ORDERED MESOPOROUS SILICA FUNCTIONALIZED WITH AMINOPROPYL GROUPS BY CO-CONDENSATION AND POST GRAFTING

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ABSTRACT

The morphology and the structural properties of mesoporous silica functionalized with aminopropyl groups by the co-condensation and the post grafting methods were evaluated. Nitrogen sorption, small angle neutron and X-ray scattering methods (SANS and SAXS) demonstrated high surface area and well-ordered hexagonal pore structure suitable for applications as adsorbents of metals from waste waters. SANS and SAXS data show that the increase of the amount of organic silica precursor in the co-condensation process leads to the decrease of the long-range order of the parallel channels and that an uneven distribution of the functional groups, by the post grafting method has been obtained. Zeta potential measurements revealed that by functionalization, the particles are stable and positively charged in a wide range of pH. The colloidal stability of the particles increases with higher amount of APTES and increases as well by using post grafting method comparatively with the co-condensation method [1, 2].

AIM

In order to obtain suitable materials with improved adsorption capacity, for the metal ion removal (pollutants from waste water): functionalization of the mesoporous silica materials; tailoring of the textural and structural properties of the materials; synthesis with varying concentrations of APTES, have been performed.

EXPERIMENTAL SECTION

Functionalization methods

Direct co-condensation
-the functional groups are inserted within the silica matrix;
-short time and involves a one-step co-condensation;
it gives a more homogeneous distribution of the functional groups;
-it produces materials with a less ordered structure.

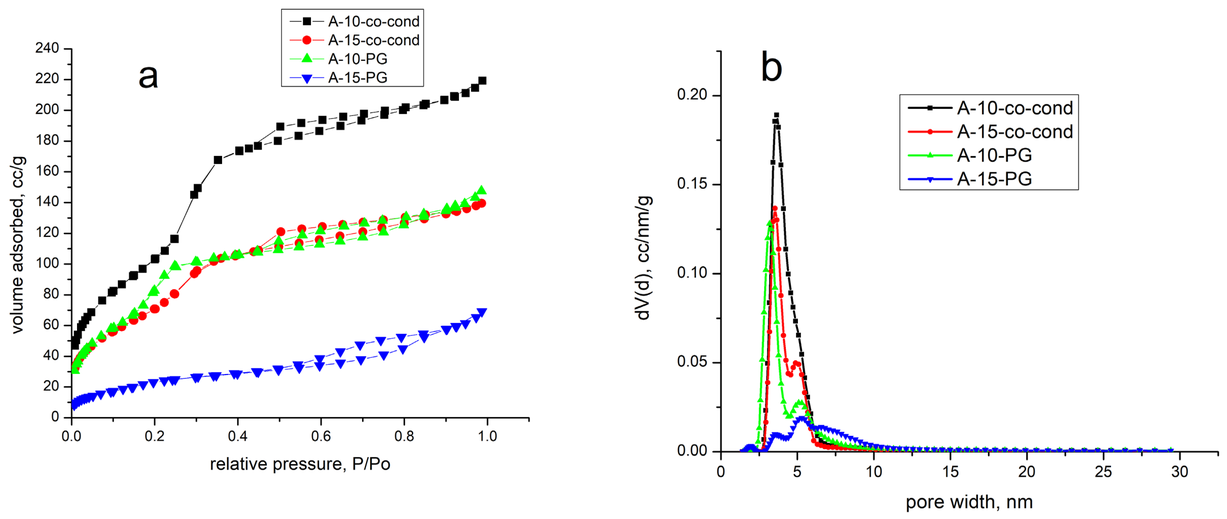
Post-grafting method
-the functional groups are attached to the surface of the nanoparticles;
-two-step procedure: synthesis and functionalization, separate stages;
-it is easier to control particle size, morphology, pore diameter and pore ordering;
-it produces non-uniformly distributed organic groups, which can also congregate on the particle external surface blocking the pore entrance.

Synthesis of functionalised mesoporous materials via co-condensation
Reactants:
CTAB (cetyl-trimethylammonium bromide)
NH_3
Ethanol/H_2O = 1: 10
TEOS
APTES
CTAB was removed by extraction with a mixture of solvents.

Synthesis of functionalized mesoporous materials via post-grafting
TEOS, CTAB, NH_3/ H_2O, ethanol
The ready prepared mesoporous silica material was added to a solution formed from:
different grams of **APTES** and 25 mL toluene,
and left for soaking 24 hours followed by 6 hours stirring.

