ORGANOFUNCTIONAL SILICA NANOMATERIALS FOR ENERGY AND ENVIRONMENTAL APPLICATIONS

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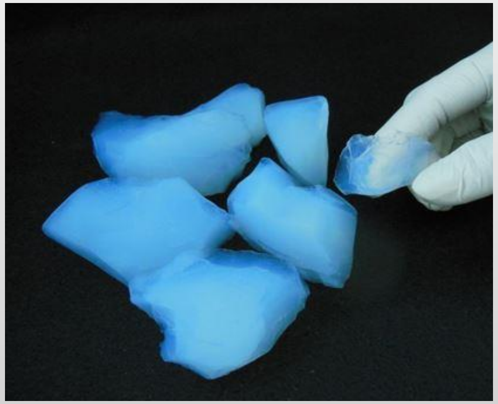
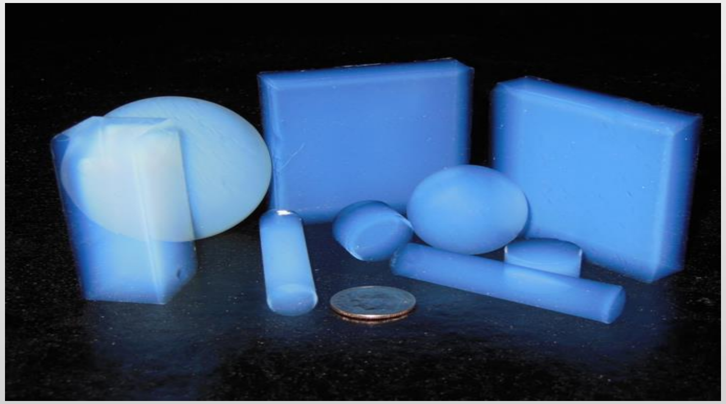
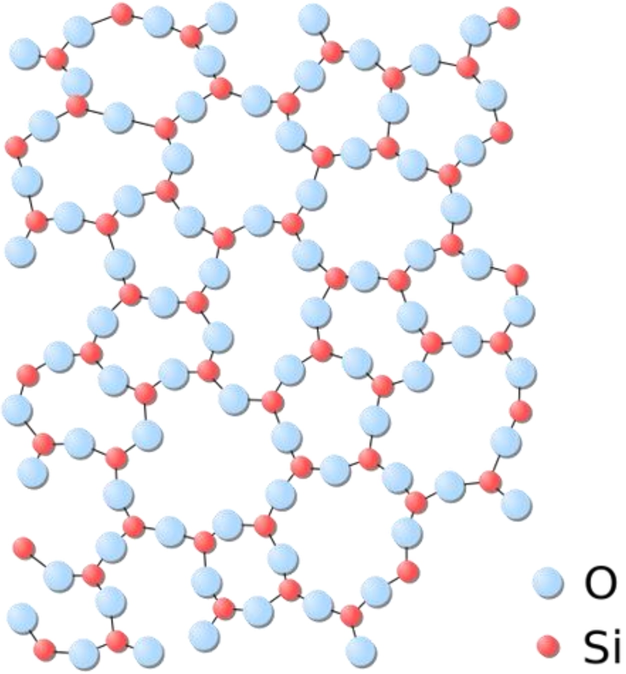


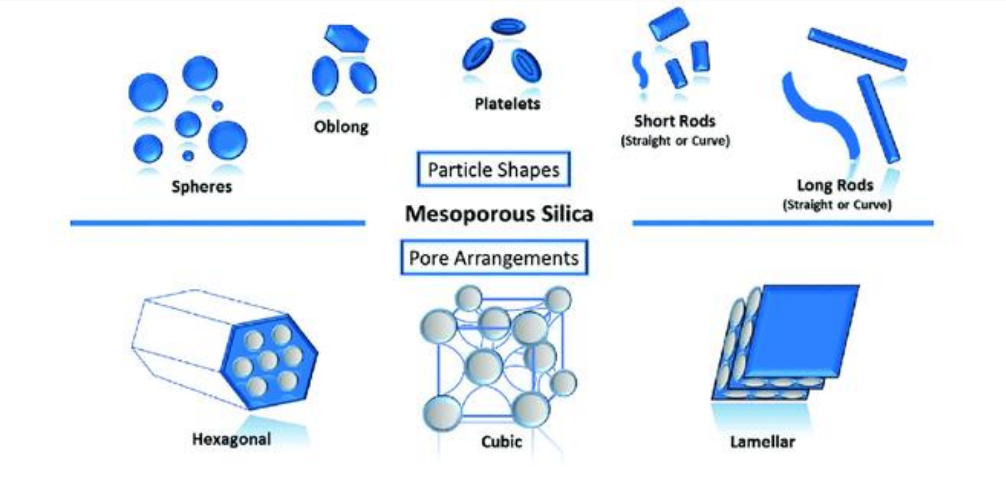
BNC Seminars

Budapest-HUNGARY, 25. 04. 2024



SILICA BASED NANOMATERIALS





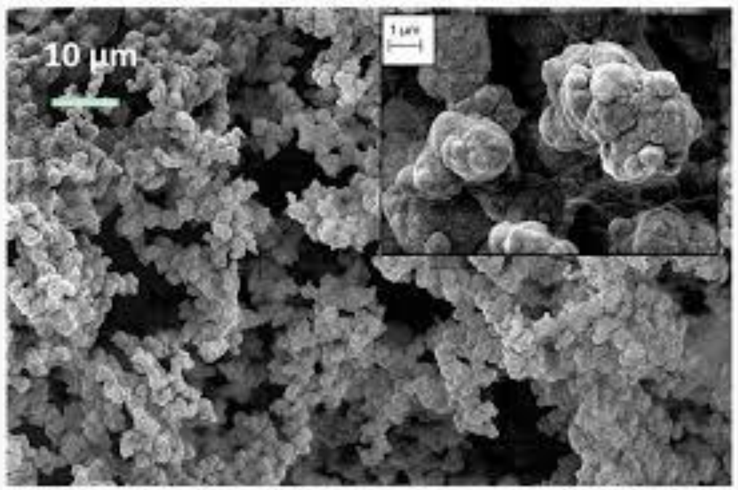
AMORPHOUS SILICA NANOMATERIALS- AEROGELS & XEROGELS

Aerogels are amongst the lightest solids known!

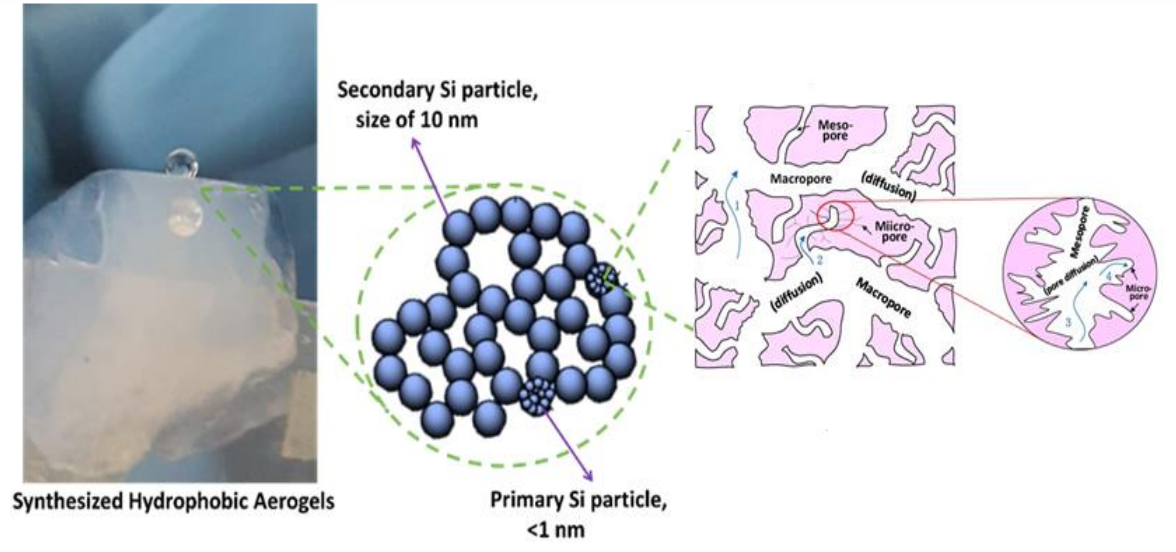
IUPAC 2022 Top Ten Emerging Technologies in Chemistry!

As a "miracle material" they possesses

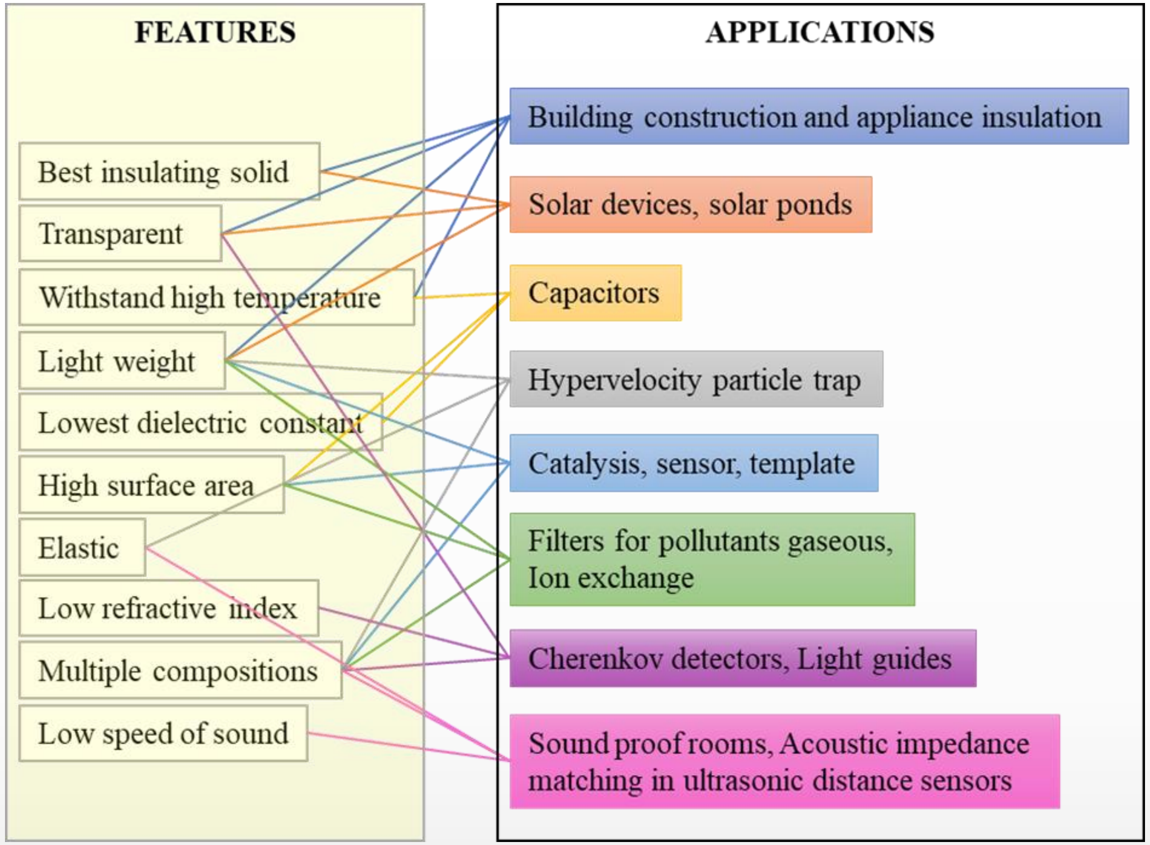
- a highly porous microstructure with an air volume of 85~99.8%,
- having a pearl necklace-like network of loosely packed and bonded particles.



SILICA AEROGELS

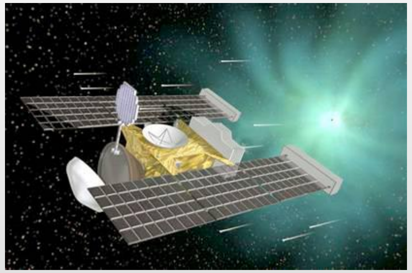


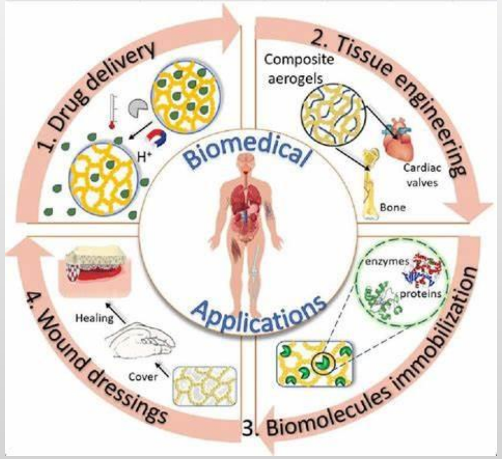
Sert Çok, S., and Gizli, N., Ceramics International, Volume 46, 2020, 27789.



With outstanding properties:

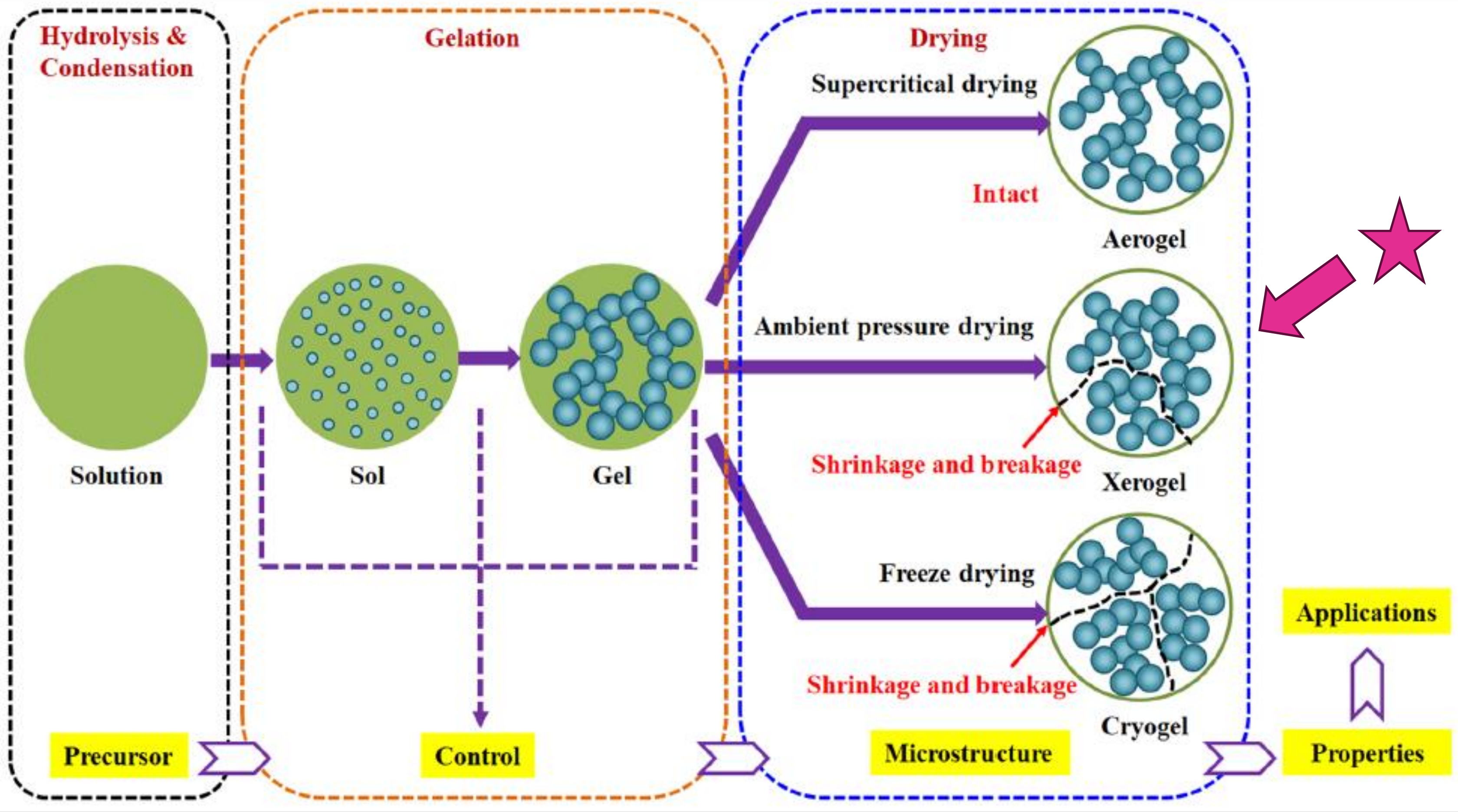
- low density (0.01-0.03 g/cm^3)
- optical transparency (~99% in the visible region)
- high acoustic insulation (low sound velocity of 100 m/s),
- high-temperature resistance (>800°C),
- high specific surface area (100-1500 m^2/g)
- Ultra-low thermal conductivity (20-50 mW/mK)

