Electronic supplementary information

Recovery of scandium from leachates of Greek bauxite residue by adsorption on functionalized chitosan-silica hybrid materials

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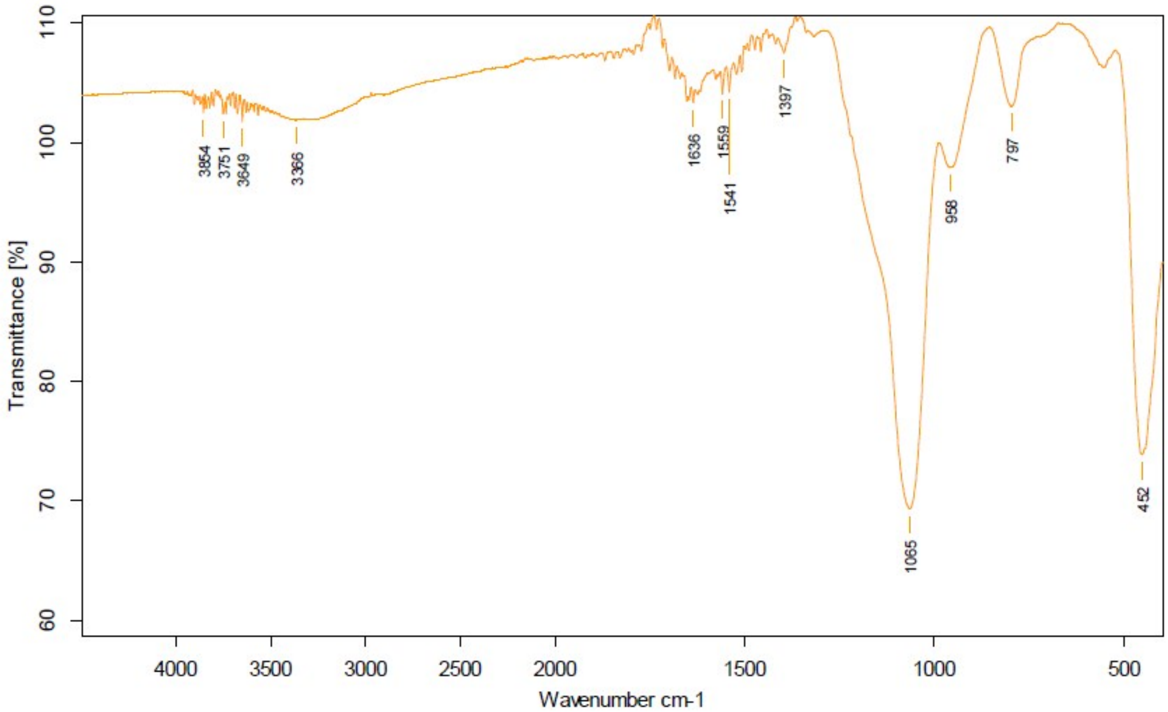
Synthesis chitosan-silica

A chitosan-silica hybrid material was made according to the method described by Rashidova et al.[1] by dissolving chitosan (2.0 g) in a 2 vol% acetic acid solution (100 mL). After the chitosan was dissolved (after approximately 1 h), tetraethyl orthosilicate (TEOS, 30 mL) was added to the pale yellow viscous solution. The solution, which was at pH 4.00, was stirred for another 30 min to induce the hydrolysis reactions during which ethoxy groups are replaced by hydroxyl groups. Afterwards, the pH was sufficiently increased by adding 200 mL of a solution of 3 vol% NH3 to catalyze the condensation reactions. The mixture was kept for about 24 h during which the chitosan-silica interpenetrating networks were formed. Then, the chitosan-silica hybrid material was filtrated and washed with demineralized water until the pH reached a neutral value. Consequently, the chitosan-silica hybrid material was washed again with ethanol to replace water in the chitosan-silica gel with ethanol. To end the washing procedure, the chitosan-silica gel was washed with n-heptane (300 mL), in which the chitosan-silica particles precipitated. The chitosan-silica gel was then air-dried for a period of 24 h and dried further in vacuum at an elevated temperature of 40 °C for another 24 h. The result of this procedure is a dry, white-coloured powder.

Synthesis DTPA-chitosan-silica

Prior to functionalization, diethylenetriamine pentaacetic acid bisanhydride (DTPABA) was made starting from DTPA (19.7 g), acetyl anhydride (20.4 g) and pyridine (23.7 g) as a solvent.[2] The reaction was done at an elevated temperature of 65 °C, with a reflux condenser and under argon atmosphere in order to minimize the water content. After two hours, the reaction was stopped and the product was immediately filtrated, washed three times with acetyl anhydride (approximately 70 mL) and dry diethyl ether (20 mL). Afterwards, the DTPABA was dried under vacuum conditions at an elevated temperature of 40 °C for 24 h. The functionalization of the chitosan-silica hybrid material with DTPA has been carried out by mixing chitosan-silica (7.5 g) in 2.0 vol% acetic acid solution (100 mL) and stirring it in order to catalyze the reaction between the DTPABA and the amino-groups of chitosan. DTPABA (15.0 g) was dissolved in pure methanol (100 mL). After adding methanol (400 mL) as solvent to the chitosan-silica mixture, the DTPABA-methanol mixture was added and stirred in order to start the functionalization process. After 24 h, the stirring was stopped and a 1.00 M NaOH solution was added until the mixture reached a pH value of 11.00, necessary to remove the excess DTPA by formation of its water-soluble sodium salt. After filtration, the particles were washed with demineralized water until pH-neutral, then with HCl 0.10 M (200 mL) and again with demineralized water until pH-neutral. After that, the DTPA-chitosan-silica material was washed with ethanol (200 mL). After drying in a vacuum oven, the particles were stored in contact with the air in order to equilibrate its water content with the water content of the air.

