

Preconcentration of heavy metals using ceria-coated silica-magnetite nanoparticles prior to their determination by ICP-OES



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1. INTRODUCTION

Nanosized metal oxides, including ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides and cerium oxides, provide high surface area and affinity for heavy metals from aqueous systems

Ceria (CeO₂) is an attractive metal oxide for many technological applications owing to its unique physicochemical properties, including high hardness, chemical inertness, high-temperature strength, and high oxide ion conductivity.

In this study, magnetic-silica nanoparticles are synthesized by a co-precipitation and sol-gel method followed by the ceria coating through a homogenous precipitation from Ce(III) - HMT. The resulting material is characterized with XRD, FTIR and SEM and is examined for its use for the non-specific preconcentration of heavy metals from environmental water samples and biological matrices. The nanoparticles are separated from the sample solution magnetically and analyzed with ICP-OES using a slurry suspension sampling approach.

2. MATERIAL AND METHODS

Synthesis of silica magnetic nanoparticles

Tetrahydrate iron(III) chloride 0.42g, hexahydrate iron(II) chloride 1.13g were mixed in 100mL of deoxygenated water, under vigorous stirring. The temperature was raised to 80°C and 5mL of 25% ammonia was added to form a black precipitate of magnetite NPs. The suspension was heated for 30min under continuous flow of nitrogen and the magnetic nanomaterial was separated from the supernatant by a magnet. The particles were subsequently coated with TEOS. The procedure consisted of placing 25mL of ethanol and 8mL of DDW into a beaker containing 0.5mg of magnetite nanoparticles. Then, 1mL of ammonia and 500µL of TEOS were added following an overnight stirring, under nitrogen. After magnetic separation, the silanized magnetic particles were thoroughly washed with ethanol.

Synthesis of ceria silica magnetic nanoparticles

Ceria-modified magnetite-silica nanoparticles were prepared by precipitating CeO₂ and in-situ formation of the modified nanoparticles from aqueous solutions of cerium (III) nitrate and HMT. The magnetic ceria nanopowder was obtained by applying an external magnetic field and after washing with deionized water and ethanol the nanomaterial was oven dried.

Preparation of ceria dispersion

For the preparation of ceria dispersion, the dried magnetic silica-ceria material was ground with an agate mortar and pestle and then added to deionized water and sonicated in an ultrasound bath cleaner, for 20min. The initial concentration of ceria was 1.0mg mL⁻¹. After sonication, the obtained dark orange dispersion was let stand undisturbed for 1h for sufficient sedimentation of the large particles. For the separation of nanoparticles a conventional magnet was applied and after the removal of the bulk water, the concentration of the suspension was adjusted to 2mg mL⁻¹.

Study and optimization of the enrichment procedure

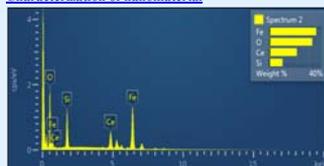
A screening and optimization study has been performed to assess the capacity of the nanomaterial to interact with metal ions and to come up with the best performance conditions. To optimize the designed procedure and set the criteria of selection, several factors were isolated from the different stages of analysis (extraction time and temperature, sample volume, slurry amount and state and ICP-OES measurement) and carefully investigated with synthetic aqueous sample solutions. For the method development, initial conditions with a sample volume of 50mL, and an analyte concentration of 3.0µg L⁻¹ for each element have been used. Regarding the amount of synthesized nanoparticles, 2.5mL of a suspension containing 5mg of particle mass per sample were added to the sample solution. All investigations were carried out with three fold replication.

Preconcentration of metals and analysis

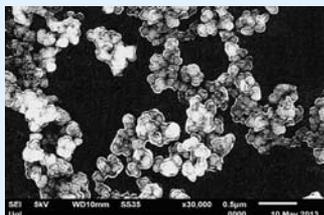
Aqueous samples with varying initial metal concentrations were used. All the experiments were carried out in 100mL capped bottles containing 50mL of standard solution (or sample) at 25 °C and the nanoparticles were added in the form of a suspension. The initial pH of the solutions was adjusted to 6.0 or 8.0 by addition of 0.1N HNO₃ or 0.1N NaOH. The procedure was carried out in a contact time period of 30min with the concentration of nanomaterial to be at 5mg/50mL sample. Stirring was maintained at 350rpm to ensure quantitative extraction using an orbital shaker. Once equilibrium was reached, the nanosorbent with the retained analytes was harvested via an external magnetic field. The remaining particles were used for the preparation of slurry after dispersion of the sorbent in 2.5mL of 2N HNO₃ and ultrasonication. For ICP-OES measurement the slurry was directly introduced into the plasma.