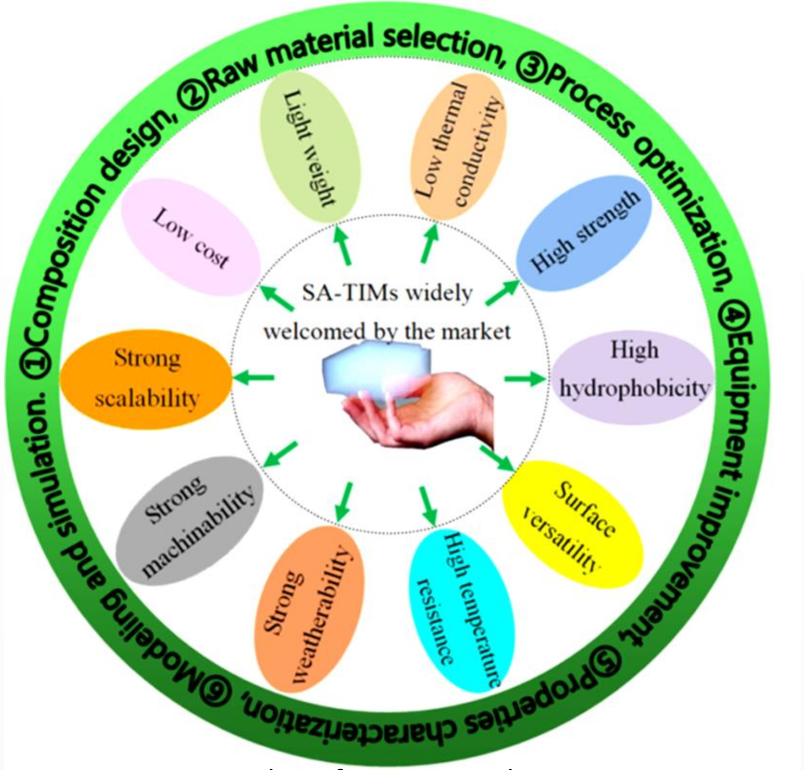




Silica aerogels are produced via

SOL- GEL METHOD





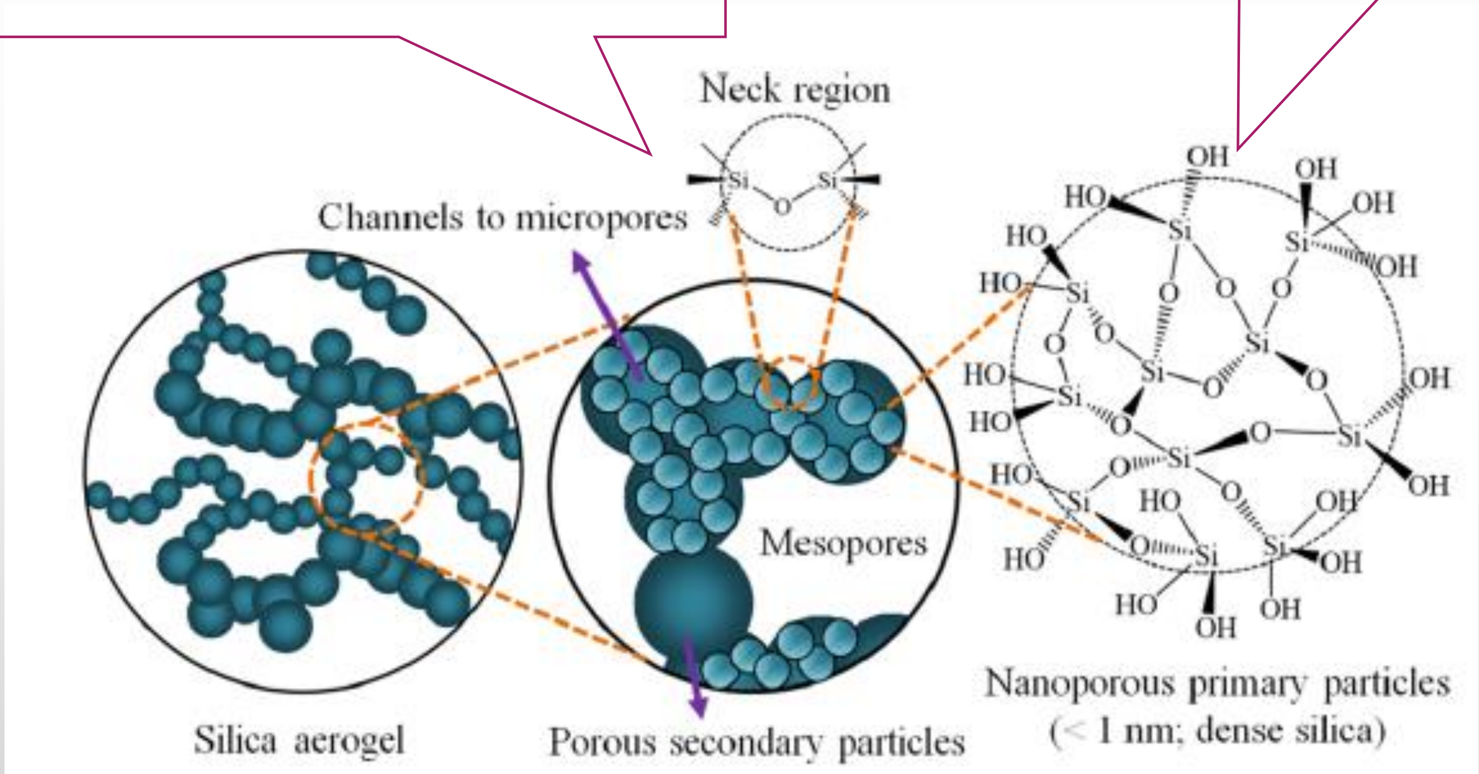
Li et.al,, J.of Non.Crys.Sol., 2020

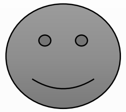
The availability of silica-aerogel related commercial products are still limited in the market so far, due to:

- the fragile structure and
- time-consuming and laborious synthesis
- and cost-intensive production (supercritical drying) technology.

The nano-scale and weakly branched silica backbones inevitably impose a low mechanical strength and inherent brittleness (especially in the neck region).

Due to the existance of hydrophilic OH groups on the silica particles, the strong tendency of absorbing mositure (hyrophilicty) also makes the processing and handling of silica aerogels difficult.





Luckily, the versatility of the sol-gel method allows:

- ✓ the incorporation of different organic functional groups to silica network for improving their low mechanical strength
- ✓ tuning their hydrophobic profile.
- ✓ Providing functionality for target applications

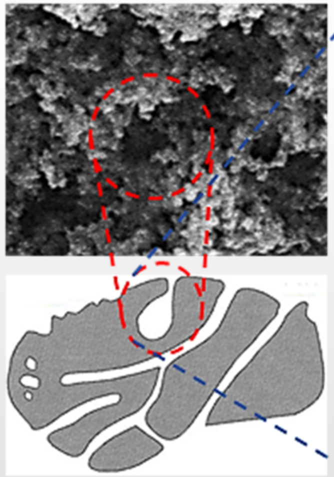
Hajar Maleki, Luisa Durães, António Portugal, Journal of Non-Crystalline Solids, 385 (2014) 55–74.

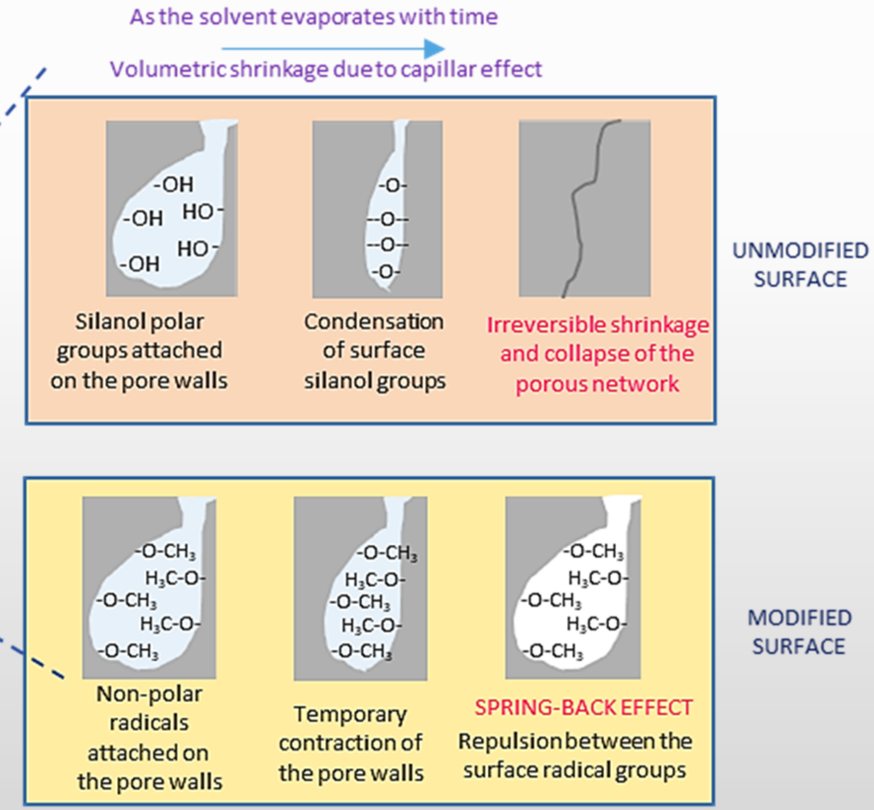
Silica xerogels prepared with conventional tetraalkoxysilanes such as tetraethylorthosilicate (TEOS), tetramethylorthosilicate (TMOS) are rich in surface silanol groups (Si-OH) which are the main source of hydrophilicity.

Sert Çok, S., Koç, F., Gizli, Journal of Hazardous Materials, Volume 408, 2021, 124858.

- Prevents material degradation caused by moisture
- Protects the porous structure against network collapse

During ambient pressure drying…





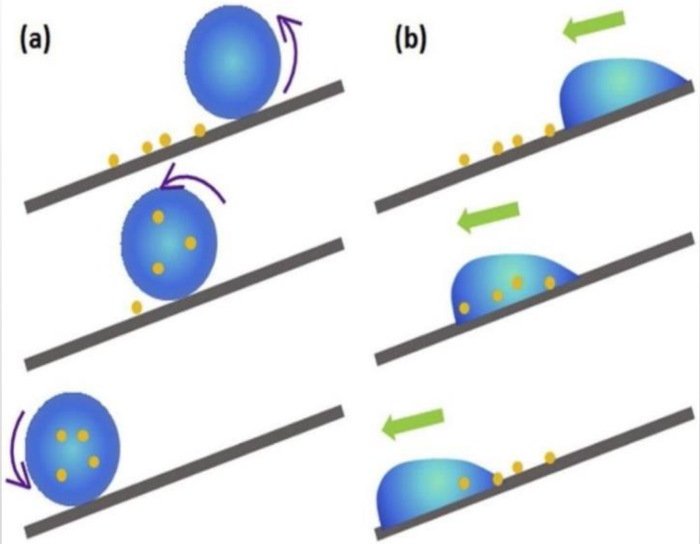
Si-OH polar groups can be replaced with hydrolytically stable Si-R (R=alkyl or aryl) groups

Sert Çok, S., and Gizli, N., International Journal of Heat and Mass Transfer, Volume 188, 2022, 122618.

Side Benefits of Hydrophobic Behaviour

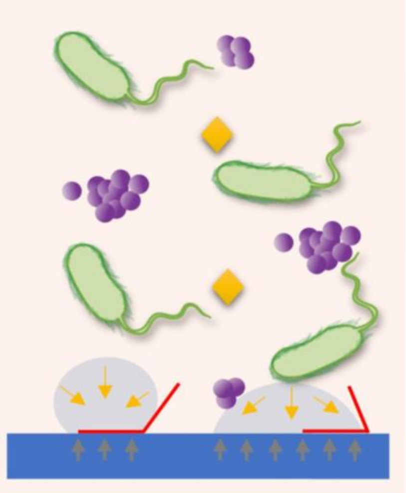
Self-Cleaning Ability

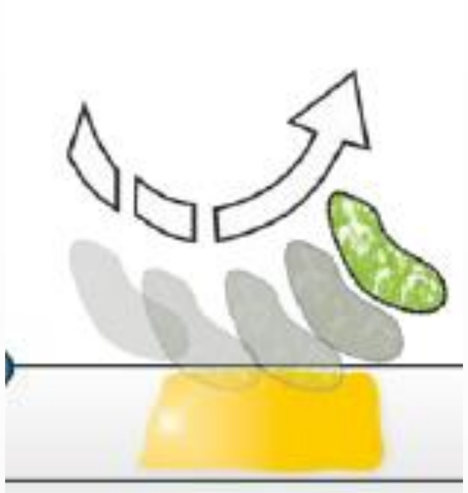
LOTUS EFFECT!

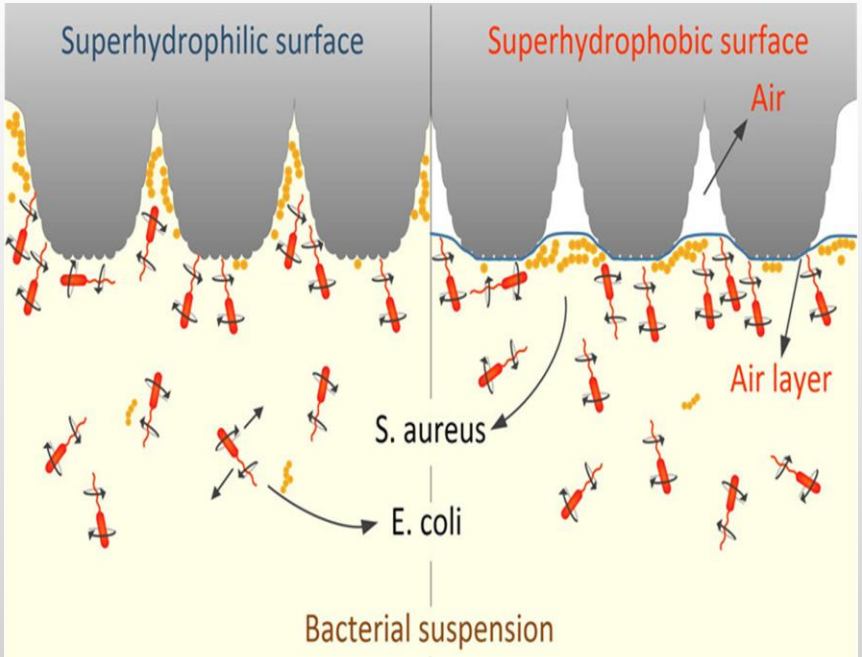


Bacteria-Repelling Ability

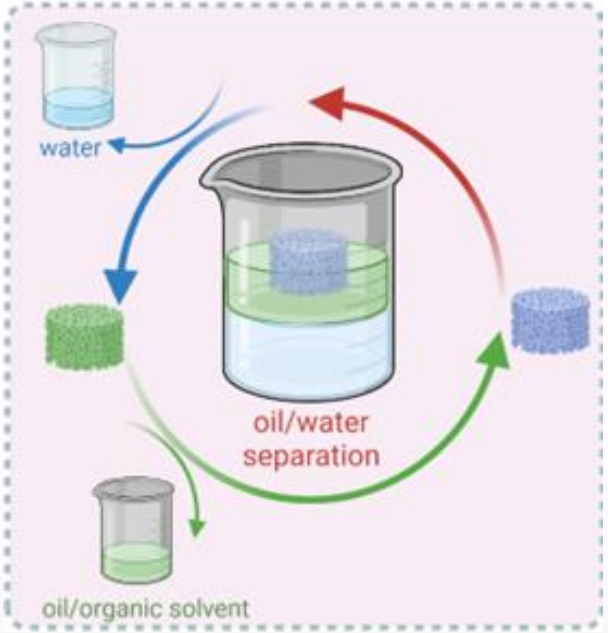
LOW ENERGY SURFACES!



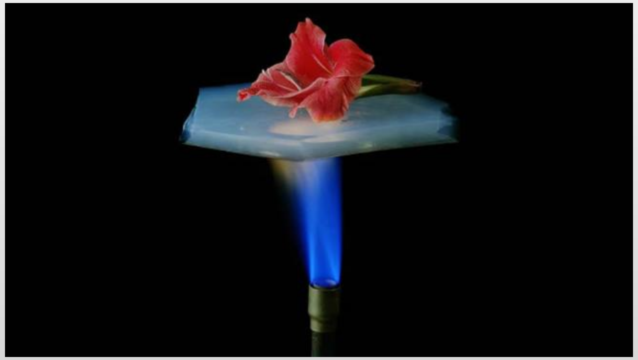




Oil/Organic Solvent Adsorption Ability

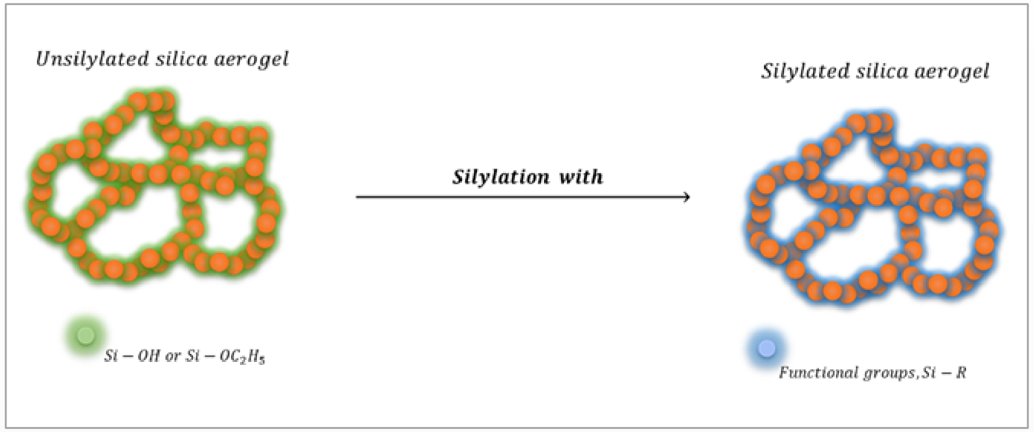


Moisture Resistent Thermal Insulation Ability



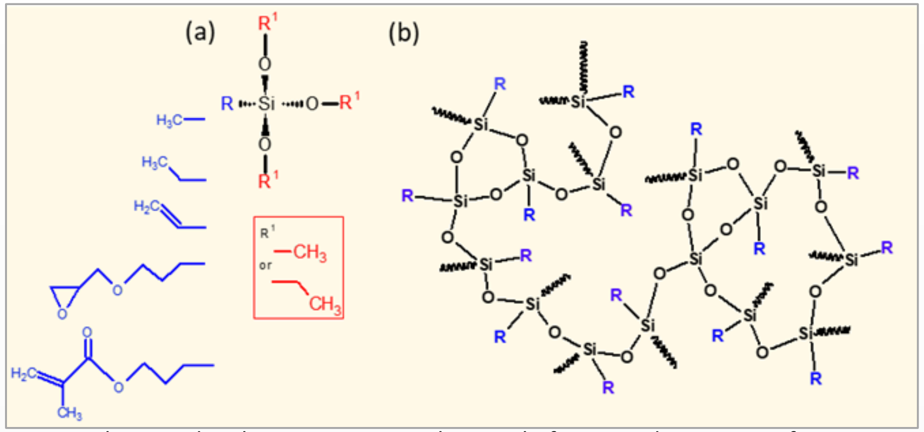
Organofunctionalized silica aerogels can be obtained either by

