

MESOPOROUS SILICA SORBENTS FOR ADSORPTION AND SEPARATION OF REE

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Abstract

A series of hybrid microadsorbents were produced by surface modification with amino polycarboxylate ligands of industrially available microparticles of Kromasil mesoporous silica nanostructured adsorbent, bearing grafted amino propyl ligands. Produced micro adsorbents bearing functions as EDTA and TTHA, original Kromasil bearing amino propyl ligands and bare particles, obtained by thermal treatment of Kromasil in air were characterized by SEM-EDS, AFM, FTIR, TGA and gas sorption techniques. Capacity of surface-modified particles to adsorb Rare Earth Elements, crucial for extraction in recycling processes, was evaluated under dynamic conditions.

Introduction

Amino polycarboxylate (APCA) ligands are attractive anchoring groups for adsorbents aimed at separation of rare earth elements (REE). In our recent studies, these groups have been grafted on the surface of dense silica nanoparticles with or without magnetic cores for application in solid phase extraction and separation of REE.¹⁻⁴ The general approach has been a two-step anchoring of the groups with first deposition of a layer of aminopropyl silane and then – attachment of the ligand function via formation of an amido bridge via one of the carboxylic groups.^{3,4} Produced adsorbents revealed high capacity at neutral pH (6.0-7.0), corresponding to the uptake of REE by the remaining carboxylic groups of APCA via the outer sphere complexation mechanism, where the adsorbent acted as poly-electrolyte.^{3,4} The desorption at intermediate pH was found to be associated with re-structuring of the complexes with loss of some fraction of the adsorbed cations and formation of inner-sphere complexes,⁴ thus opening for very pronounced selectivity, related to the nature of ligand and the size of the REE cation.^{3,4} This behaviour was indicative of the potential of such materials in chromatographic separation. A study of industrial mesoporous silica adsorbent, Kromasil®, already grafted with aminopropyl ligands and further modified via attachment of the DTPA, i.e. diethylene triamine pentaacetic acid, provided an adsorbent with characteristics quite resembling those of hybrid materials based on dense nanosilica.⁵ In the present contribution we

continued the investigation of Kromasil® based adsorbents and investigated synthesis and functional characteristics of materials grafted with ethylene diamine tetraacetic acid (EDTA) and triethylene tetramine hexaacetic acid (TTHA).

Results and discussion

The grafting of ligands occurred in analogy with the pathways earlier observed for attachment of DTPA. The material did not change its appearance (white powder) unless the temperature exceeded the stability limit for the APCA ligand (typically about 120°C). If the temperature limit was reached, the powder turned brownish and the adsorption capacity of the resulting material turned drastically decreased. The grafting of the ligand via an amide bond on the matrix was confirmed by FTIR. The powders kept their mesoporous nature as could be followed by the appearance of their low-temperature nitrogen adsorption isotherms, belonging to the type IV characteristic of mesoporous solids. The pore volume decreased quite distinctly from original Kromasil® to the EDTA, DTPA and finally to TTHA modified material. The morphology of the adsorbent is spherical with sphere diameters ranging 4-15 nm as revealed by SEM. The inner structure is built up of supposedly dense silica spheres 20-30 nm in diameter according to AFM data.

As revealed by TGA measurements, the organic component content in Kromasil® is about 12-14 %. The EDTA-functionalized material loses adsorbed solvents below 180 °C (4.57 %) undergoes then dehydration, associated, most probably, with formation of anhydrides and amides and further decomposition leading to complete destruction of ligands in a broad temperature interval 180-500 °C (loss of 11.04 %) and finally burning out of the residual organic carbon at above 500 °C (loss of just 1.04 %). The total weight loss of the organic ligands is 16.65%, corresponding to content of the grafted EDTA 0,101 mmol/g. For the TTHA functionalized material, the solvent loss occurs below 130°C (14.2 %) and is followed by the first decomposition step at around 250°C (loss of 23.1%). The multi-step further destruction is maximized at around 400 °C (loss of 16.5 %) and is then going over into slow burn out of residual carbon at 500-665 °C (loss of 11.4 %). This corresponds to grafted TTHA content of 2.3 mmol/g.

The adsorption capacity measurements demonstrate that both Kromasil-EDTA and Kromasil-TTHA are highly potent adsorbents. All three adsorbents (including earlier investigated Kromasil-DTPA) showed comparable adsorption capacity. This is a clear discrepancy to what has been earlier proved for derivatives of dense nano silica, where the uptake was mostly due to outer-sphere complexes, corresponding to 1:1 ratio between REE³⁺-cation and carboxylate function. In case of mesoporous materials reported here, the uptake is not directly related to the amount of ligand, indicating that other mechanisms than just complex formation with amino carboxylate ligands are invoked. It can be hypothesized, that other types of complexes involving non-modified amino propyl ligands and non-substituted silanol

groups are contributing to the total uptake capacity. This is supposedly this combination of different factors that led to enhanced selectivity revealed by hybrid mesoporous adsorbent in chromatographic separation.

Table 1: REE uptake by EDTA and TTHA functionalized Kromasil

Sample Solution concentration	REE uptake (mmolREE/gsample)	REE uptake (mgREE/gsample)
Kromasil-EDTA-Dy ³⁺ (0.104 mM)	1.27 ± 0.05	206.4 ± 8.1
Kromasil-EDTA-Nd ³⁺ (0.114 mM)	1.08 ± 0.05	155.8 ± 7.2
Kromasil-TTHA-Dy ³⁺ (0.107 mM)	0.89 ± 0.05	144.6 ± 8.1
Kromasil-TTHA-Nd ³⁺ (0.115 mM)	0.90 ± 0.05	129.8 ± 7.2

Acknowledgments

The authors are indebted to ERA-MIN MetRecycle project for support of this work. Swedish Research Council (Vetenskapsrådet) is acknowledged for support of the project 2018-04841 Multifunctional hybrid adsorbents for water purification.

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