Kinetic and equilibrium studies for the sorption of benzene and phenol from water on functional MCM-41 silicas

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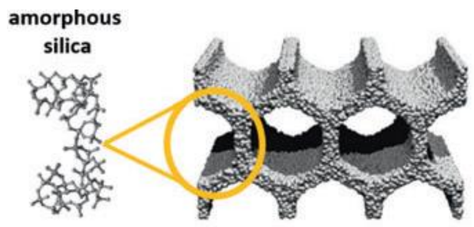
Mobile Crystalline Materials (MCM-41):

- ❑ regular channel type structures
- ❑ high surface area
- ❑ large pore volume and diameter
- ❑ excellent hydrothermal, thermal and hydrolytic stabilities
- ❑ active silanols on the surface

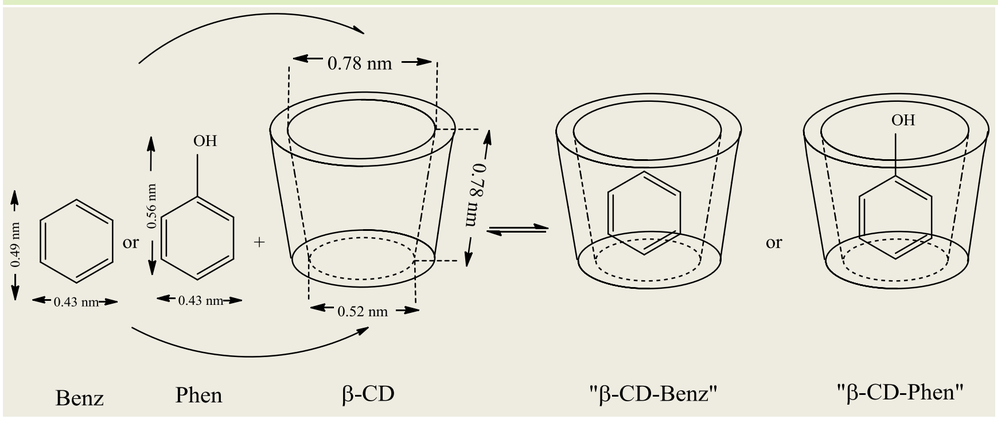


Schwanke, Anderson & Balzer, Rosana & Pergher, Sibele. (2017). Microporous and Mesoporous Materials from Natural and Inexpensive Sources. 10.1007/978-3-319-68255-6_43.

β-Cyclodextrin (β-CD):

- ❑ cyclic oligosaccharide formed of 7 glucopyranose units linked by α-(1,4)-glycosidic bonds
- ❑ torus-like macro-ring with primary and secondary OH-groups on its edges (hydrophilic sites)
- ❑ hydrophobic cavity lined with hydrogen atoms and glycosidic oxygen bridges

Benzene and its derivatives are flammable, toxic, carcinogenic and/or mutagenic industrial pollutants, which can contaminate the aquatic environment and drinking water because of theirs high volatility, spreading, and low biodegradability.