Ex-situ modification

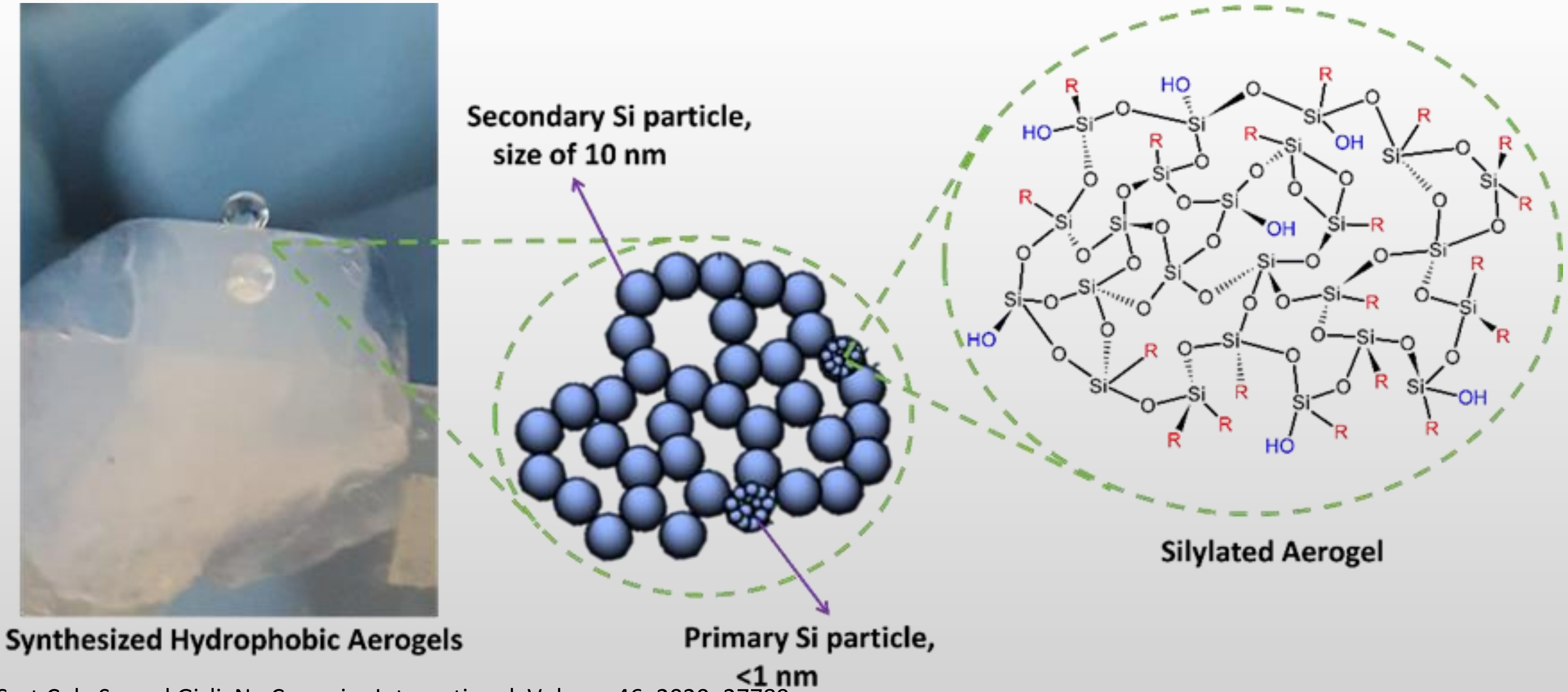


Sert Çok, S., Koç, F., Gizli, Journal of Hazardous Materials, Volume 408, 2021, 124858.

in-situ modification



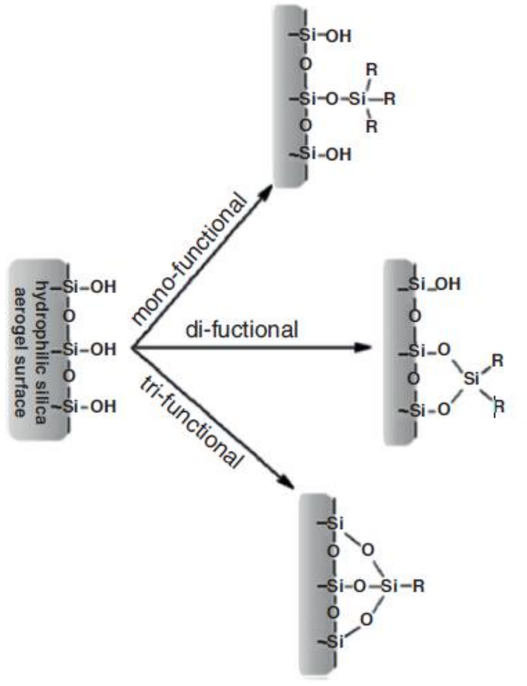
Sert Çok, S., and Gizli, N., International Journal of Heat and Mass Transfer, Volume 188, 2022, 122618.



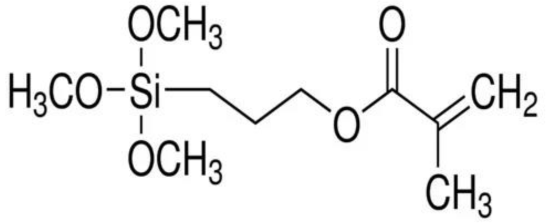
Sert Çok, S., and Gizli, N., Ceramics International, Volume 46, 2020, 27789.

In both strategies, organically modified silica precursors (i.e., alkylsilanes or arylsilanes of type $R_{4-x}Si(OR')_x$ serve as the chemical modifiers of the silica particles derived from the silicon alkoxide ($Si(OR')_4$)) precursor.

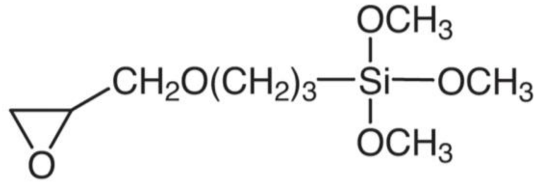
ORGANICALLY MODIFIED SILICA (ORMOSIL) AEROGELS



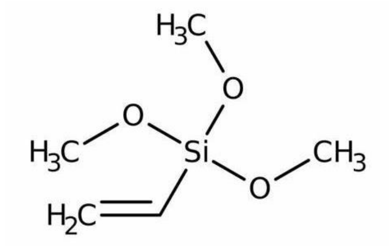
Organofunctional Silanes



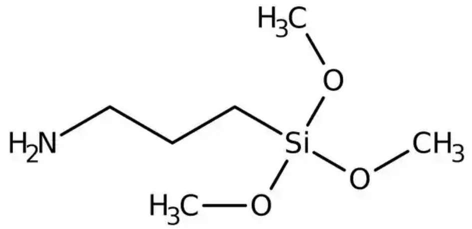
3-methacryloxypropyltrimethoxysilane



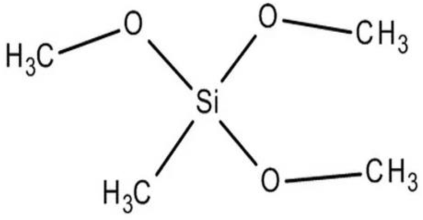
3-Glycidyloxypropyltrimethoxysilane



Vinyltrimethoxysilane



(3-Aminopropyl)trimethoxysilane



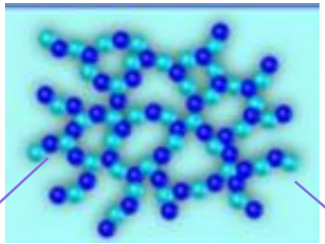
Methyltrimethoxysilane

Benefits from:

- functionality coming from organic groups
- high surface area and stability of inorganic silica host

• IN-SITU MODIFICATION APPROACH

Sol preparation
↓
Gel formation
↓
Ambient pressure drying



WET GEL

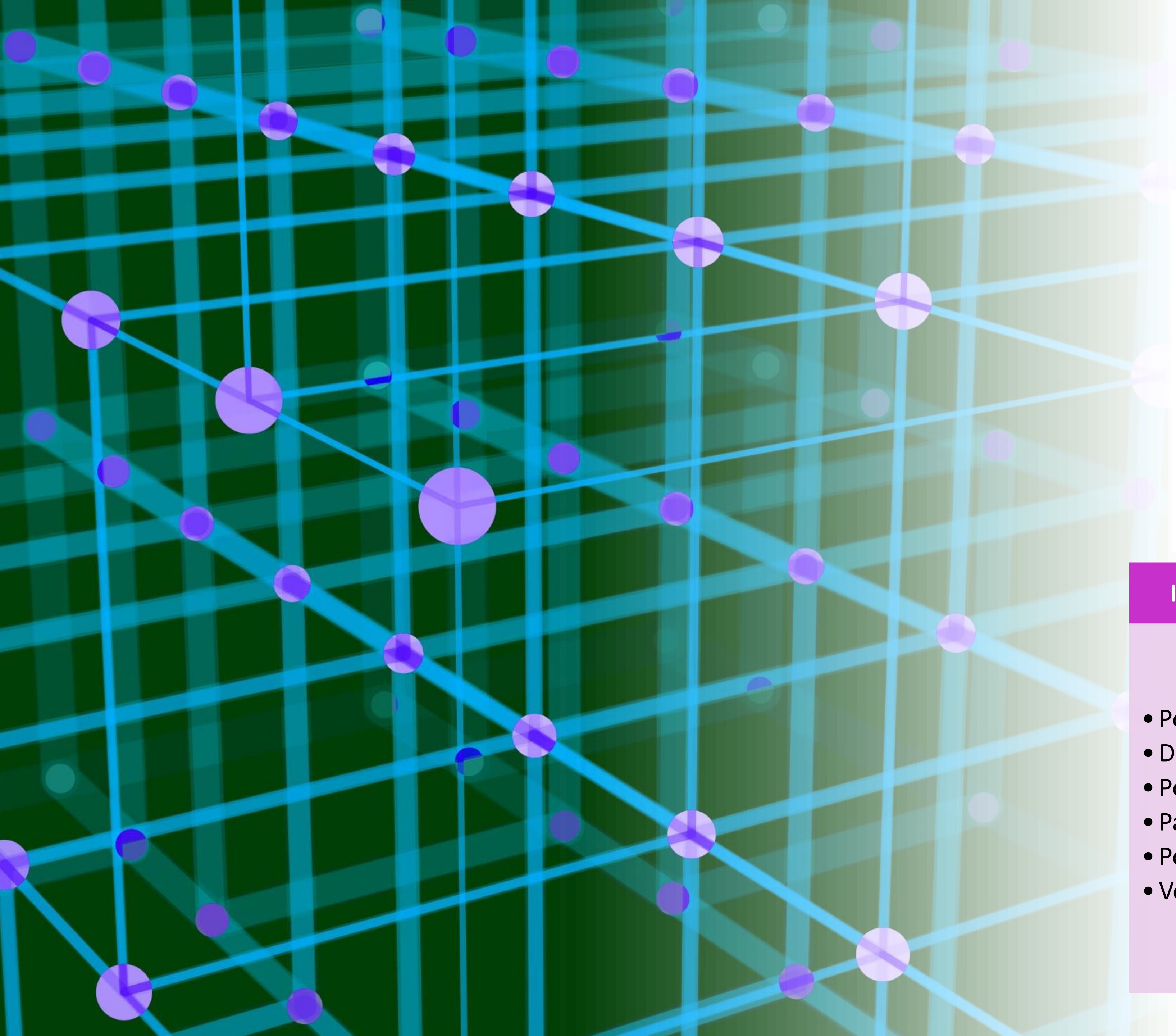
• EX-SITU MODIFICATION APPROACH

Sol preparation
↓
Gel formation
↓
Aging
↓
Solvent exchange
↓
Surface Modification
↓
Ambient pressure drying

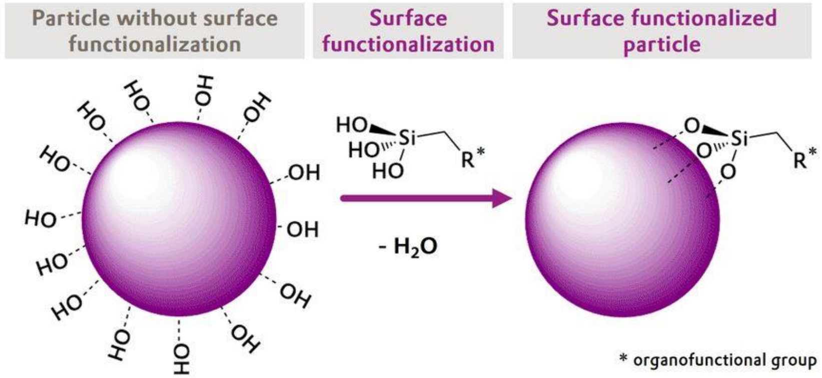
post-gelation treatments (Aging, Solvent exchange, Surface Modification)

- ➢ cost-effective
- ➢ time-saving
- ➢ looser solid matrix
- ➢ possiblity to retain monolithic structure

- ➢ Effective in achieving high hydrophobicity
- ➢ Slightly a time-consuming strategy



Structure-activity relationship



INTRINSIC PROPERTIES		ACTIVITY
• Porosity • Density • Pore Size • Particle Size • Pore Distribution • Versatile surface	⟷	• Lightweight form • High Specific Surface Area • Low thermal conductivity • Low dielectric constant • Low refractive index • Tunable transparency • Tunable Hydrophobicity • Multiple Composition • Flexibility • High mechanical strength

PHYSICOCHEMICAL AND MICROSTRUCTURAL VARIATIONS CAUSED BY ORGANIC SUBSTITUION ARE MONITORED BY:

