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National Recovery and Resilience Plan
OF THE REPUBLIC OF BULGARIA

NEW COMPOSITE MATERIALS FOR SELECTIVE DETERMINATION OF TOXIC FORMS OF CHEMICAL ELEMENTS IN ENVIRONMENTAL SAMPLES (GRANT № 70-123-469)

Newly designed organic-inorganic nanocomposite membrane for simultaneous determination and speciation analysis of chromium and manganese in water samples

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Motivation and goals

Chromium is a relatively abundant element in the earth's crust, existing in the environment mainly as Cr(III) and Cr(VI) oxidation states, which have quite different biological activity, chemical behavior and toxic effects. Manganese is an essential element for humans and animals. The most prevalent oxidation states of manganese are Mn(II) and Mn(VII). Mn(II) is toxic to mitochondria in cells at high concentrations, whereas Mn(VII) is widely used as an oxidizing agent in synthesis procedures as well as in analytical chemistry and also as a disinfectant. Therefore, accurate information on the toxicity of Cr and Mn could be obtained by the development of analytical methods capable to determine not only the total Cr and Mn in the different environmental samples but also allowing determination of their species separately with sufficient precision and sensitivity.

Direct determination of low levels of these two metal species in real samples appears to be a difficult task by the atomic absorption spectrometry, inductively coupled plasma-optical emission spectrometry, inductively coupled plasma-mass spectrometry, etc. due to some matrix interferences.

The main goals in this research were directed towards preparation of novel hybrid nanosorbent of membrane type (PVA-PEO-TEOS-AuNPs) and developing a procedure based on this simple solid phase extraction system for quantification of low levels of inorganic Mn and Cr species in different water samples. The analytical method is based on the experimental fact that Mn(II) and Cr(III) cations could be quantitatively retained on the PVA-PEO-TEOS-AuNPs membrane, whereas Mn(VII) and Cr(VI) oxyanions remained in the solution without retention.

Experimental

Synthesis of Au@Starch NPs

Starch solution, 0.2 % + $HAuCl_4$, 0.001 mol/L
→ Sonication 15 min
→ Au-Starch complexes + D-glucose, 0.1 mol/L
→ Sonication 15 min
→ NaOH, 0.1 mol/L + Reaction mixure
→ Sonication 60 min
→ Au@Starch NPs aqueous dispersion

Preparation of PVA-PEO-TEOS-AuNPs hybrid membranes

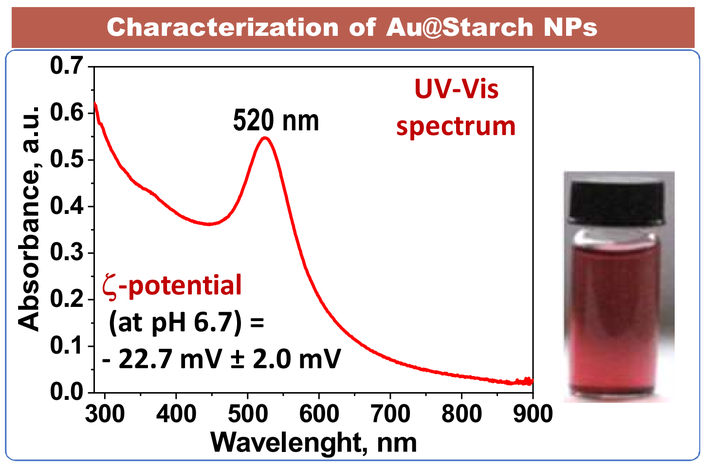
PVA-PEO-TEOS polymer matrix solution + Au@Starch NPs aqueous dispersion
→ Magnetic stirrer, 15 min
→ PVA-PEO-TEOS-AuNPs hybrid matrix dispersion
→ Casting and drying at 50 °C for 15 h
→ Hybrid nanocomposite membranes PVA-PEO-TEOS-AuNPs

