Raffinose-stabilized silver nanoparticles as a novel sorbent for separation, preconcentration and speciation of chromium

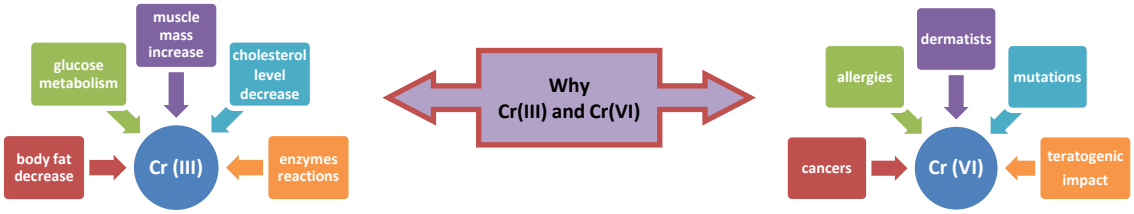
L. Djerahov[1], P. Vasileva[2*], I. Karadjova[3]

[1] Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry, Department of Analytical Chemistry,
Faculty of Chemistry and Pharmacy, University of Sofia "St. Kliment Ohridski", Bulgaria
[2*] Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia "St. Kliment Ohridski", Bulgaria
[3] Department of Analytical Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia "St. Kliment Ohridski", Bulgaria
*Corresponding author's e-mail: pvasileva@chem.uni-sofia.bg

Synthesis of raffinose – stabilized silver nanoparticles

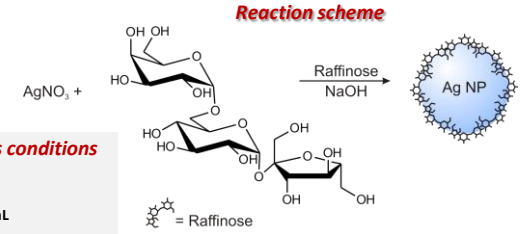
Analytical problem Cr(III)? Cr(VI)?

Developing of simple and sensitive method for chromium speciation in surface water



GREEN SYNTHESIS AND CHARACTERIZATION OF Ag-NPS

Reaction scheme

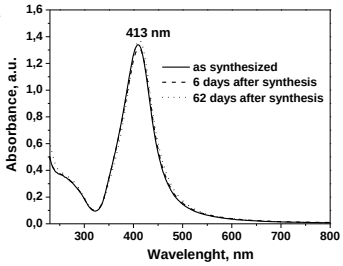


Optimal synthesis conditions

$c(AgNO_3)$ = 0,001 mol/L
n(Ag+):n(Raff) = 1:20
V(NaOH solution) = 4 mL
Temperature - 30 °C
Ultrasound bath: 38 kHz, 100 W

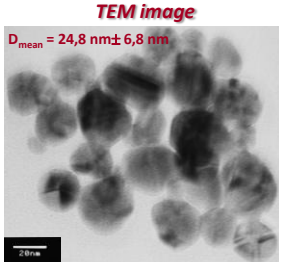
UV-visible absorption spectrum

Photograph of Ag NPs aqueous dispersion



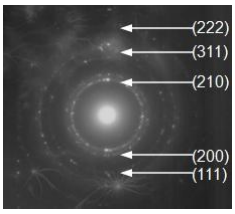
- Absorption measurement of the light yellow aqueous solution of silver nanoparticles shows an UV-visible spectrum with a maximum at 413 nm.
- The registered reproduction of the optical characteristics of the nanoparticles in different period of time demonstrated their high colloidal stability at storage. Measured value of negative ζ-potencial confirmed this stability.

TEM image



- The resulting product mainly consisted of quasi-spherical silver nanoparticles.
- Some polyhedral nanoparticles are easily observed.
- About 150 NPs counted from TEM images

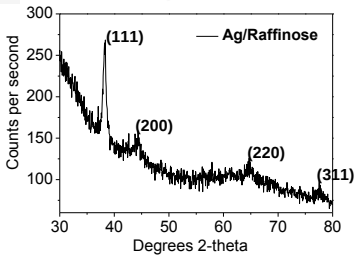
SAED pattern



- The polycrystalline nanoparticles with fine nanocrystallite nature are observed.