RESULTS

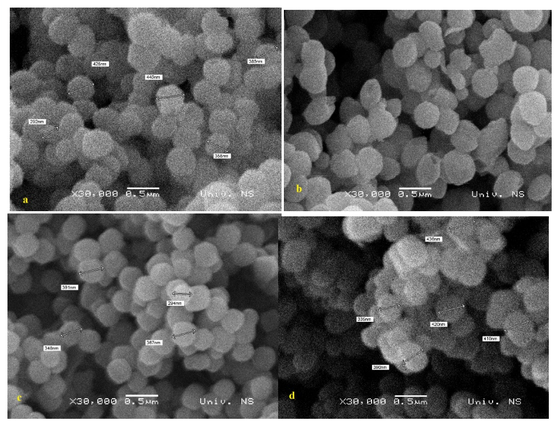
Nitrogen adsorption/desorption isotherms and the pore size distributions revealed by the DFT method



Textural parameters

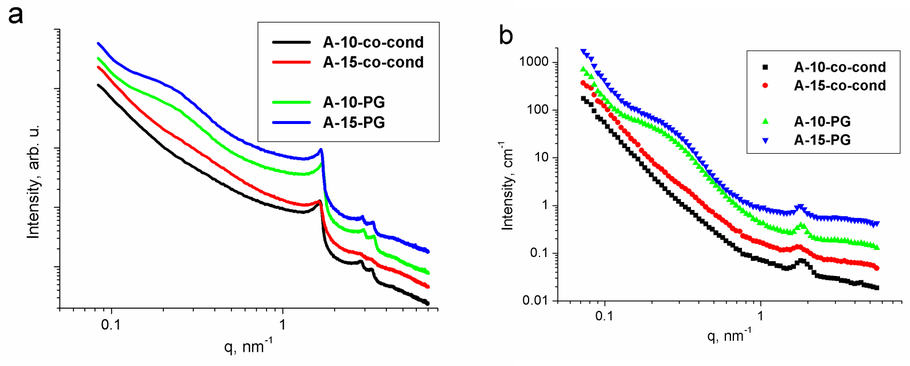
Samples	SBET (m2/g)	Micropore area (m2/g)	D DFT (nm)	VT (cm3/g)
A-10-co-cond	500	183	3.6	0.34
A-15-co-cond	323	145	3.5	0.22
A-10-PG	416	289	3.2	0.23
A-15-PG	93	37	5.3	0.11

SEM images:
A-10-co-cond (a), A-15-cocond (b) A-10-PG (c), and A-15-PG (d)



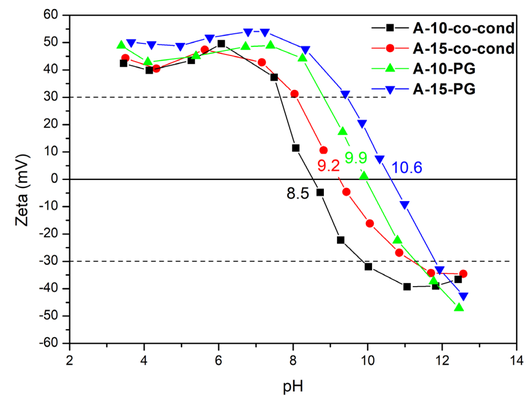
Sample, Adsorption Capacity
A-10-co-cond, 85.4 mg/g
A-10-PG, 9.4 mg/g

Small angle X-ray Scattering (SAXS) (a) and Small Angle Neutron Scattering (SANS) b)
scattering curves of the functionalized mesoporous silica samples



Characteristic cluster size, D = 2/q*, giving a value of 20–30 nm.

Zeta potential of the samples measured as a function of pH.



Particles are stable and positively charged in a wide range of pH.

Higher colloidal stability of the particles increases: with higher amount of APTES and by post grafting method.

Functionalization with APTES leads to the positively charged particle surface, making it suitable for adsorption of the of negatively charged anion groups.

Conclusions

- **The sample obtained by co-condensation had an increased affinity for Cr(VI) ions compared to the post-grafted material.**

It may be explained by: the increased specific surface area and of the pore volume of this material, and the possibly higher amount of amine groups in the pore channels due to their even distribution provided by the co-condensation method.

- **SAXS and SANS analyses data show that: the increase of the amount of organic silica precursor in the co-condensation process leads to the decrease of the long-range order of the parallel channels; and an uneven distribution of the functional group, by the post grafting method.**

References:
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2. Putz A.M., Almásy L., Len A., Ianăşi C., Fuller. Nanotub. Carbon Nanostructures 27 (2019) 323-332.

Acknowledgments:*The authors thank the Romanian Academy;* ***to the Inter-Academic Exchange Program between Romanian Academy and the Hungarian Academy of Sciences; and Research grant within the framework of scientific cooperation between Romania and Joint Institute for Nuclear Research, Dubna.***

13th ON-LINE Edition of symposium with international participation - New trends and strategies in the chemistry of advanced materials with relevance in biological systems, technique and environmental protection – October, 7-8, 2021.