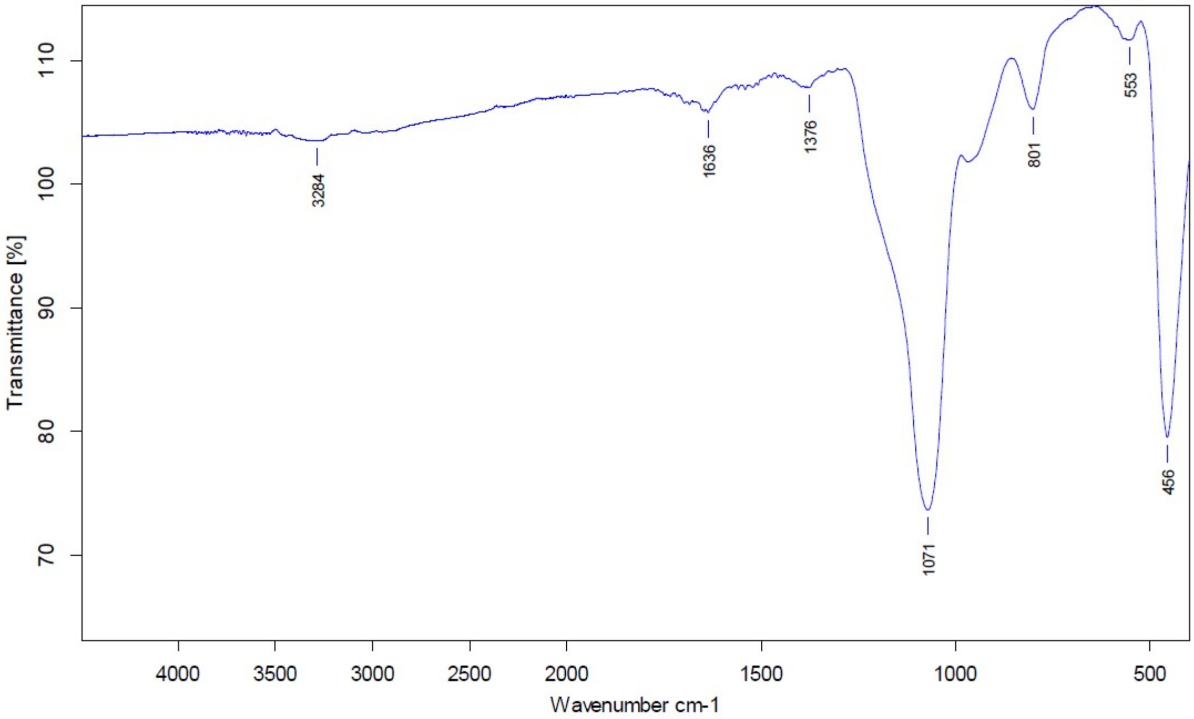
IR spectrum:



Synthesis EGTA-chitosan-silica

EGTA (3.2 g) was dissolved in demineralized water (100 mL) and chitosan-silica (7.5 g) was added. The mixture was heated till 60 °C and stirred for 4 h. After the heating and stirring, the mixture has been cooled down to 40 °C after which 1.00 M NaOH (10 mL) and N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC, 2.0 g) were added in order to initiate the gelation of the mixture. EDC is a water soluble crosslinking agent that activates carboxyl groups for the coupling of primary amines. The mixture was stirred for 1 h at 40 °C after which the mixture was stirred for 16 h at room temperature. The gel was washed with acetic acid 5 m% (50 mL). A 4:2:1 MeOH-AcOH-Ac_2O 5 % solution (140 mL) was added and stirred for 3 h. The gel was successively washed with 0.10 M NaOH, demineralized water, 0.10 M HCl, demineralized water and n heptane. Since filtration of the slurry took a huge amount of time, the washing steps have been carried out by centrifuging the slurry multiple times. Since centrifuging could not remove all of the moisture without spilling functionalized particles, the last washing step has been conducted by doing a (time consuming) filtration. The washed EGTA-chitosan-silica has been dried for 24 h at 60 °C in vacuum.

IR spectrum:



[1] S. S. Rashidova, D. S. Shakarova, O. N. Ruzimuradov, D. T. Satubaldieva, S. V. Zalyalieva, O. A. Shpigun, V. P. Varlamov, B. D. Kabulov, J. Chromatogr. B 2004, 800, 49-53.

[2] V. Montembault, J.-C. Soutif, J.-C. Brosse, F. Hilldré, J.-J. Le Jeune, Reactive and Functional Polymers 1997, 32, 43-52.