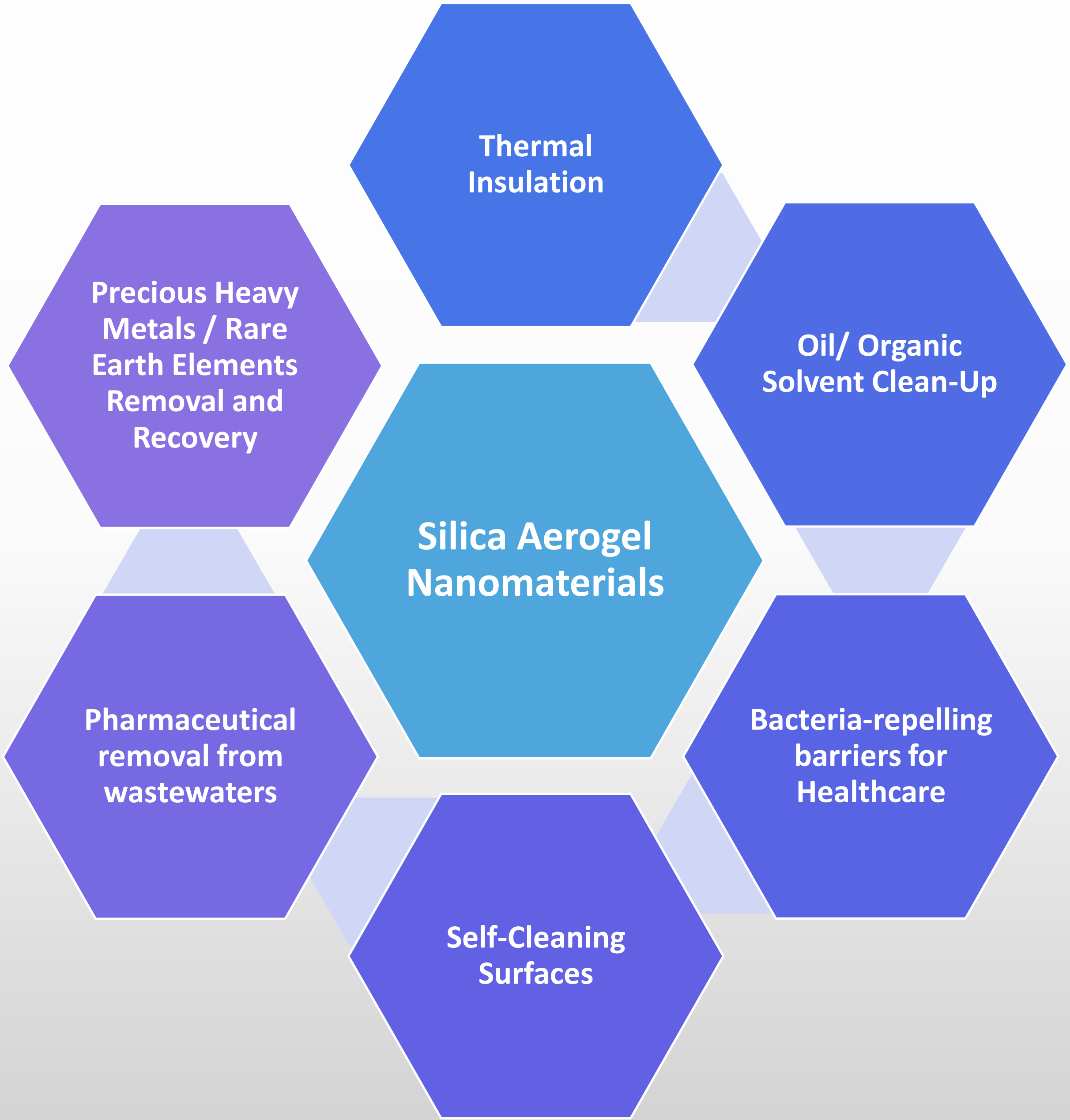
Basic Characterizations

- FTIR
- SEM
- N2 Porosimetry
- TGA
- TEM

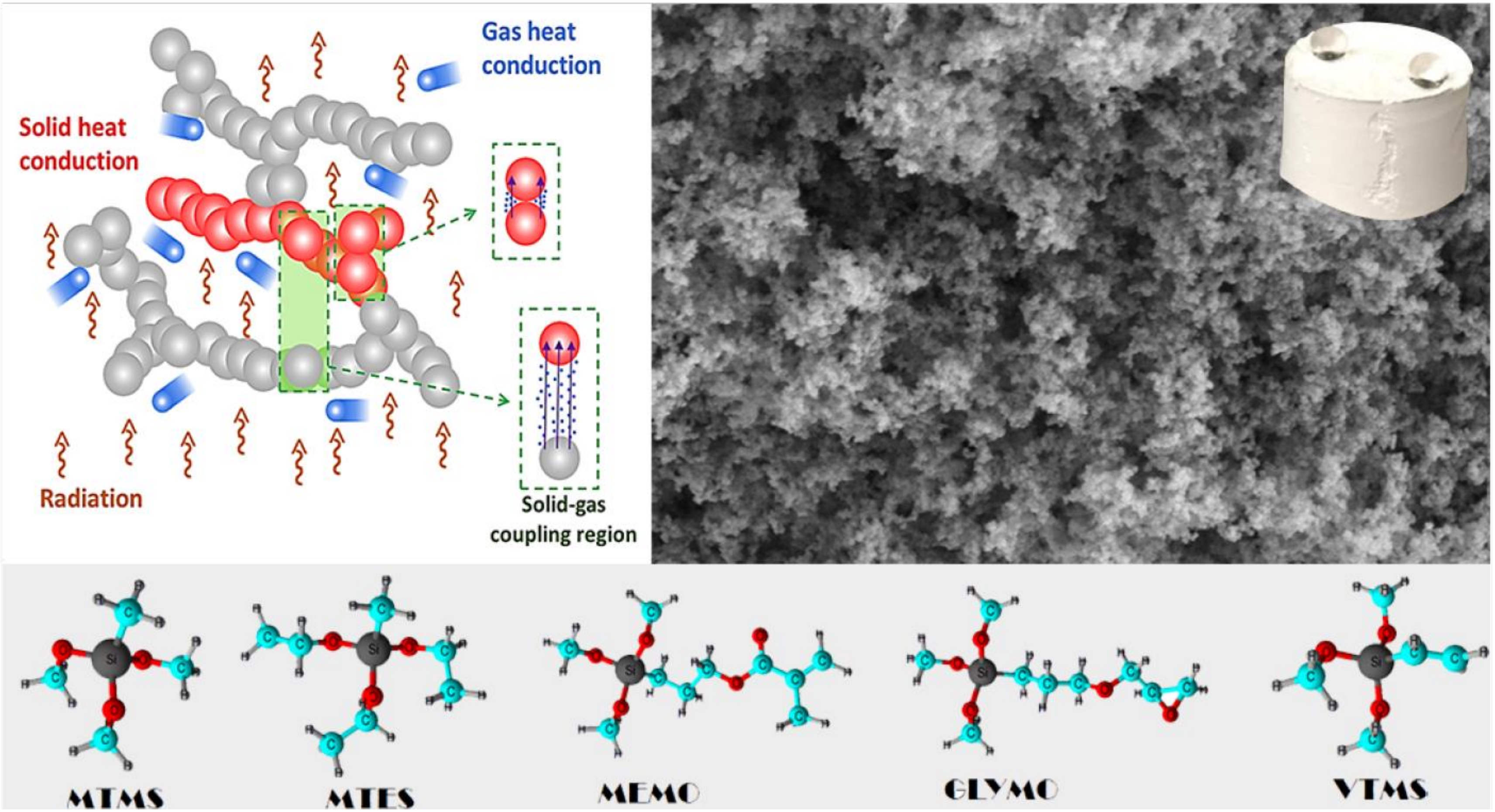
Complementary Characterizations

- ssNMR
- SAXS
- SANS

SO FAR..



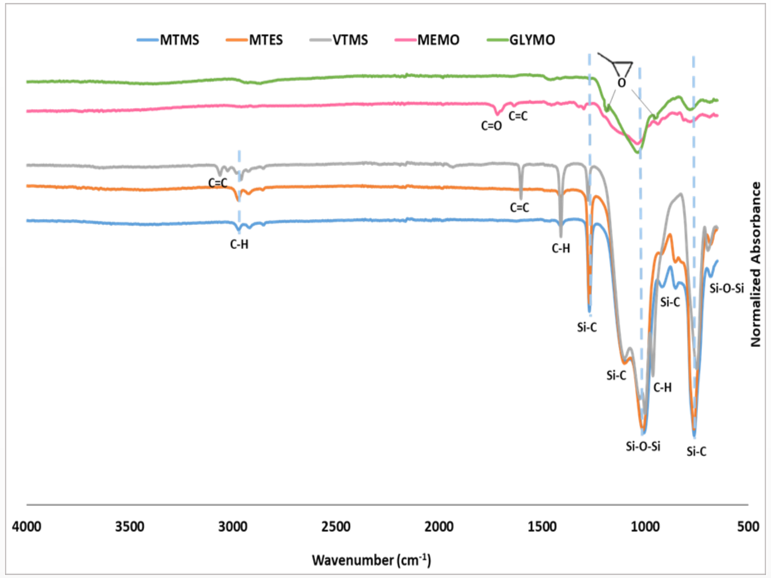
ORGANICALLY MODIFIED SILICA (ORMOSIL) AEROGELS AS THERMAL INSULATORS



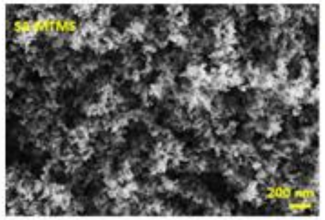
Sert Çok, S., and Gizli, N., Int J of Heat and Mass Transfer, Volume 188, 2022, 122618.

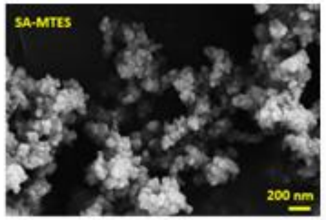
Samples	*S-MTMS*	*S-MTES*	*S-VTMS*	*S-MEMO*	*S-GLYMO*
Physical Appearance					
Density (kg/m³)	92	120	114	380	457
Porosity (%)	95.8	94.5	94.8	82.7	79.2
Gelation time (h)	0.5	1	2	8	8
Total synthesis time (h)	49	69	72	48	48

Chemical Properties



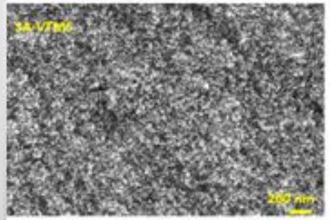
Microstructure

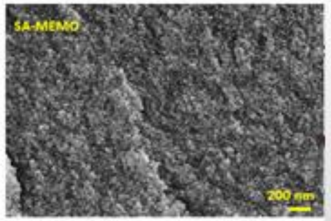


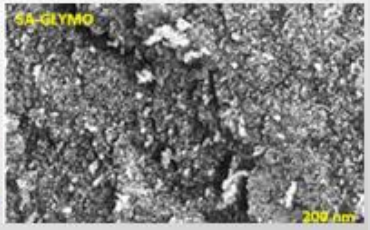


distinct and uniformly distributed pores and fine silica particles

particles aggregated as clusters
globular aggregated morphology



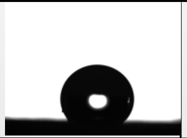
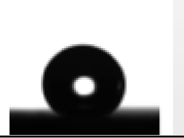
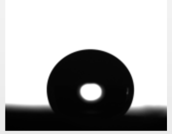




the clusters consisted of densely packed nanoparticles
more compact morphology

some large pores existed

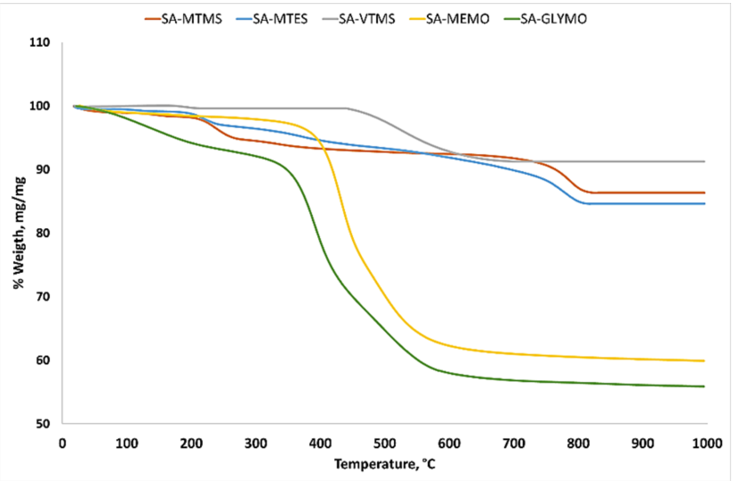
Hydrophobicity

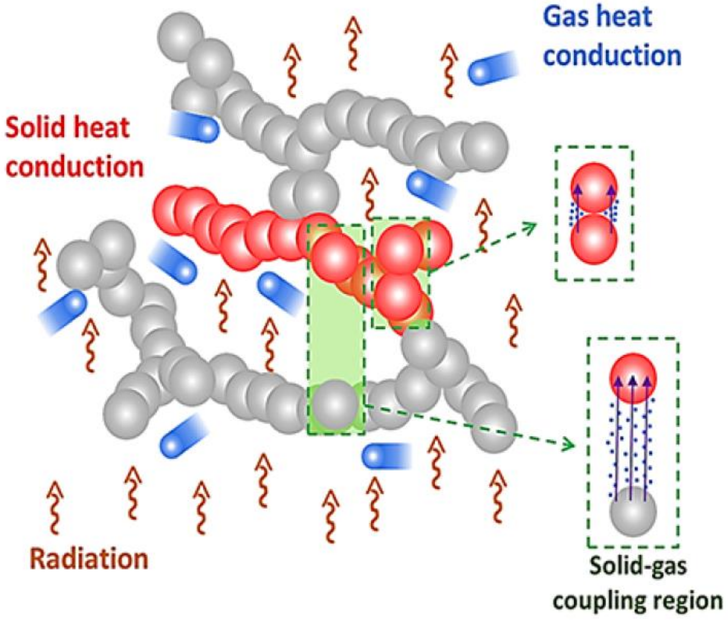
Sample ID	SA-MTMS	SA-MTES	SA-VTMS	SA-MEMO	SA-GLYMO
Contact Angle Image					-
Contact Angle Value (°)	141	147	140	120	-

Textural Properties

SAMPLE ID / PROPERTIES	SA-MTMS	SA-MTES	SA-VTMS	SA-MEMO	SA-GLYMO
S_{BET} (m²/g)	367	315	308	326	531
D (nm)	2.3	2.8	3.2	3.7	6

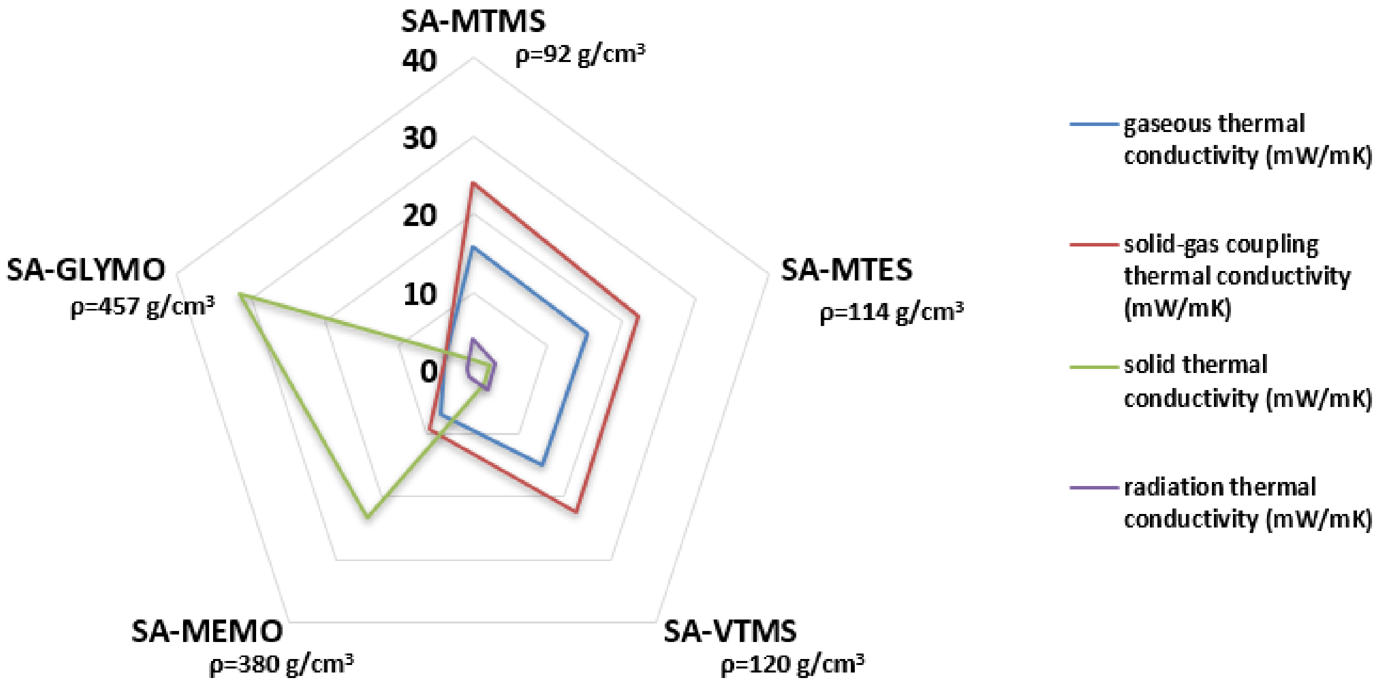
Thermal Stability



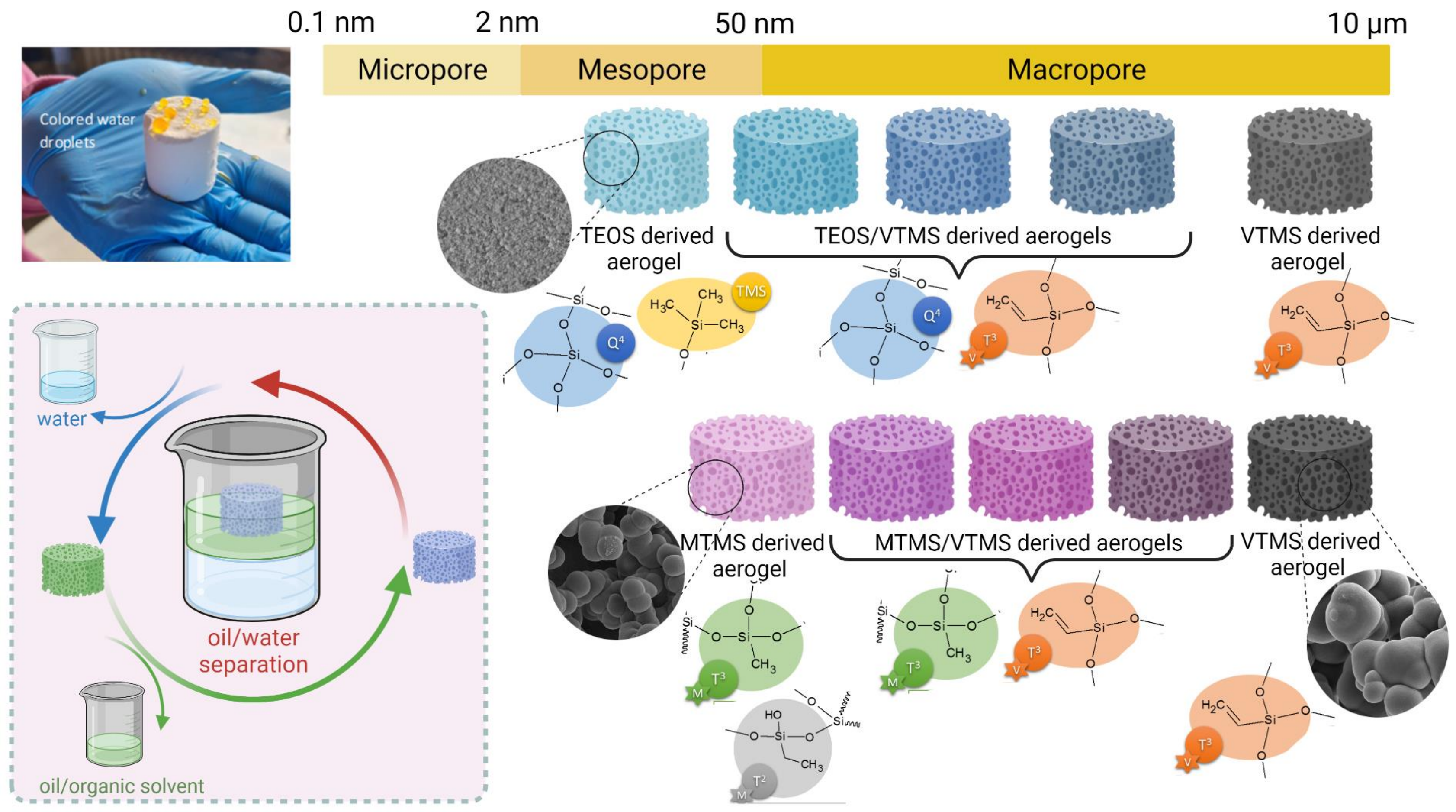


Thermal Conductivity

SAMPLE ID / PROPERTIES	SA-MTMS	SA-MTES	SA-VTMS	SA-MEMO	SA-GLYMO
$\rho\ (kg/m^3)$	92	114	120	380	457
$\lambda_{exp}\ (mW/mK)$*	**45±0.23**	**44±0.25**	**43±0.20**	**42±0.37**	**47±0.39**