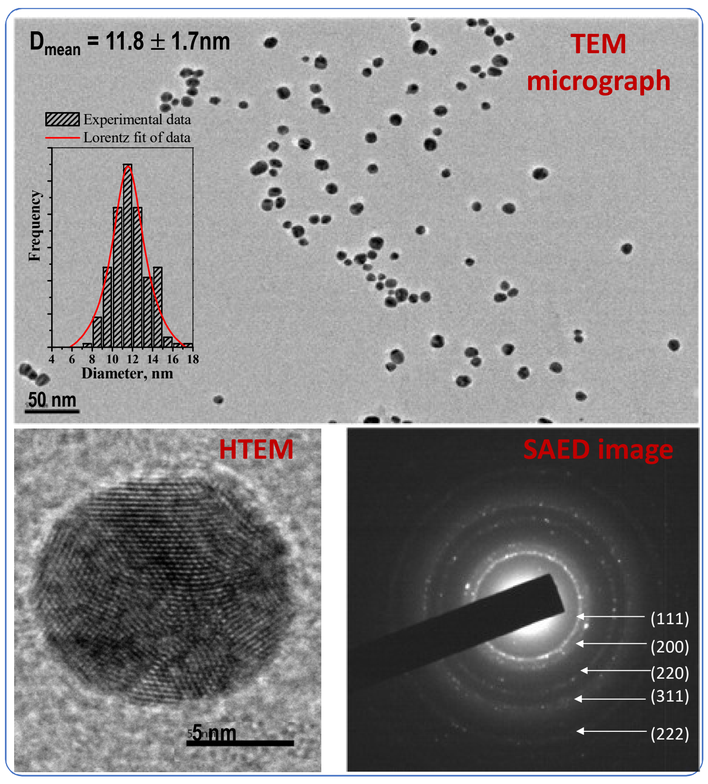
Methodology

- The organic polymers employed, poly(vinyl alcohol) (PVA) and poly(ethylene oxide) 400 (PEO), are renowned for their biocompatibility and non-toxicity. Tetraethoxysilane (TEOS) served as a precursor for the inorganic polymer silica.
- A solution containing PVA, PEO, and pre-hydrolyzed TEOS was combined with pre-synthesized starch-coated AuNPs to form a cast hybrid nanocomposite membrane.
- The characterization of both the gold nanoparticles and the hybrid membrane was conducted using UV-visible spectroscopy,, transmission and scanning electron microscopy, DSC measurements.
- The extraction efficiency of PVA-PEO-TEOS-AuNPs membrane toward Cr(III) and Mn(II) was investigated under various pH in batch mode.
- The adsorption behavior of Cr(III) and Mn(II) was analyzed by four isotherm (Langmuir, Freundlich, Temkin, Dubinin–Radushkevich (DRK)) and three kinetic (pseudo-first order, pseudo-second order, sigmoidal) models.

