubtedly showed synergetic sorption effect of nanocomposite material CS-AgNPs which ensures quantitative sorption for all tested analytes over CS film (extraction efficiencies 39–59%) and AgNPs (extraction efficiencies 83–93%). Analogous results were found for PVA film and composite sorbent PVA-AgNPs. The sorption of analytes on PVA membrane is due to the partial deprotonation of hydroxyl groups and their interaction with positively charged metal species. The degree of sorption is increased on PVA-AgNPs composite film, yet not quantitative due to the absence of amino groups on the film surface.

3.2.2. Effect of the AgNPs content in the nanocomposite films. The chemical activity of AgNPs in the nanocomposite film requires optimization of their content. The experiments were carried out with films containing from 540 to 1080 µg Ag and constant CS mass of 25 mg in the film matrix. The results showed that 540 µg Ag was sufficient for the quantitative sorption of all studied analytes. Lower AgNPs amount were not tested as far as they play also role of crosslinker for CS ensuring a good mechanical stability of the nanocomposite films.

3.2.3. Effect of elution parameters. The CS-AgNPs nanocomposite films demonstrate very good mechanical stability, so it was attempted to elute sorbed analytes with relatively low concentrations of HNO$_3$ (2–4 mol/L). Unfortunately results obtained showed that process of elution is relatively long (more than 4 h), degree of elution is in the range 50–70% for all studied analytes and composite film is not suitable for next sorption cycle. That is why complete film dissolution with minimum amount of conc. HNO$_3$ was accepted as more efficient procedure for quantitative recovery of retained analytes. The process of film dissolution is accelerated at elevated temperatures (80 °C was accepted as optimal) and could be finalized in 4–5 min.

Brief conclusion – CS-AgNPs composite film is an efficient sorbent, ensures quantitative sorption of Al(III), Cd(II), Ni(II) and Pb(II) for 24 h at pH 8–8.5 (adjusted with NH$_4$OH), elution of retained analytes is achieved by complete dissolution with small amount HNO$_3$. The whole separation and concentration procedure could be performed in one analytical vessel (in which the composite film is synthesized).

![Fig. 4. Effect of pH on Al(III), Cd(II), Ni(II) and Pb(II) sorption by CS-AgNPs nanocomposite film in (a) NaOH and (b) NH$_3$](image)

Table 1. Comparative results for the degree of sorption of Al(III), Cd(II), Ni(II) and Pb(II) ions with sorbents: upon solid ph CS-AgNPs nanocomposite film, PVA-AgNPs composite film, CS film, PVA film and AgNPs (pH 8–8.5, NH$_4$OH), three parallel experiments

<table>
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<tr>
<th>Sorbents</th>
<th>Degree of sorption, %</th>
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<tr>
<td></td>
<td>Al(III)</td>
</tr>
<tr>
<td>CS-AgNPs</td>
<td>99±3</td>
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<td>CS</td>
<td>39±5</td>
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<td>AgNPs</td>
<td>83±4</td>
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<td>PVA-AgNPs</td>
<td>73±4</td>
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<td>PVA</td>
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3.3. Analytical application

3.3.1. Determination of Cd(II), Ni(II) and Pb(II) in surface waters. Samples of 30 ml sea water (Black sea, Bourgas) and river water (Iskar) are spiked with known amounts (ranged between 0.01–0.1 µg/L) of Cd(II), Ni(II) and Pb(II) and passed through the optimized procedure described in Paragraph 2.6. Recoveries achieved varied in the range 94–97%, 95–98% and 93–96% for Cd(II), Ni(II) and Pb(II), respectively. Relative standard deviation is between 5 and 11% for all studied elements in this concentration range. Detection limits achieved are 0.002 µg/L, 0.02 µg/L and 0.04 µg/L for Cd(II), Ni(II) and Pb(II) respectively and completely satisfy requirements of European legislation (Directive 2008/105/EO) for priority pollutants in surface waters.

3.3.2. Determination of Al(III), Cd(II) and Pb(II) in solutions for hemodialysis. The solution for hemodialysis usually contained high concentrations of alkali chlorides and direct instrumental determination of controlled elements concentrations is difficult. Separation procedure in this case is required for elimination of matrix interferences. Model saline hemodialysis solutions with matrix concentrations: 10% w/w, 15% w/w and 20% w/w were spiked with known amounts (ranged between 0.1–0.2 µg/L) of Al(III), Cd(II), and Pb(II) are passed through the optimized procedure described in Paragraph 2.6. Recoveries achieved for 10% w/w and 15% w/w saline solutions varied in the range 91–95%, 93–96% and 92–95% for Al(III), Cd(II) and Pb(II) respectively. Recoveries for 20% w/w saline solution were below 85%, most probably due to the slow diffusion of analytes to the film surface in this highly saline solution. Optimized analytical procedure for the determination of Al(III), Cd(II) and Pb(II) in hemodialysis solutions is characterized with detection limits: 0.01 µg/g for Al, 0.001 µg/g for Cd and 0.05 µg/g for Pb and fulfils the requirements of European Pharmacopoeia.

4. CONCLUSION

Cast nanocomposite film of biocompatible polymer CS with embedded AgNPs was prepared and characterized for its optical and structural properties. The extraction efficiency of nanocomposite film toward Al, Pb, Cd and Ni was studied and analytical procedures for determination of Cd, Ni and Pb in surface waters and Al, Cd and Pb in hemodialysis solutions were proposed.

REFERENCES

СРЕБЪРНИ НАНОЧАСТИЦИ, ВГРАДЕНИ В БИОСЪВМЕСТИМИ ПОЛИМЕРИ: ЕКСТРАКЦИОННА ЕФЕКТИВНОСТ СПРЯМО МЕТАЛИ

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(Резюме)

Нанокомпозитни филми от (CS) или поливинилов алкохол (PVA), с вградени в тях предварително синтезирани сребърни наночастици (AgNPs), са получени с помощта на „зелен” химичен подход и са приложени като ефективни сорбенти за твърдофазна екстракция на различни метали. Процедурата за получаване на филмите се състои от два етапа: получаване на дисперсия от AgNPs и разтвори на биосъвместими полимери, смесването им при разбъркване и следващо изпаряване на разтворителя при контролирана температура. Получените нанокомпозитни филми са с много добри химични и механични свойства; филмите са стабилни поне три месеца след получаването им и могат да се използват без допълнително третиране. Оптичните свойства, структурата и морфологията на AgNPs и нанокомпозитните филми са охарактеризирани с UV-Vis, TEM и SEM. Изследвана е тяхната екстракционна ефективност спрямо често определяни метали. Резултатите показват, че при оптimalни условия нанокомпозитният филм CS-AgNPs осигурява количествено разделяне и концентриране на Al, Cd, Ni и Pb. Разработени са процедури за твърдофазна екстракция и определяне на приоритетните замърсители Cd, Pb и Ni в повърхностни води, и Al, Cd и Pb в разтвори за хемодиализа. Постигнатите граници на определяне удовлетворяват допустимите концентрации за тези метали, което прави предлагените аналитични процедури и новия нанокомпозитен сорбент подходящи за рутинната аналитична практика.