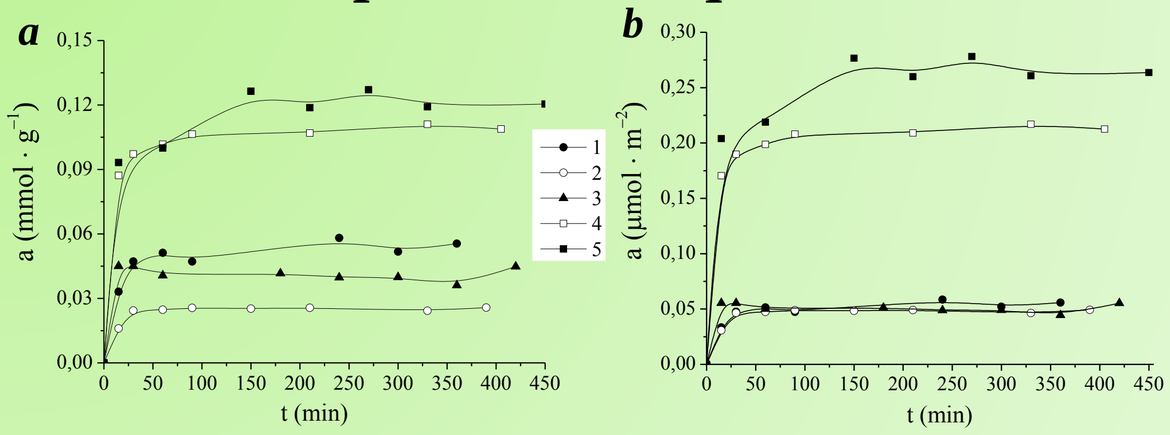


Aromatic compounds and β-CD could form 1 : 1 "host–guest" inclusion complexes in aqueous solutions. The formation of "β-CD–aromatic compounds" complexes is spontaneous and thermodynamically profitable exothermal process.

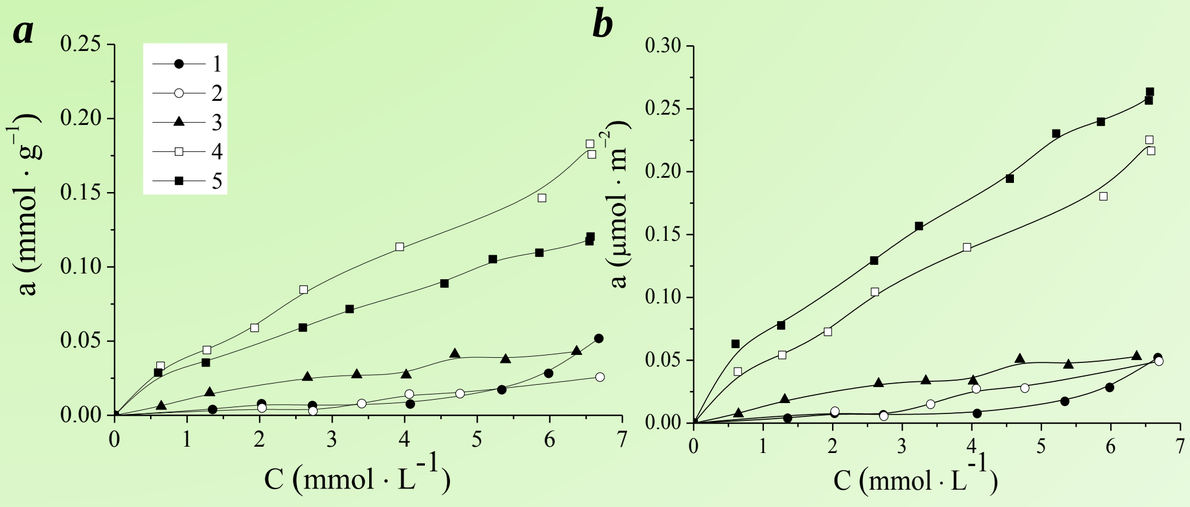
Chemical composition and structural parameters of synthesized silicas

Silica	X-ray diffraction		Nitrogen adsorption-desorption			Chemical analysis			
	d_{100}, nm	a, nm	S_{BET}, m^2/g	V_t, cm^3/g	D_{DFT}, nm	$[-(CH_2)_3NH_2]$		[β-CD]	
						mmol/g	μmol/m^2	mmol/g	μmol/m^2
MCM-41 (1)	4.17	4.82	995	0.75	3.7; 5.1	-	-	-	-
NH_2-MCM-41 (2)	4.02	4.64	523	0.86	3.7; 5.1	0.44	0.84	-	-
β-CD-APTES-MCM-41 (3)	4.11	4.75	812	1.06	3.9; 5.1	0.05	0.06	0.018	0.022
β-CD-$APTES_3$-MCM-41 (4)	3.93	4.54	512	0.60	2.5; 3.3; 5.1	0.11	0.21	0.072	0.141
β-CD-$APTES_5$-MCM-41 (5)	4.11	4.74	457	0.69	2.4; 3.1; 4.7	0.12	0.26	0.095	0.208