DEVELOPMENT OF VINYL/METHYL DECORATED SILICA-BASED AEROGEL-LIKE MATERIALS AND THEIR PERFORMANCE EVALUATION AS NOVEL ADSORBENTS FOR OIL/ORGANIC SOLVENTS



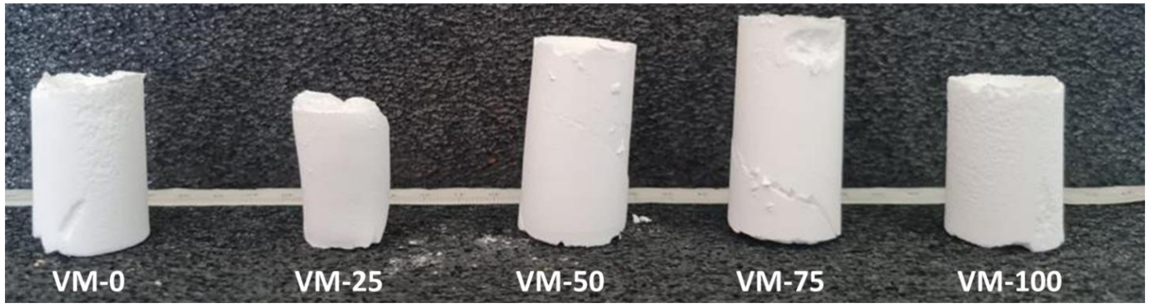
Chemical functionality and the microstructural variations induced by the vinyl substitution, various complementary characterization techniques like:

- ^{29}Si-NMR,
- Small angle neutron/X-ray scatterings (SANS and SAXS)

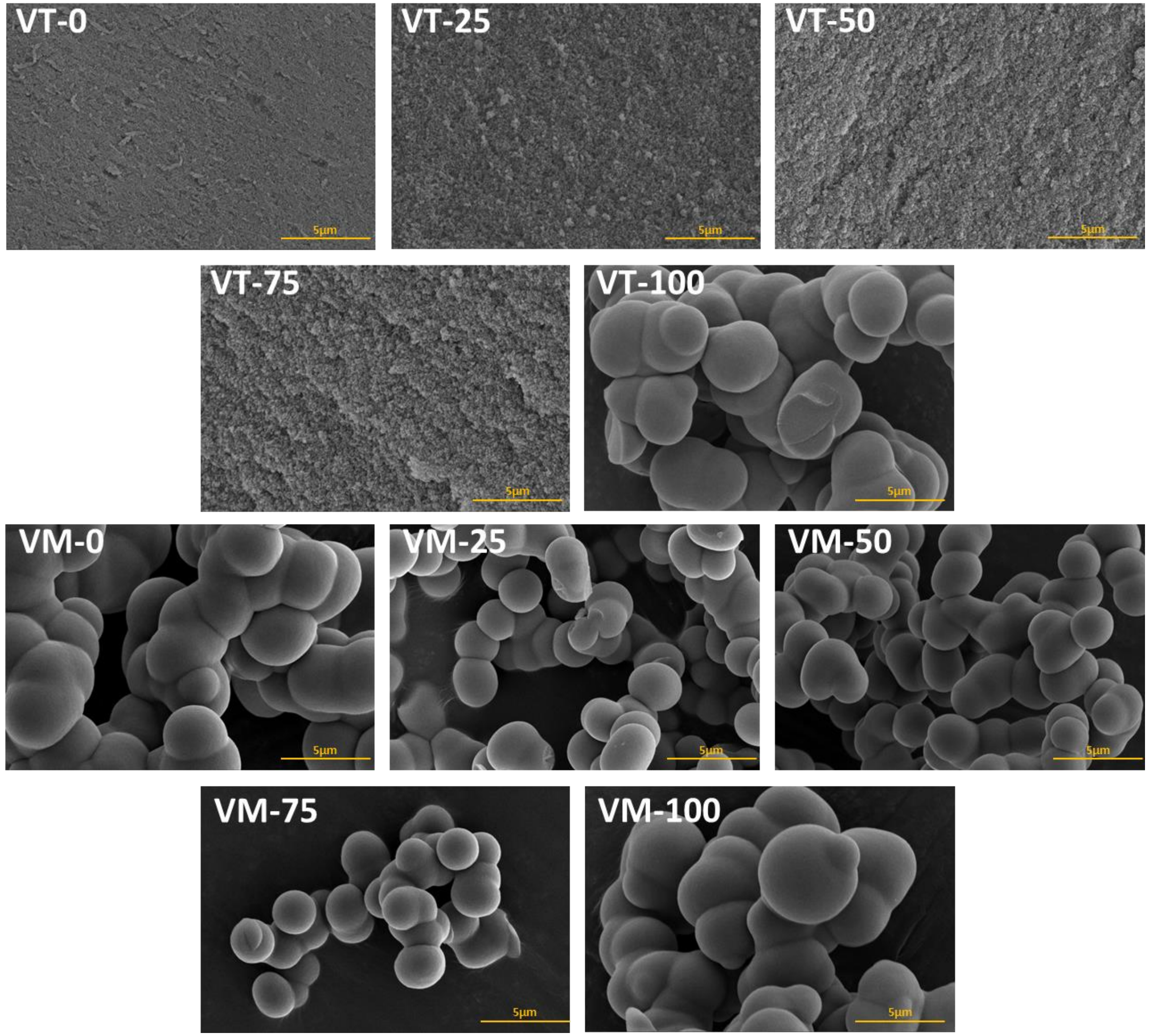
in addition to basic characterizations like

- FTIR,
- N_2 Sorption
- SEM.

Sert Çok S., Koç F., Len A., Gizli N., Dudás Z., The role of surface and structural properties on the adsorptive behavior of vinyl-methyl decorated silica aerogel-like hybrids for oil/organic solvent clean-up practices, 2023, Separation and Purification Technology, Vol.334, 125958.



Microstructure- SEM

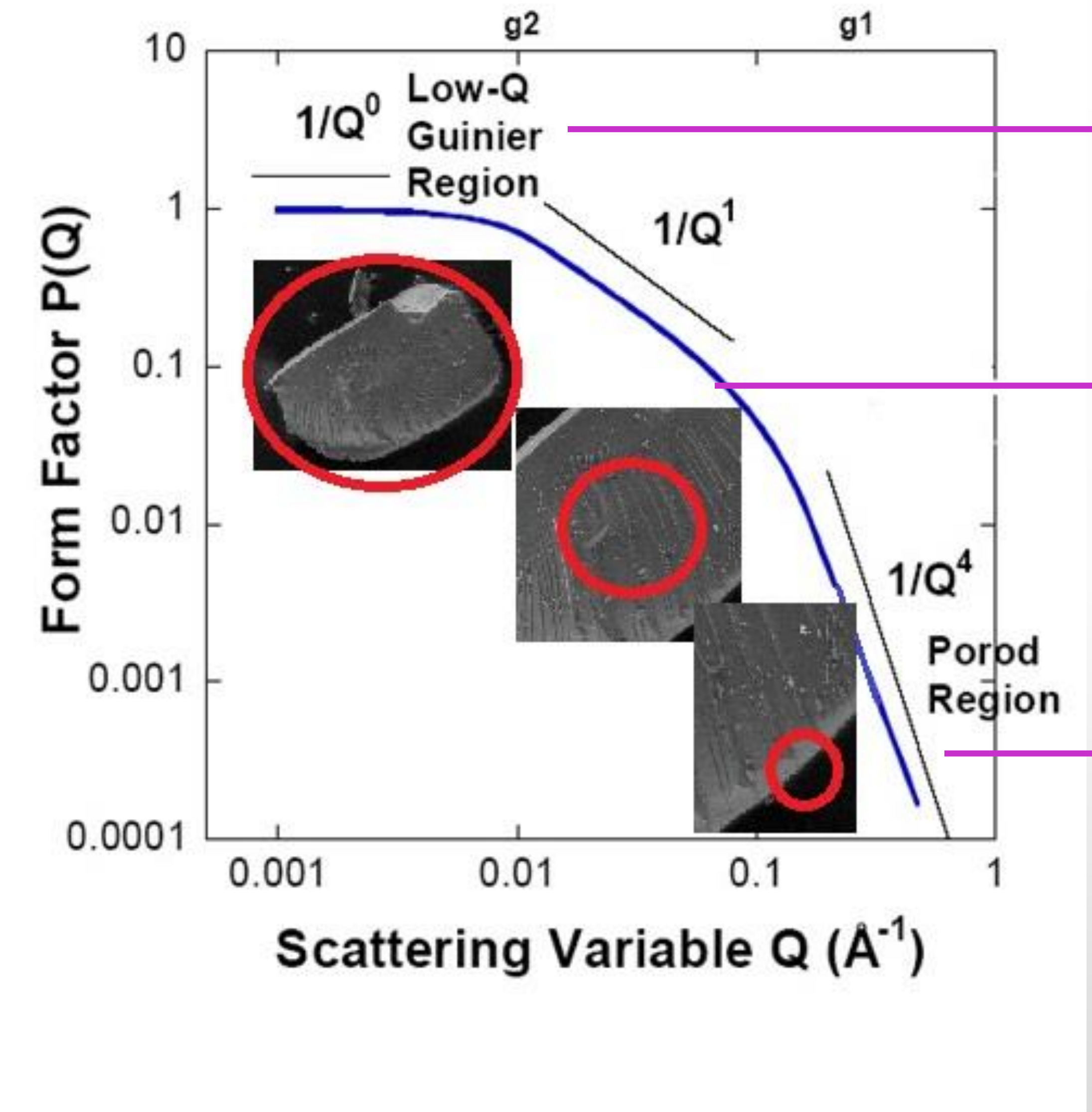


Pore Properties- N_2 Sorption

Sample ID	Surface Area Multipoint BET (m^2/g)	Total Pore Volume (cm^3/g)	DR Method Micropore Volume (cm^3/g)	NLDFT average pore diameter (nm)	Bulk Density (g/cm^3)	Porosity (%)	Volumetric Shrinkage (%)
VT-0	792	1.75	0.250	8.14	0.072	94.9	-
VT-25	1021	1.84	0.340	4.09	0.098	93.1	-
VT-50	889	1.70	0.400	4.88	0.131	90.8	-
VT-75	855	1.18	0.310	6.07	0.110	92.3	-
VT-100	145	0.19	0.027	4.09	0.115	91.9	4.6
VM-0	8.7	0.1	-	-	0.109	92.3	5.9
VM-25	44	0.07	-	-	0.182	87.2	21 .2
VM-50	16	0.08	0.009	-	0.095	93.3	6.8
VM-75	21	0.05	0.010	-	0.087	93.9	8.1
VM-100	4.4	0.03	0.002	-	0.125	91.2	5.8

Sert Çok S., Koç F., Len A., Gizli N., Dudás Z., The role of surface and structural properties on the adsorptive behavior of vinyl-methyl decorated silica aerogel-like hybrids for oil/organic solvent clean-up practices, 2023, Separation and Purification Technology, Vol.334, 125958.

INTRODUCTION –SANS measurements



Low-Q Guinier ($1/Q^0$) region: Gives the details about the particle size of the material

$1/Q^1$ region: Gives the details about the porosity the material

Porod ($1/Q^{4)}$ region: Gives the details about the surface properties of the material

Microstructure- SANS

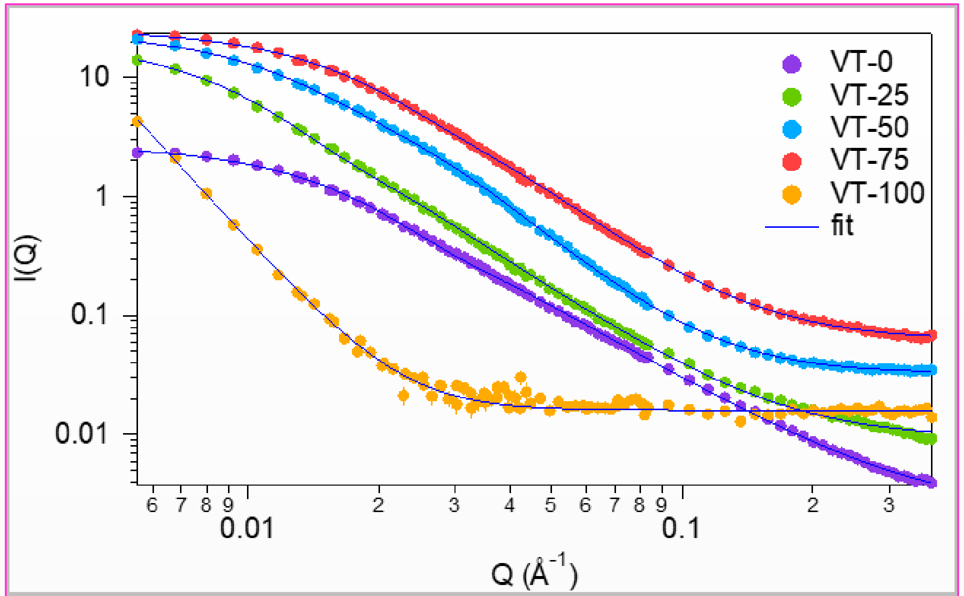
Fitted SANS parameters for the VT and VM series

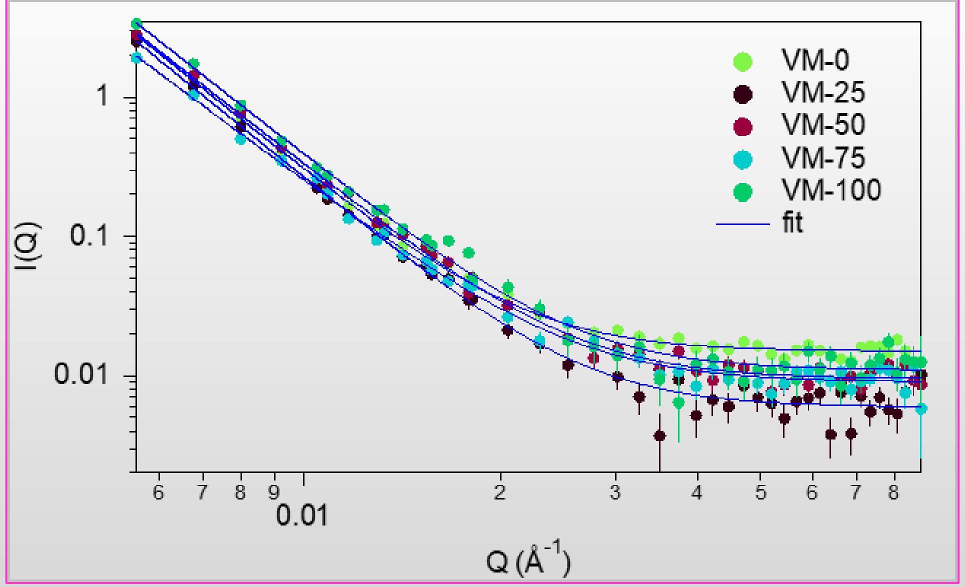
Sample	p	Rg (Å)	Estimated diameter (nm)	Sample	SANS p
VT-0	2.04 ± 0.01	115 ± 1	30	VM-0	3.82 ± 0.03
VT-25	2.38 ± 0.01	211 ± 2	55	VM-25	3.84 ± 0.04
VT-50	2.63 ± 0.01	150 ± 2	39	VM-50	3.70 ± 0.03
VT-75	3.02 ± 0.01	108 ± 1	28	VM-75	3.53 ± 0.03
VT-100	4.00 ± 0.03	-	-	VM-100	3.71 ± 0.04

- VT-0 -75 samples showed volume fractal-like behavior characteristic for multilevel particle system.
- The VT-100 sample showed smooth interfaces between the pores and micrometer-sized particles.

- The VT series showed average estimated particle sizes from 28 to 55 nm, except for the VT-100.
- The VM series does not contain pores or particles in the size range of 20 nm to 100 nm.

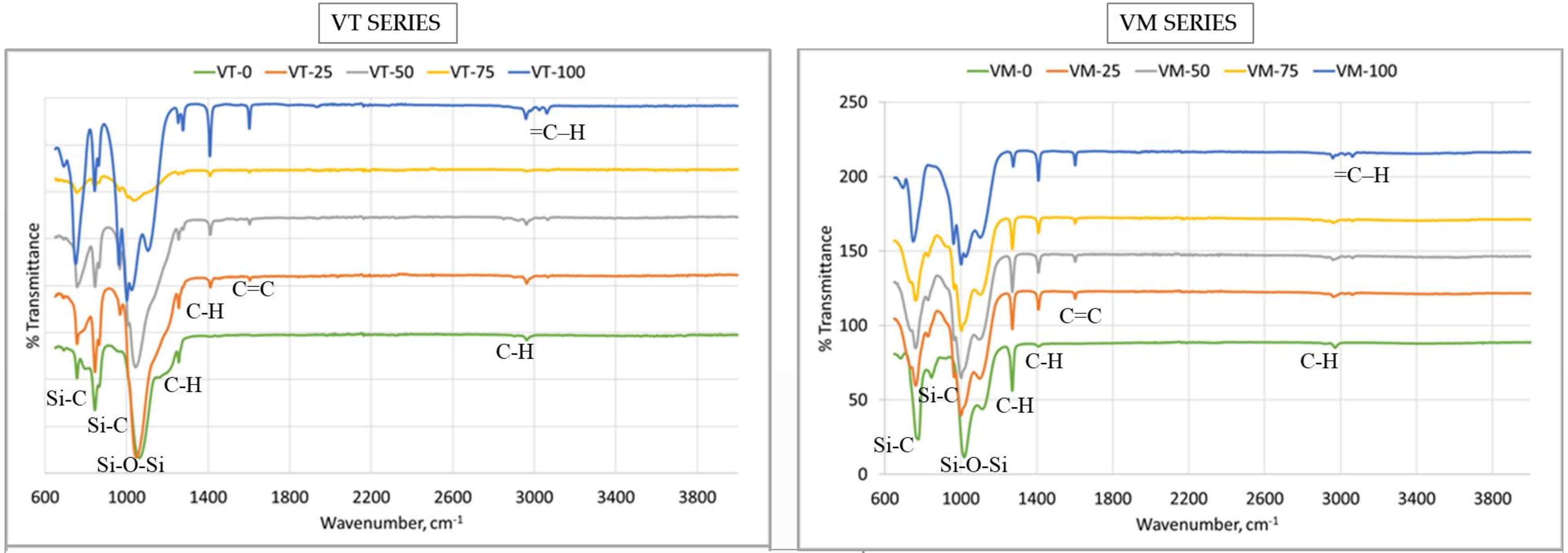
- The VM shows fractal-like behavior with the calculated p exponents
- Characteristic of surface fractals and describes a rough interface between the micrometric pores and particles.