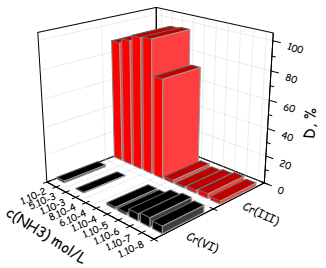
XRD pattern

- The XRD pattern of Ag NPs showed four relatively broad diffraction peaks with 2θ of 38.2°, 44.4°, 64.6° and 77.4° corresponding to the (111), (200), (220) and (311) planes, respectively, of the fcc silver, confirmed by SAED pattern from TEM observation. The broad diffraction peaks with relatively low intensity indicate the formation of complexes between crystalline Ag NPs and raffinose as their capping agent.

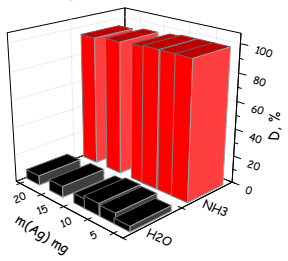


CHROMIUM SPECIATION USING Ag-NPS SORBENT

Sorption in NH_3 solution
Cr (III) vs Cr (VI) ???

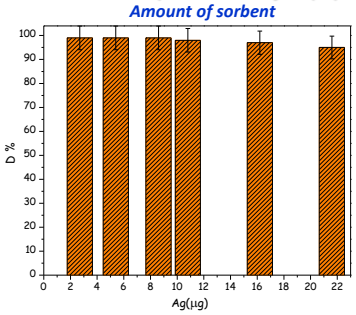


Sorption of Cr (III)
NH_3 vs H_2O solution ???

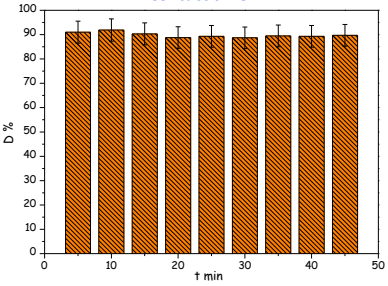


Optimization of Cr (III) sorption conditions in NH_3 solution

Amount of sorbent



Contact time



ANALYTICAL PROCEDURE

- The method developed consists of two steps:
  - After addition of Ag NPs to a mixture of Cr(III)+Cr(VI), adjusted at pH 9.5 by NH_3 solution, Cr(III) is selectively sorped, removed and determined by ICP-MS;
  - determination of total chromium after the reduction of Cr(VI) to Cr(III) with ascorbic acid.

Finally, the amount of Cr(VI) is calculated by subtracting Cr(III) concentration from total Cr concentration.

CONCLUSIONS

- Raffinose-stabilized silver nanoparticles (Ag-NPs/Raff) were produced via green chemical reduction method and characterized by several techniques such as UV-Vis spectroscopy, XRD, TEM and SAED.
- Ag-Raff NPs were used as a selective sorbent for Cr(III) in the NH_3 solution at pH 9.5.
- The detection limit for Cr(III) and Cr(VI) was found to be 0.005 $\mu g L^{-1}$ and 0.008 $\mu g L^{-1}$, respectively; RSD varied from 4% to 9% and from 5% to 11%, respectively.
- Analytical procedure have been developed for chromium speciation in surface waters.
- The method was validated by comparative analysis of surface waters using the proposed method and analytical procedure based on liquid/liquid extraction.

Recoveries of Cr (III) and Cr(VI) for tap and mineral water samples

Cr species	LOD µg/L	RSD, %	Recovery, %	
			Tap water	Mineral water
Cr (III)	0.005	4-9	96±3	95±3
Cr (VI)	0.008	5-11	95±4	94±4

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