Phenol uptake from aqueous solutions



Kinetic curves of phenol sorption on silicas per g (a) or per m^2 (b) of materials

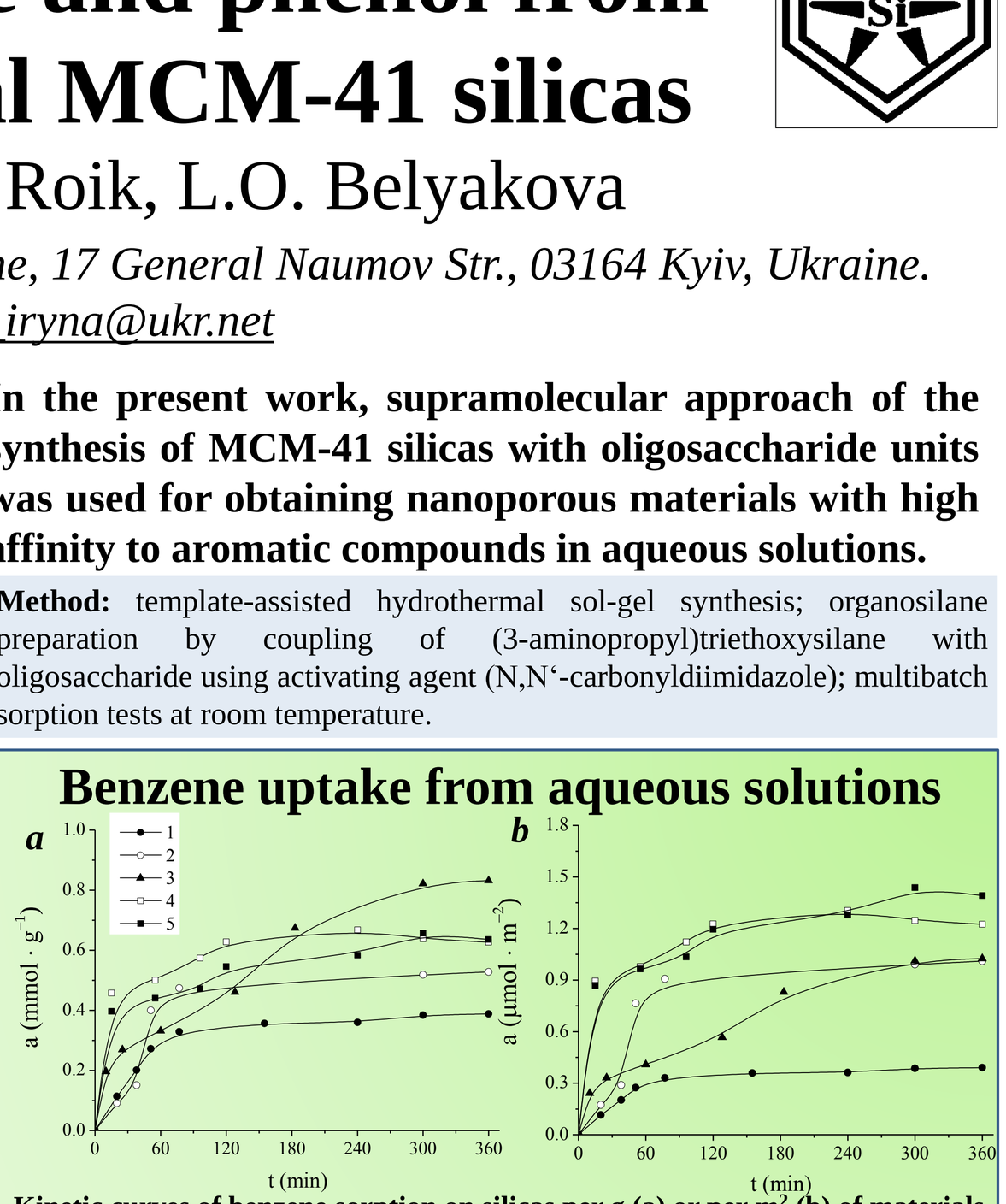


Phenol sorption isotherms on silicas per g (a) or per m^2 (b) of materials

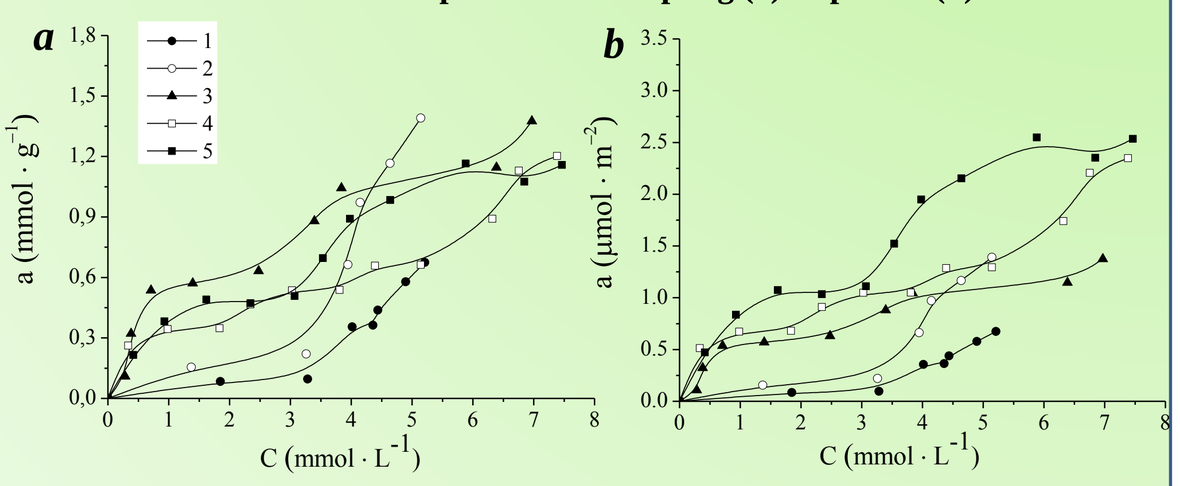
In the present work, supramolecular approach of the synthesis of MCM-41 silicas with oligosaccharide units was used for obtaining nanoporous materials with high affinity to aromatic compounds in aqueous solutions.

Method: template-assisted hydrothermal sol-gel synthesis; organosilane preparation by coupling of (3-aminopropyl)triethoxysilane with oligosaccharide using activating agent (N,N'-carbonyldiimidazole); multibatch sorption tests at room temperature.

Benzene uptake from aqueous solutions



Kinetic curves of benzene sorption on silicas per g (a) or per m^2 (b) of materials



Benzene sorption isotherms on silicas per g (a) or per m^2 (b) of materials

CONCLUSIONS

- MCM-41-type silicas with different content of β-CD-containing functional groups (in the range 0.018-0.095 mmol/g) were synthesized by hydrothermal sol-gel co-condensation of tetraethyl orthosilicate and oligosaccharide-containing organosilanes in the presence of cetyltrimethylammonium bromide as template.
- Nitrogen sorptometry experiments exhibited the decrease of high surface area (from 812 to 457 m^2/g) and the average pore diameter (from 1.06 to 0.60 cm^3/g) of synthesized silicas with increasing of immobilized oligosaccharide groups.
- The results of sorption experiments proved that β-cyclodextrin immobilization on the surface of silicas leads to the increase of aromatic compounds uptake from aqueous solutions.
- Prepared MCM-41 silicas demonstrate stronger affinity towards benzene than to phenol that could be very promising for selective removing of hazardous compounds in water treatment processes.