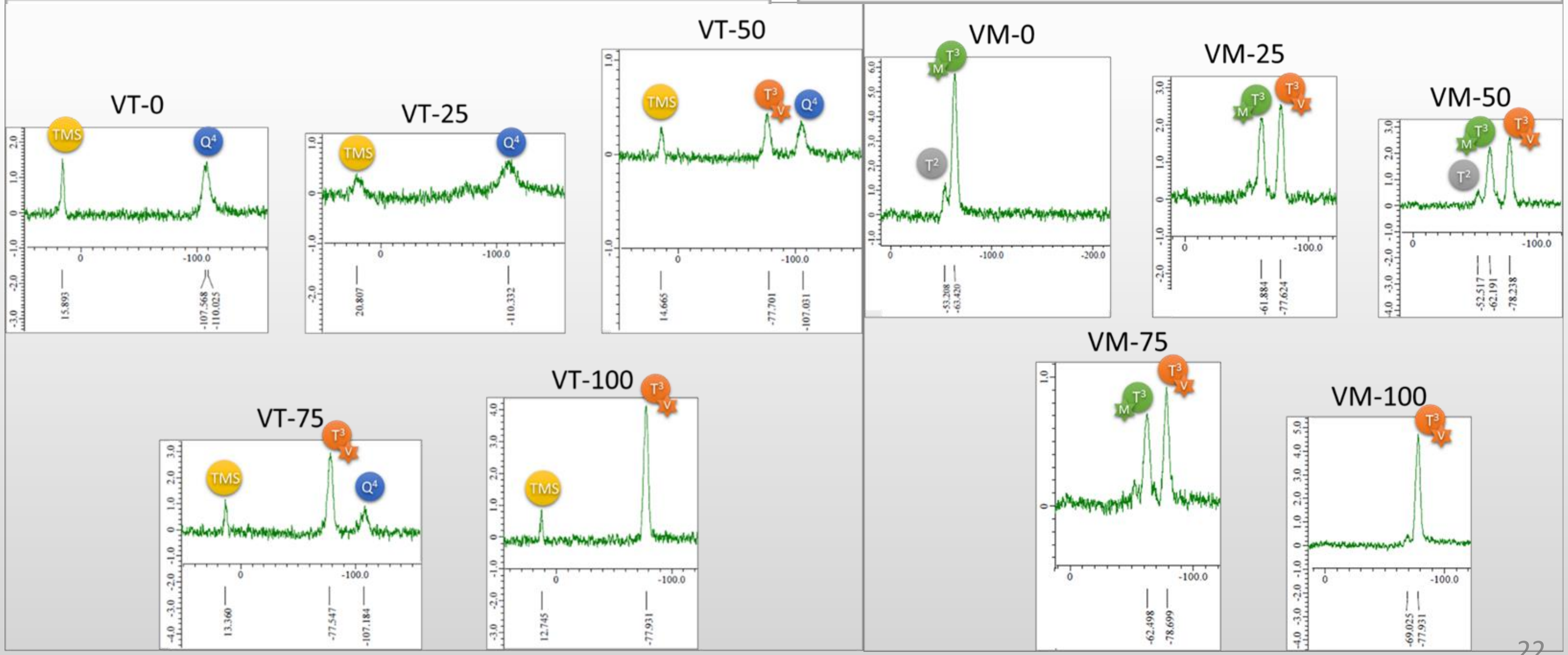
Sert Çok S., Koç F., Len A., Gizli N., Dudás Z., The role of surface and structural properties on the adsorptive behavior of vinyl-methyl decorated silica aerogel-like hybrids for oil/organic solvent clean-up practices, 2023, Separation and Purification Technology, Vol.334, 125958.

FTIR



Chemical Properties

^{29}Si-NMR



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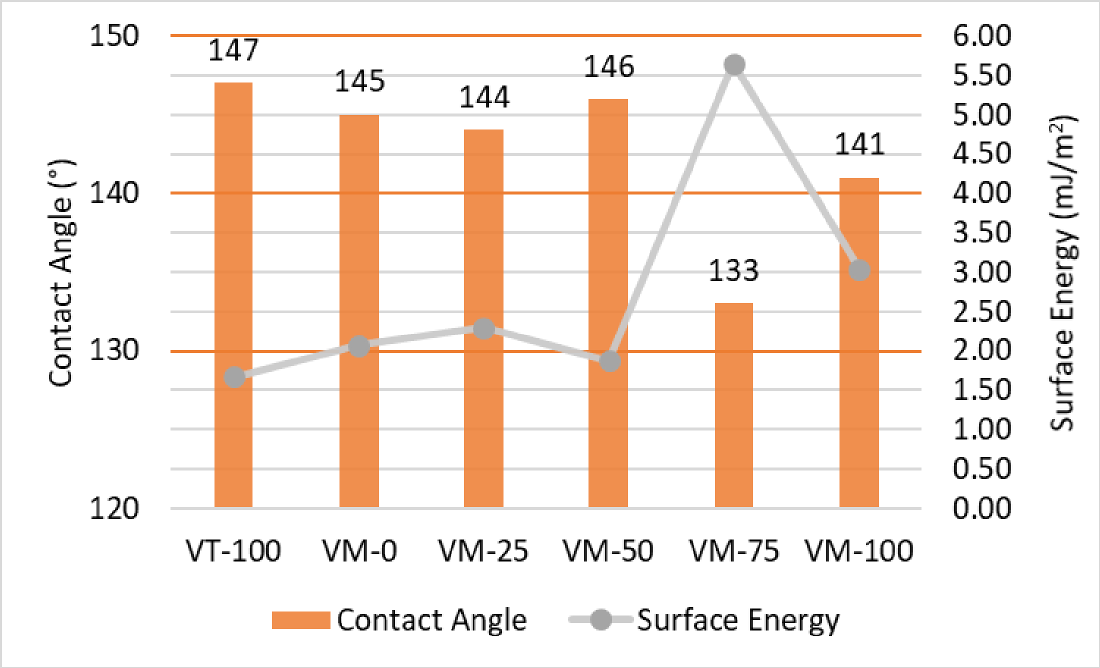
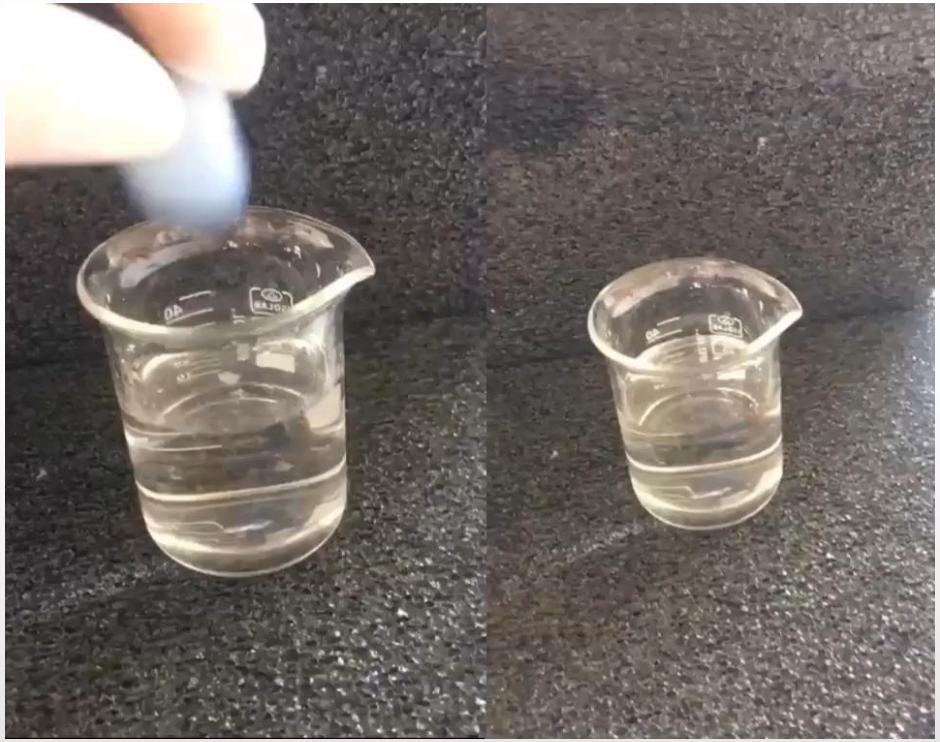
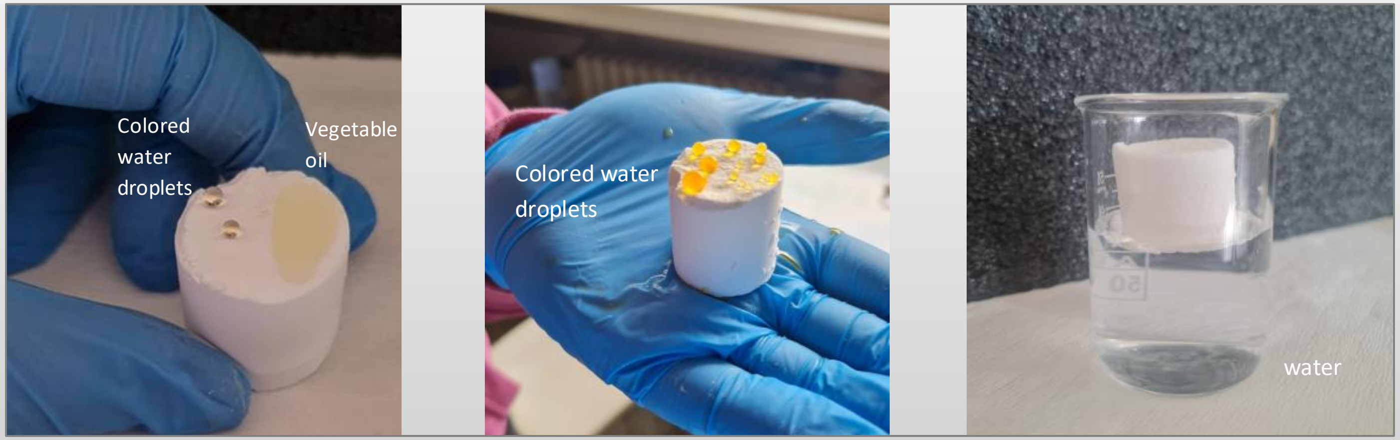
SURFACE PROPERTIES- CONTACT ANGLE MEASUREMENTS



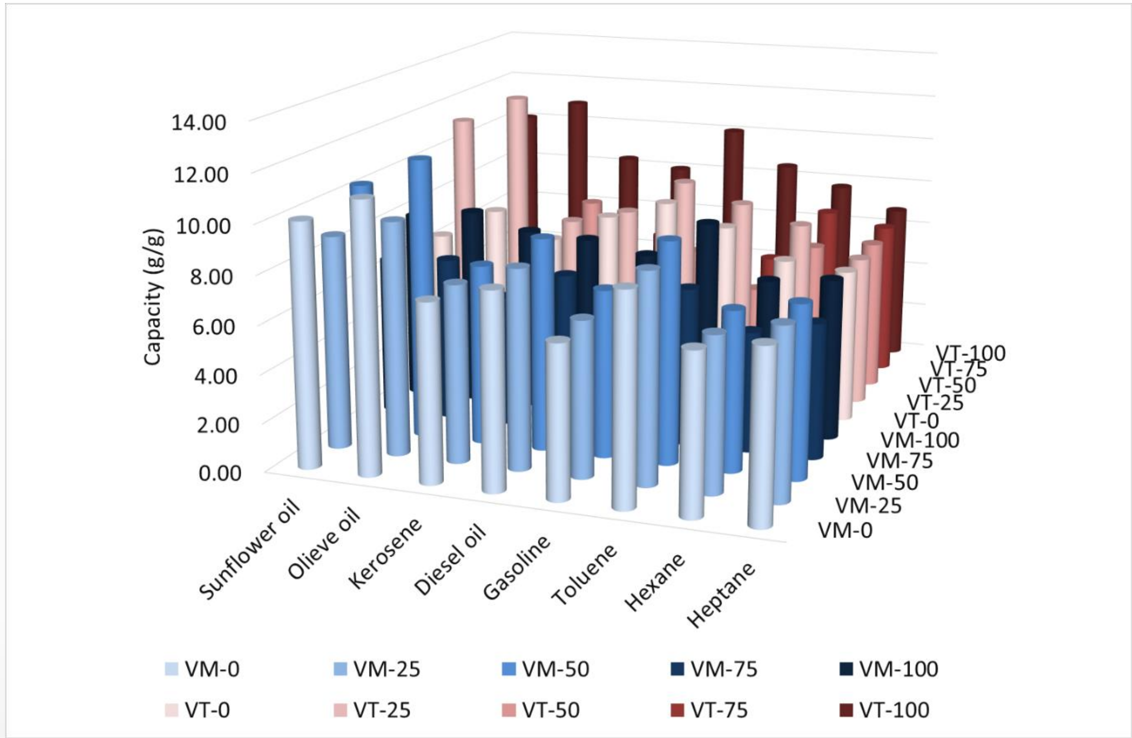
Hydrophobic behaviour of the samples in VT series

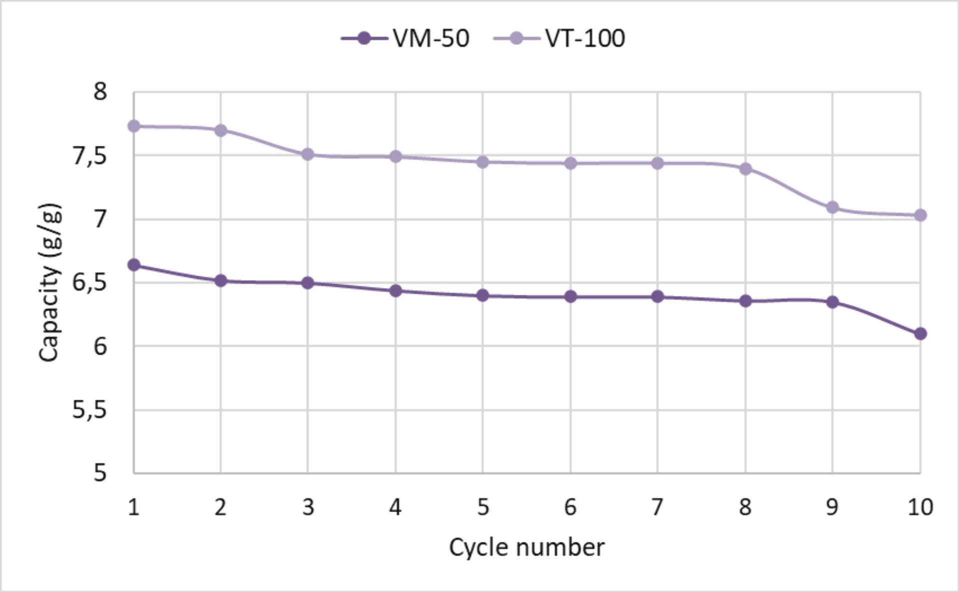


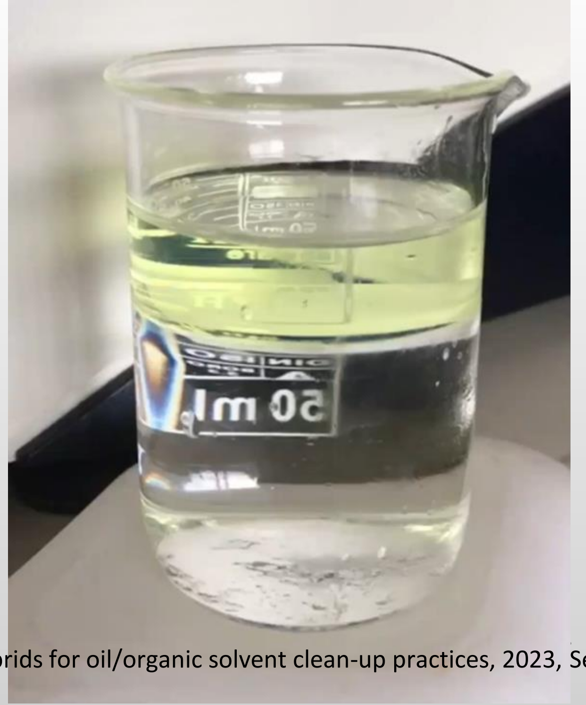


Sert Çok S., Koç F., Len A., Gizli N., Dudás Z., The role of surface and structural properties on the adsorptive behavior of vinyl-methyl decorated silica aerogel-like hybrids for oil/organic solvent clean-up practices, 2023, Separation and Purification Technology, Vol.334, 125958.

OIL/ORGANIC SOLVENT SORPTION STUDIES







- All samples reached over 90% of their capacity after less than 5 min of exposure, confirming fast sorption kinetics.
- VT-100 and VM-50 had the highest uptake capacity for the majority of the pollutants.