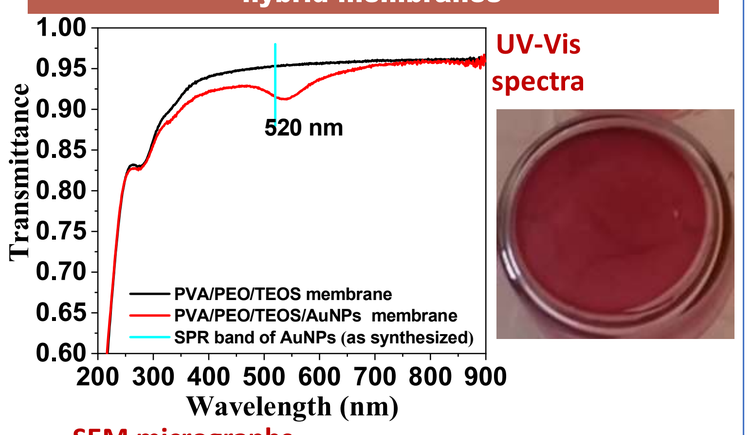
Results

Characterization of Au@Starch NPs

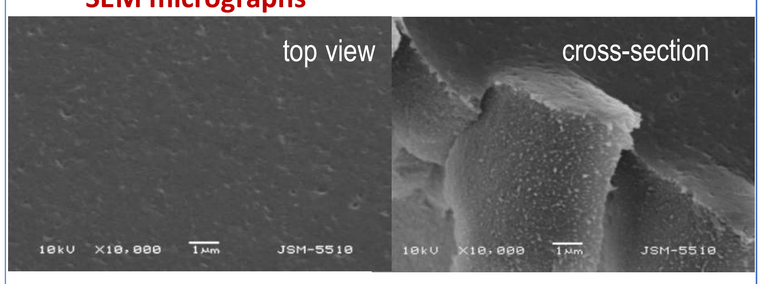




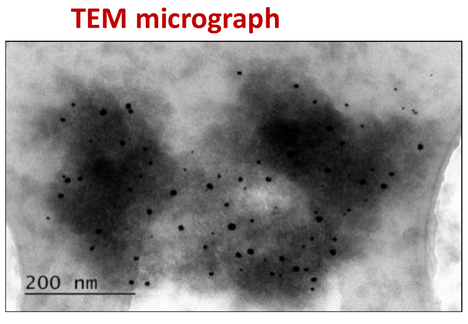
Characterization of PVA-PEO-TEOS-AuNPs hybrid membranes



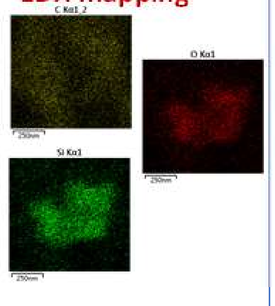
SEM micrographs



TEM micrograph



EDX mapping



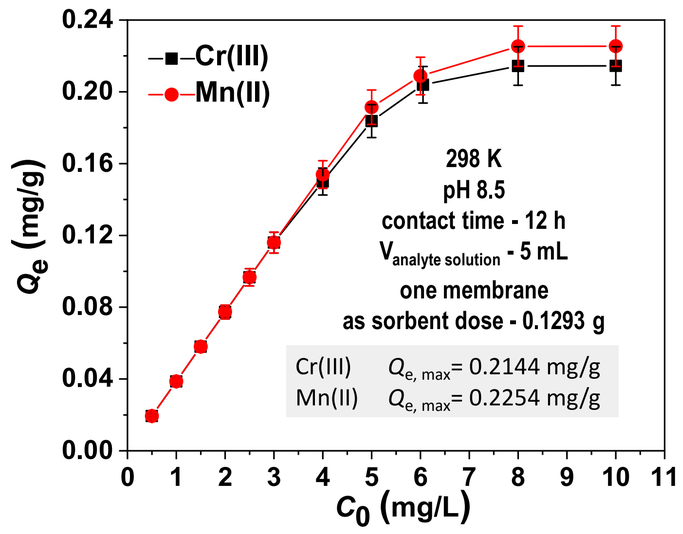
Quantitate data from DSC measurements

Sample	Composition	Temperature (°C)		ΔH_m (J g^{-1})	Degree of crystallinity X_c (%)
		T_g	T_m		
PVA membrane	PVA 100 %	87.5	224.2	65.074	46.95
PVA/PEO membrane	PVA 87,5 % PEO 2,5 % PEO:PVA = 0.14	95.0	218.9	45.678	37.66
PVA/PEO/TEOS membrane	PEO:PVA = 0.14 PVA 70.0 %	95.0	213.9	9.776	10.08
PVA/PEO/TEOS/ AuNPs membrane	PEO 10.0 % TEOS (as SiO_2) 20 %	104.0	213.4	26,277	27.08