3. RESULTS

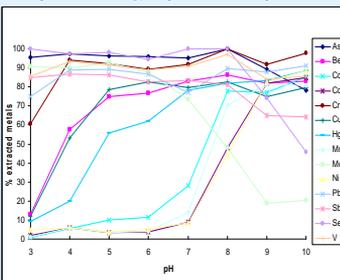
Characterization of nanomaterial



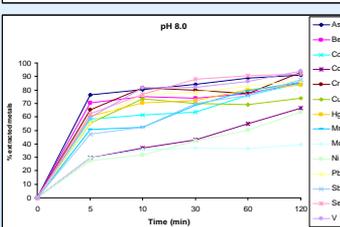
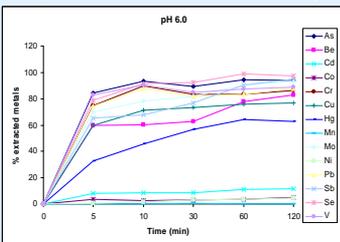
EDS of ceria-silica-magnetite



Scanning electron microscopy image of ceria-silica-magnetite



Effect of pH on the extraction of metals on ceria-coated silica-magnetite.



Percent of extracted metals as a function of time, at pH 6.0 and pH 8.0

Table 2. Limits of quantitation and preconcentration factors for the studied metals using the slurry suspension sampling and ceria-coated silica-magnetite

Analyte	LOQ (µg L ⁻¹)	Preconcentration factor
As	0.46	18
Be	0.15	19
Cd (pH 8)	0.05	18
Co (pH 8)	0.12	14
Cr	0.61	18
Cu	0.51	17
Hg	0.10	16
Mn (pH 8)	0.14	18
Mo	0.22	14
Ni (pH 8)	0.14	14
Pb	0.51	17
Sb	0.29	19
Se	0.24	19
V	0.23	19

Spectral lines of ICP-AES measurements, and values of slope ± standard error of the calibration curves and limits of quantitation.

Analyte	Spectral line	Slope of aqueous standard calibration	Slope of slurry suspension calibration	Correlation coefficient
As	189.0	0.04±0.01	0.04±0.01	0.9989
Be	313.0	0.67±0.02	0.65±0.03	0.9996
Cd	226.5	0.80±0.02	0.73±0.03	0.9996
Co	228.6	1.41±0.05	1.31±0.07	0.9999
Cr	267.7	0.20±0.02	0.18±0.02	0.9962
Cu	324.7	0.48±0.02	0.55±0.03	0.9989
Hg	184.9	0.08±0.01	0.08±0.01	0.9945
Mn	257.6	1.20±0.05	1.17±0.06	0.9999
Mo	202.0	0.39±0.02	0.35±0.03	0.9989
Ni	221.6	0.68±0.03	0.74±0.04	0.9987
Pb	220.3	0.06±0.01	0.05±0.01	0.9983
Sb	206.8	0.08±0.01	0.08±0.01	0.9989
Se	196.0	0.05±0.02	0.06±0.01	0.9985
V	292.4	0.08±0.02	0.07±0.02	0.9997

Mean concentrations (n = 3) of heavy metals in environmental and biological samples (µg L⁻¹)

Analyte	Well water*	Reservoir water*	Urine**
As	3.0±0.2	3.0±0.3	nd
Be	0.4±0.1	0.5±0.1	0.7±0.2
Cd (pH 8)	0.4±0.1	0.2±0.1	nd
Co (pH 8)	0.21±0.03	0.21±0.03	nd
Cr	0.12±0.03	nd	5.1±0.9
Cu	4.7±0.4	8.3±	5.1±0.3
Hg	nd	nd	nd
Mn (pH 8)	1.1±0.2	1.4±0.3	0.9±0.1
Mo	1.9±0.1	1.3±0.3	4.9±0.3
Ni (pH 8)	19.7±0.4	3.2±0.3	nd
Pb	3.4±0.2	3.2±0.4	nd
Sb	4.3±0.3	2.2±0.2	nd
Se	20±1	2.1±0.2	23±1
V	23±1	7.2±0.3	nd

4. CONCLUSION

A novel microextraction / preconcentration procedure for the multielement enrichment prior to analysis with ICP-OES has been introduced. The procedure combines the magnetic and non-specific, metal extracting properties of a composite magnetite-silica ceria nanomaterial with a slurry suspension sampling approach and ICP-OES slurry measurement. By using 50 mL of sample volume and 5 mg of the ceria dispersion enrichment factors of 14 to 19 could be achieved. Compared to conventional solid-phase extraction this method includes advantages like simplicity, low cost and consumption of solvents and shows distinct advantages for nanosorbent handling and memory effects by implementing the slurry sampling. This feature of the developed procedure establishes access to sorbent materials with irreversible bonding mechanisms for sample pretreatment. The proposed method is also rapid with negligible sample preparation and offers good detection limits and acceptable precision for routine analysis of liquid environmental and biological samples. Conceivably, the detection limits can further be improved using higher content of nanoparticles in the slurries in combination with higher sample volumes but with a reasonable sacrifice of the precision of the final slurry measurement.

5. ACKNOWLEDGEMENTS

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