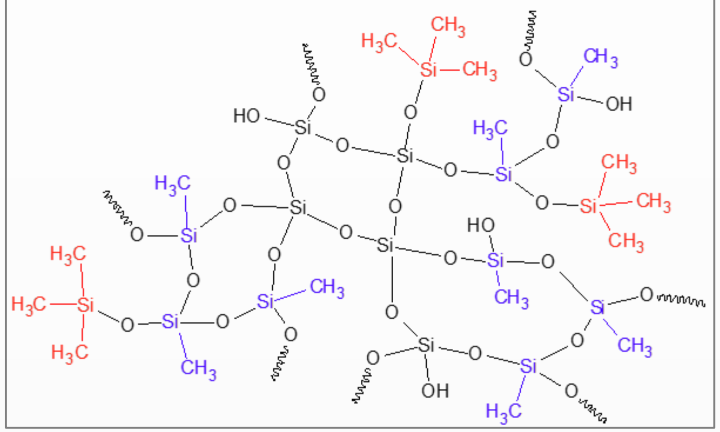
Sert Çok S., Koç F., Len A., Gizli N., Dudás Z., The role of surface and structural properties on the adsorptive behavior of vinyl-methyl decorated silica aerogel-like hybrids for oil/organic solvent clean-up practices, 2023, Separation and Purification Technology, Vol.334, 125958.

FEASIBILITY OF METHYLATED SILICA XEROGELS AS SUPERHYDROPHOBIC, SELF CLEANING MATERIALS WITH BACTERIA REPELLING PROPERTY

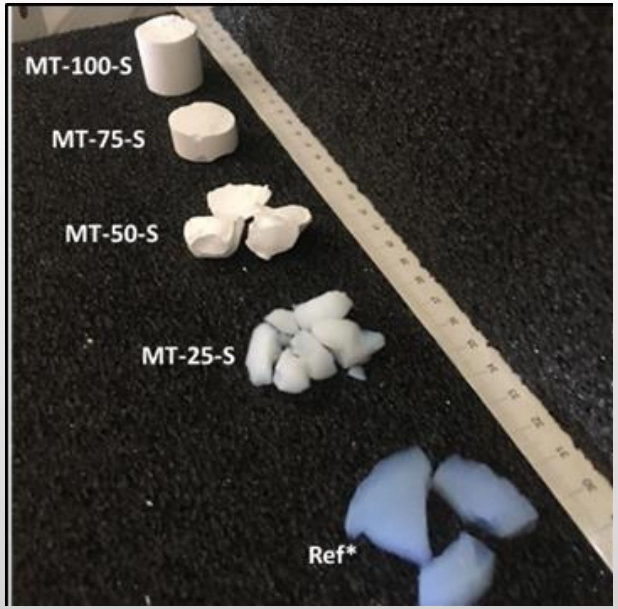
Sol preparation → Gel formation → Aging → Solvent exchange → Surface Modification → Ambient pressure drying

- MTMS content (MTMS/TEOS) was varied 0%, 25%, 50%, 75%, 100% by vol.
- To improve the methyl functionality, heat treatment at 250°C for 4 h was applied to all samples.

TEOS/MTMS aerogel with TMCS silylation



MT-0-S MT-25-S MT-50-S MT-75-S MT-100-S

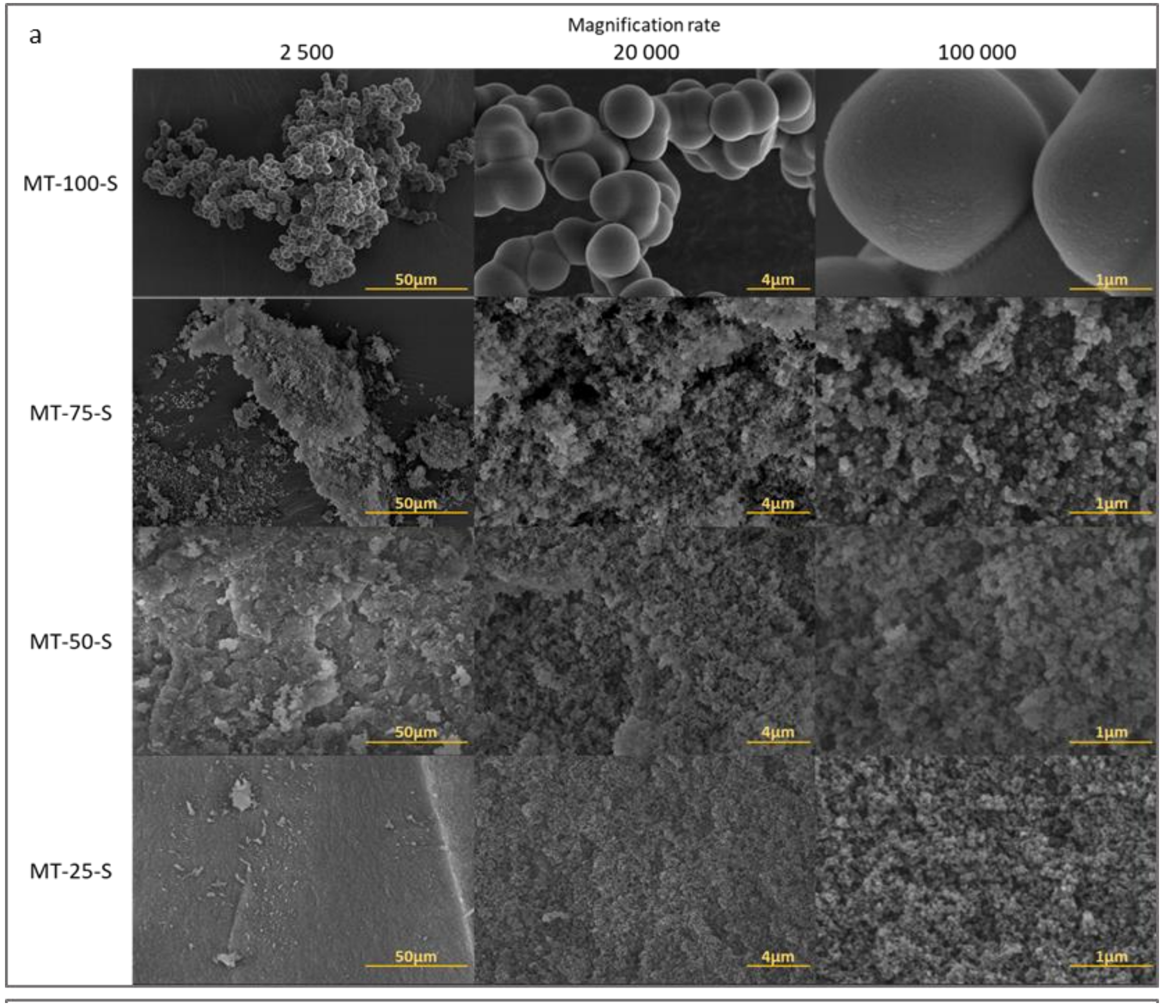


Sample ID	Surface Area, m^2/g	Ave. Pore Diameter, nm		Total pore vol., cm^3/g		Exp.bulk density, g/cm^3	Porosity, %	% linear shrinkage
	S_{BET}	$d_{p,BET}$	d_p*	$V_{p,BET}$	V_p*	ρ_b		
MT-100-S	39	1.4	1014	0.12	9.89	0.096	95	2.86
MT-75-S	302	11	100	0.99	7.57	0.121	92	3.57
MT-50-S	613	1.7	34	4.25	5.32	0.166	88	-
MT-25-S	844	1.4	24	4.05	5.06	0.173	87	-

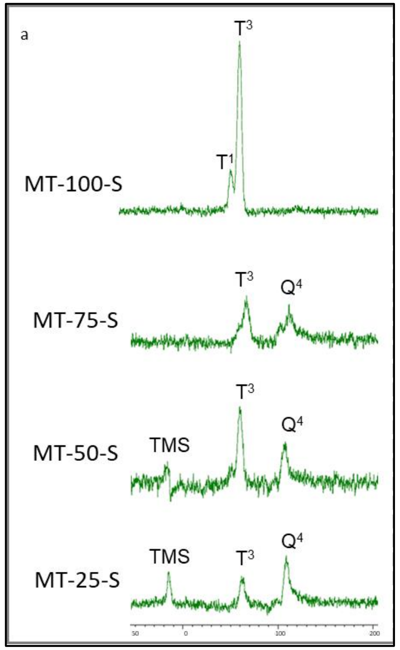
*: properties calculated depending on experimental bulk and skeletal density.

Sert Çok S., Koç F., Dudás Z., Gizli N., Methyl Functionality of Monolithic Silica Xerogels Synthesized via the Co-gelation Approach Combined with Surface Silylation, 2023, Gels, Vol.9, 33.

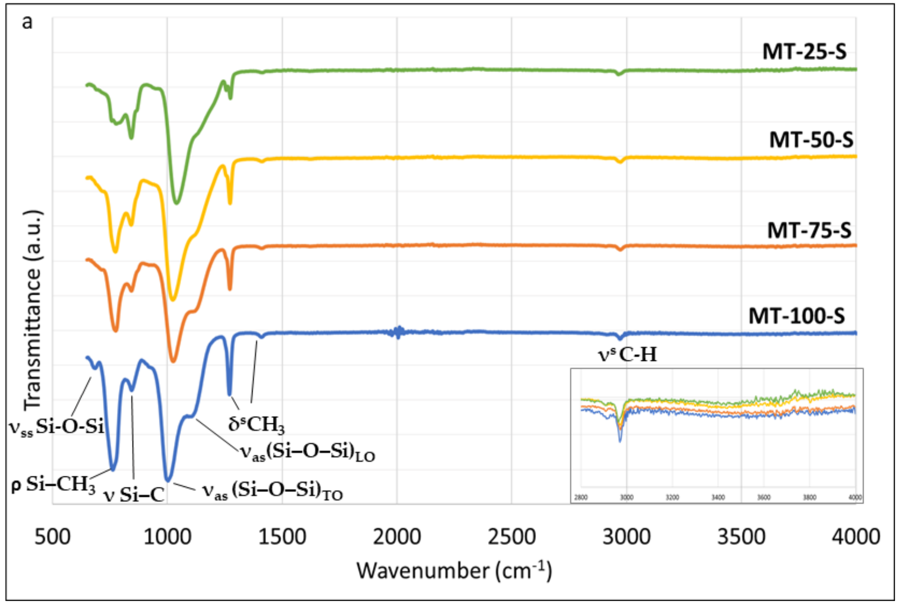
SEM MICROGRAPHS



^{29}Si-NMR SPECTRA



FTIR SPECTRA



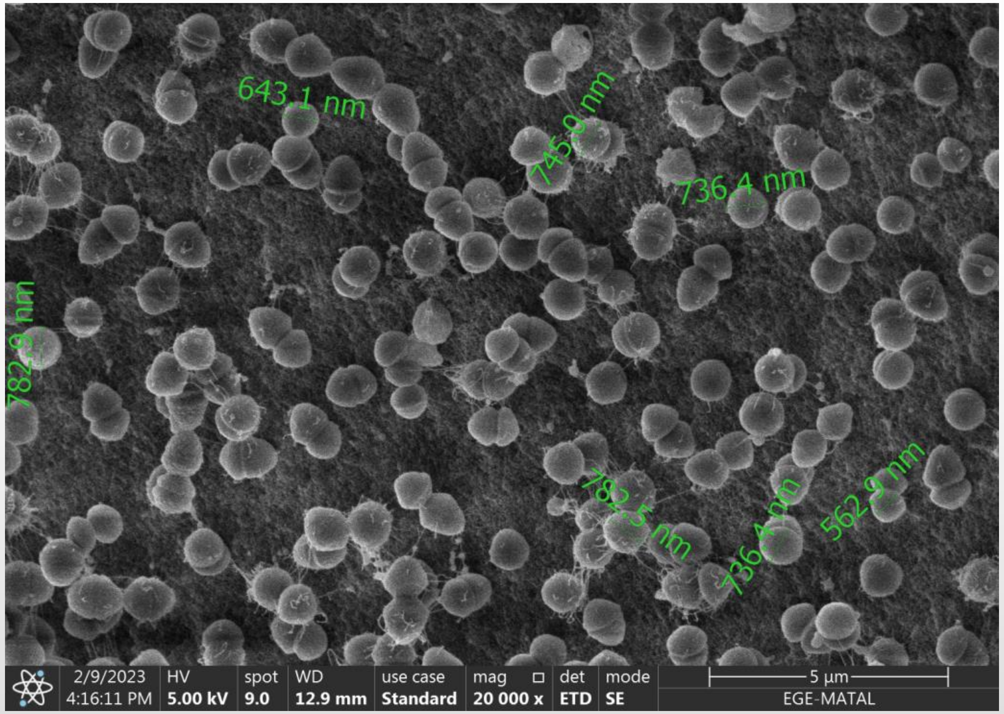
Sert Çok S., Koç F., Dudás Z., Gizli N., Methyl Functionality of Monolithic Silica Xerogels Synthesized via the Co-gelation Approach Combined with Surface Silylation, 2023, Gels, Vol.9, 33.

Bacterial Adhesion Tests:

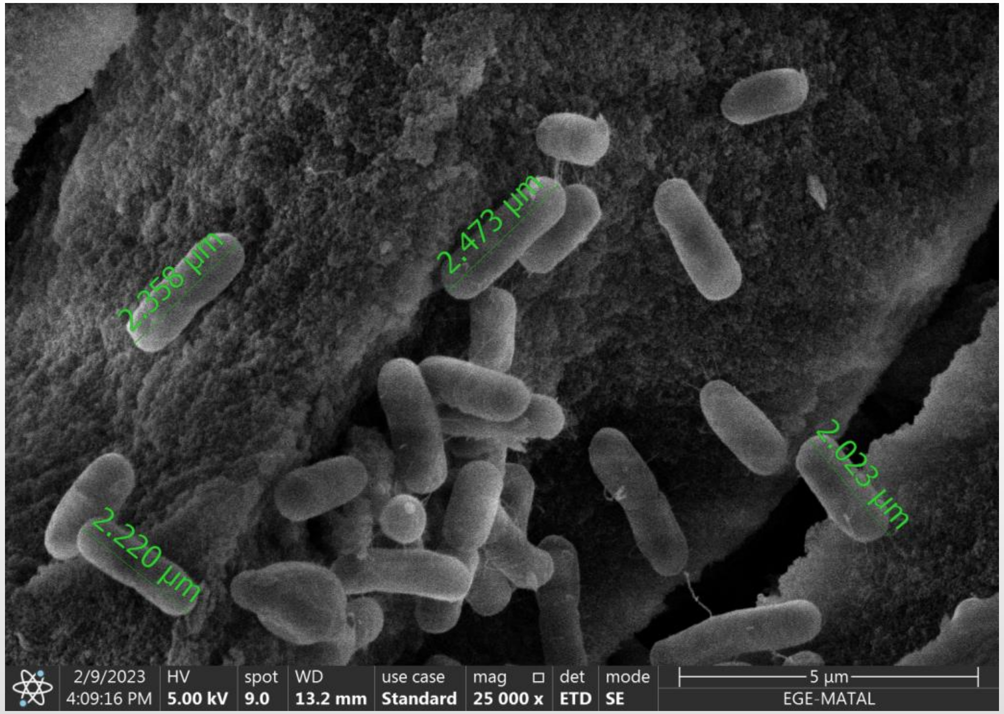
- Staphylococcus aureus and Escherichia coli O157:H7 were selected as reference gram-positive and gram-negative bacteria.
- Working cultures were obtained by inoculating them into tryptic soy broth.
- Aerobic incubation of the strains was carried out at 37 °C for 24 hours (≈ 9 CFU/ml).
- Before the inoculation, the hydrophobic aerogels and hydrophilic aerogel as a reference were well sterilized by submerging them into 70 % Ethanol.
- Inoculation was carried out under ambient conditions for 6 hours.
- After inoculation, bacterial attachments on both hydrophilic and hydrophobic aerogels were observed by SEM analysis.