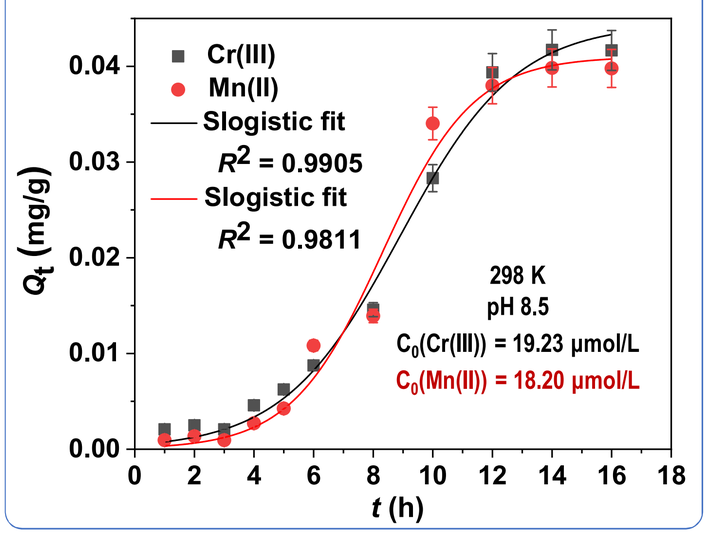
Results

Sorption Isotherms and kinetics

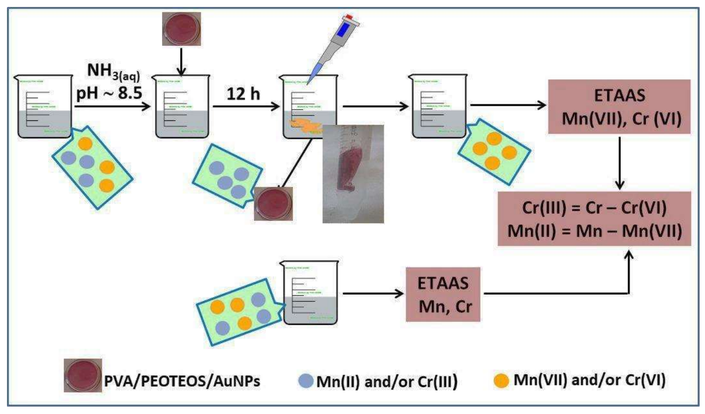
Best fit: Langmuir isotherm model $C_e/q_e = C_e/Q_m + 1/(Q_m \times K_L)$



Best fit: sigmoidal kinetic model $Q_t = Q_e/(1 + \exp(-k \times (t-\tau)))$



Analytical procedure



LOD: Cr(III), Cr(VI) - 0.001, 0.05 μg/L; Mn(II), Mn(VII) - 0.0005 ; 0.05 μg/L
RSD: Cr 5 ÷ 9 % ; Mn 6 ÷ 11 %
Recovery: Cr and Mn 95 ÷ 108 %

Conclusions

- Completely green method for the synthesis of hybrid nanocomposite membranes loaded with AuNPs is proposed; the synthesis procedure is with very good repeatability and the membranes obtained were with excellent uniformity, high mechanical strength and allowed easy manipulation.
- Selective adsorption of Cr(III) and Mn(II) occurred on the membrane surface within 12 hours at optimum pH of 8.5, while Cr(VI) and Mn(VII) remained in the effluent solution and were quantified using ETAAS; subsequent to dissolving the membrane in aqua regia, Cr(III) and Mn(II) concentrations were measured using ETAAS.
- The adsorption data exhibited the best fit with the Langmuir model, while the kinetics followed a sigmoidal model.
- A simple SPE extraction procedure is developed for selective determination of Cr(VI) and Mn(VII), based on preliminary quantitative retention of Cr(III) and Mn(II) on hybrid polymer membrane loaded with gold nanoparticles.
- The determination limits achieved for toxic species Cr(VI) and Mn(VII) fulfil the requirements for their monitoring in surface water bodies under the demand of Water Frame Directive.
- The developed analytical method was applied to the simultaneous speciation of chromium and manganese in river water samples from national monitoring points.

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