SEM MICROGRAPHS OF HYDROPHILIC AND HYDROPHOBIC AEROGELS

Hydrophilic Reference Aerogels

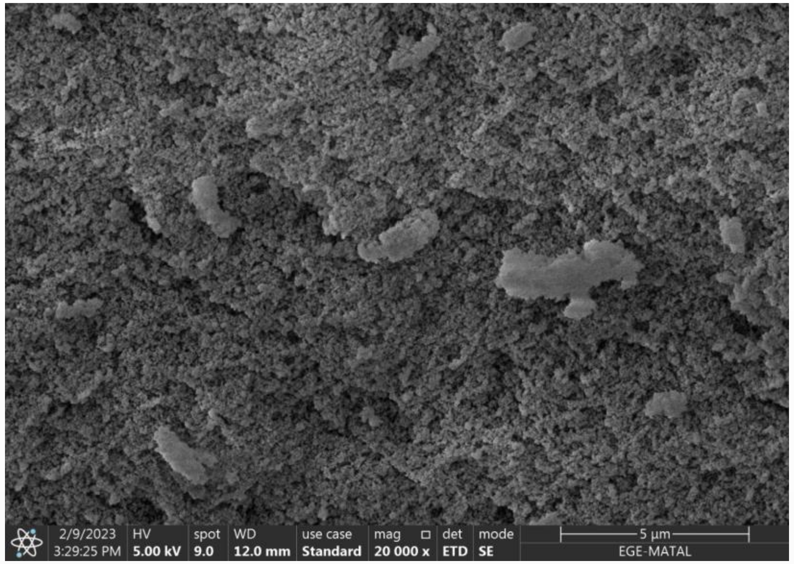


S.aureus

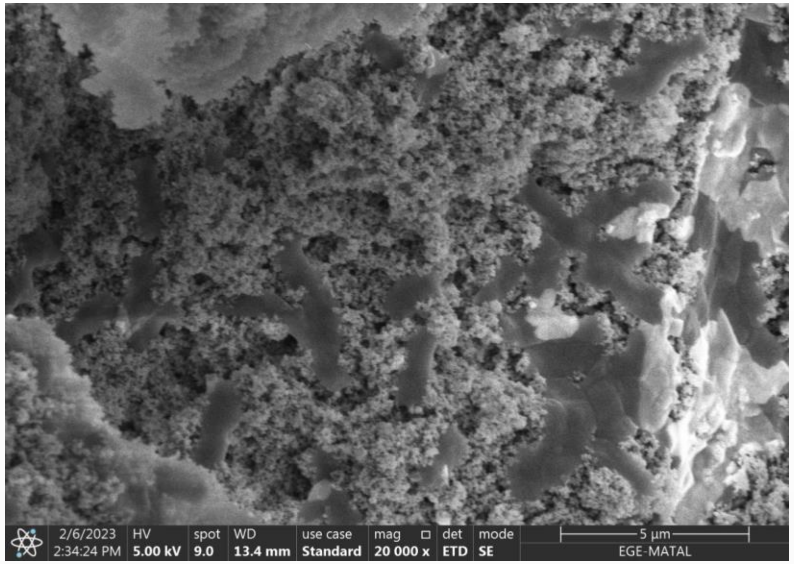


E.Coli

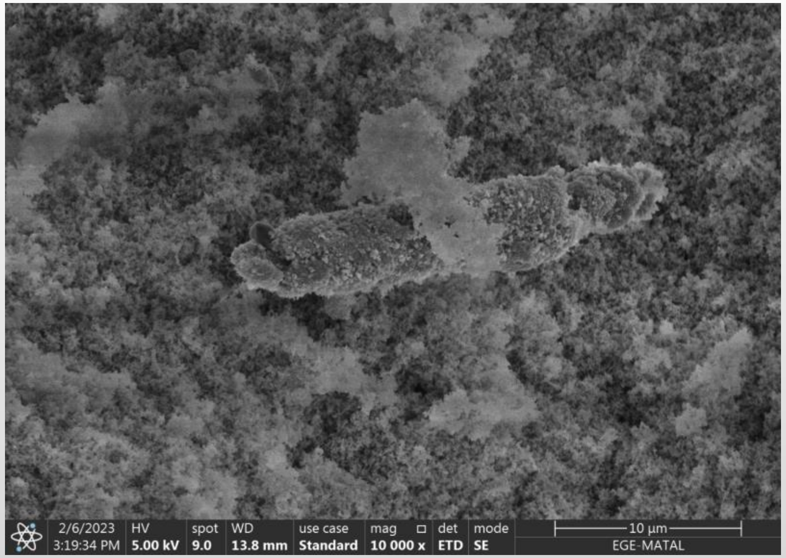
E.Coli Adhesion



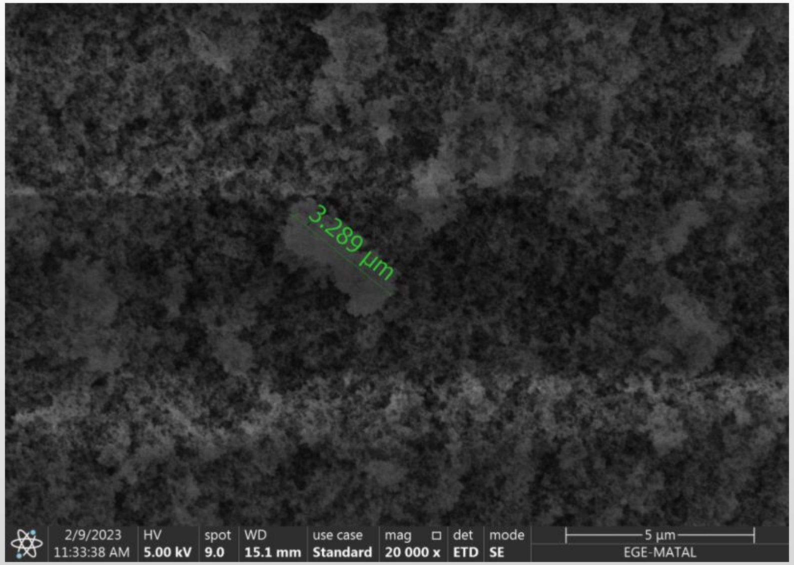
MT-25-S



MT-50-S



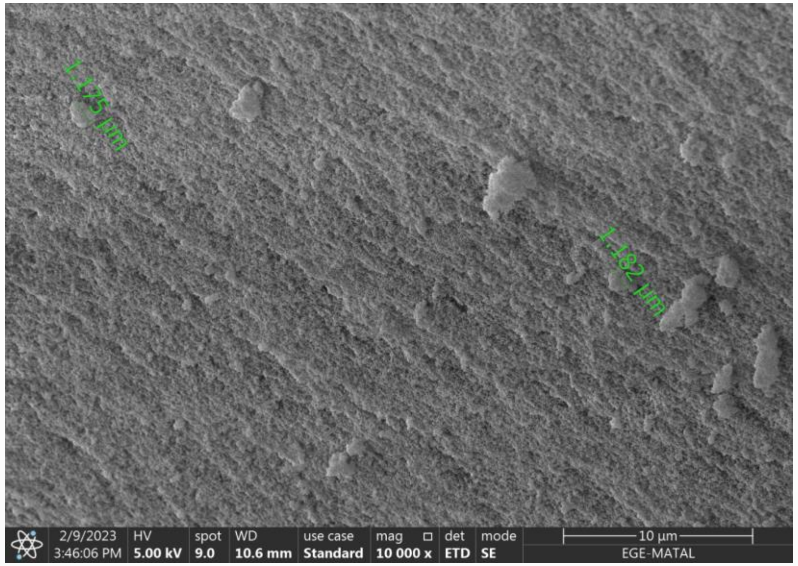
MT-75-S



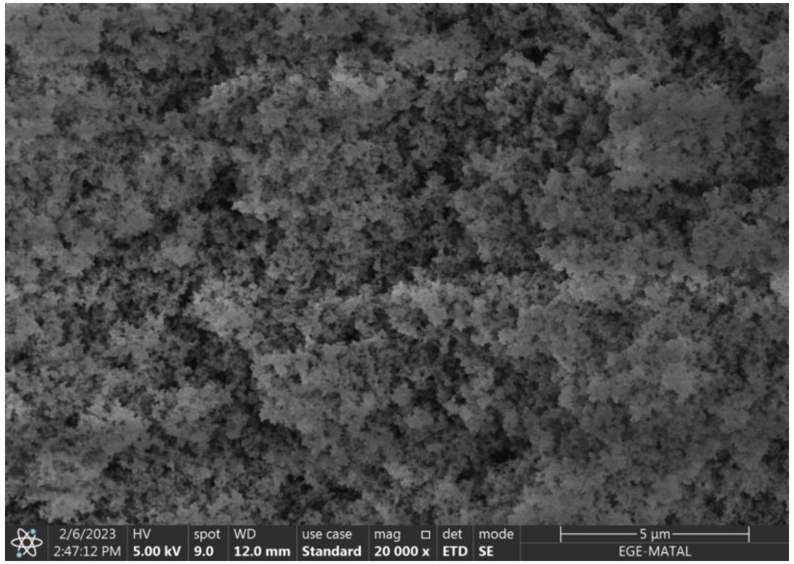
MT-100-S

- ✓ E.Coli adhesion was restricted in the entire series compared to reference samples.
- ✓ On the other hand, the most intense bacterial adhesion was observed in MT-25-S and MT-50-samples and decreased significantly in MT-75-S and MT-100-S samples depending on the methyl content.

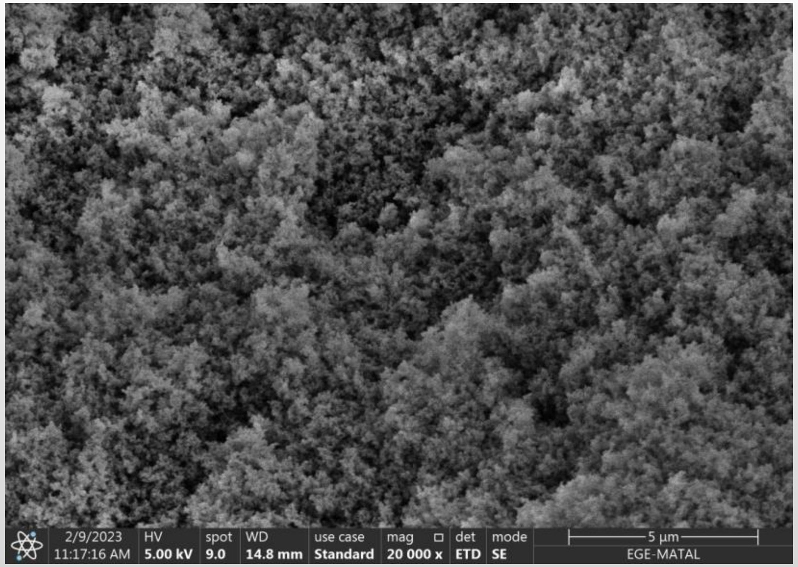
S.Aureus Adhesion



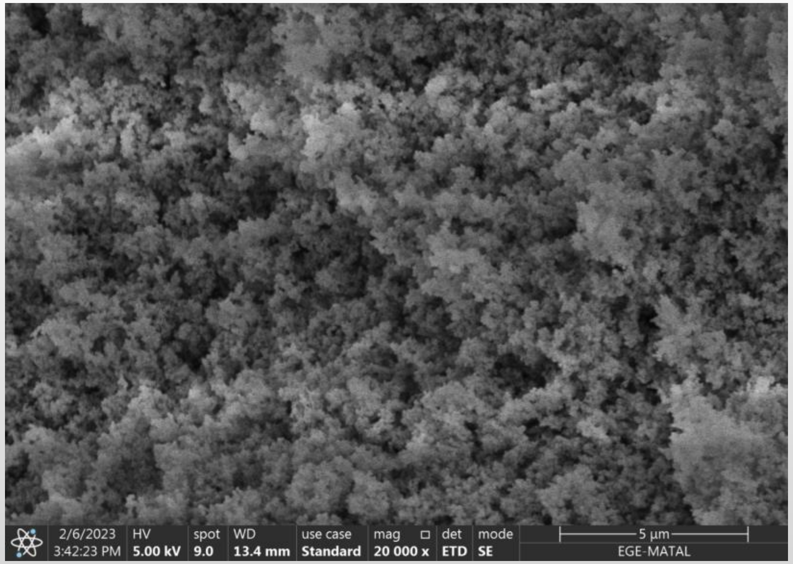
MT-25-S



MT-50-S



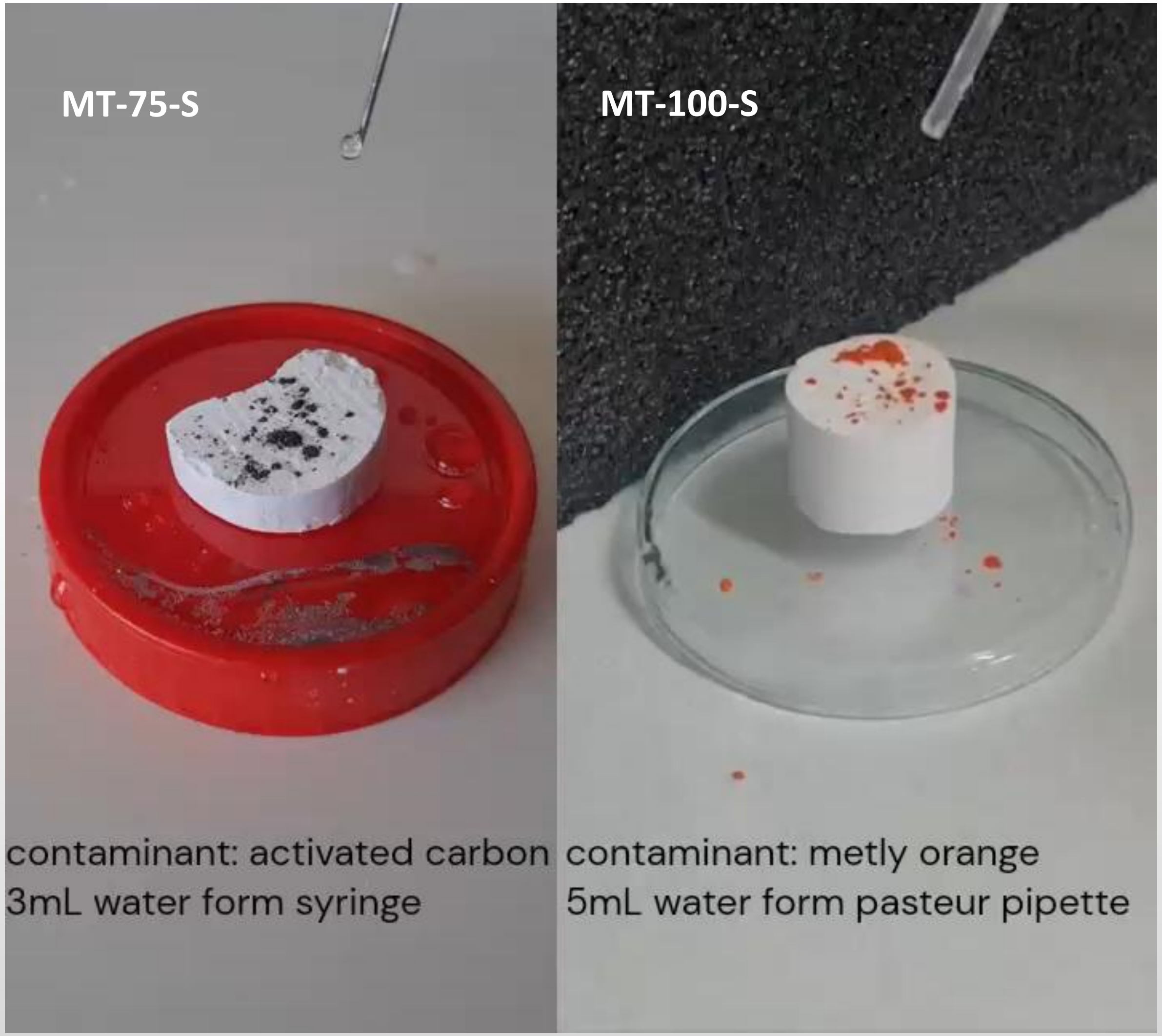
MT-75-S



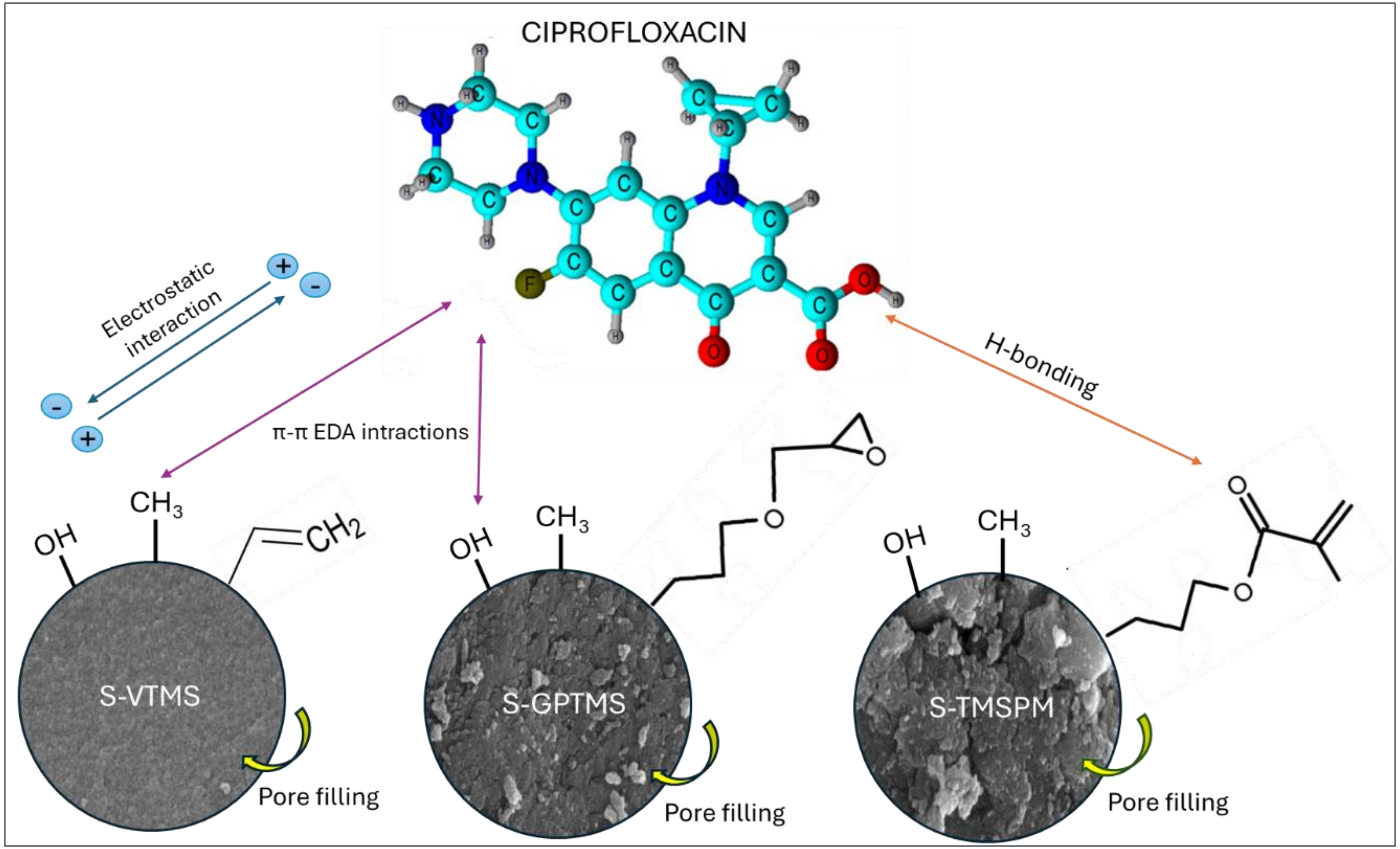
MT-100-S

- ✓ S.Aureus adhesion was prevented much better in all samples than E.Coli adhesion.
- ✓ While S. Aureus adhesion was only evident in the MT-25-S sample with low methyl content, MT-50-S, MT-75-S and MT-100-S samples showed almost no bacterial attachment in the scanned areas.

SELF-CLEANING PROPERTY



VINYL, EPOXIDE, METHACRYLATE FUNCTIONAL SILICA AEROGELS FOR THE REMOVAL OF CIPROFLAXACIN FROM WATER BY ADSORPTION



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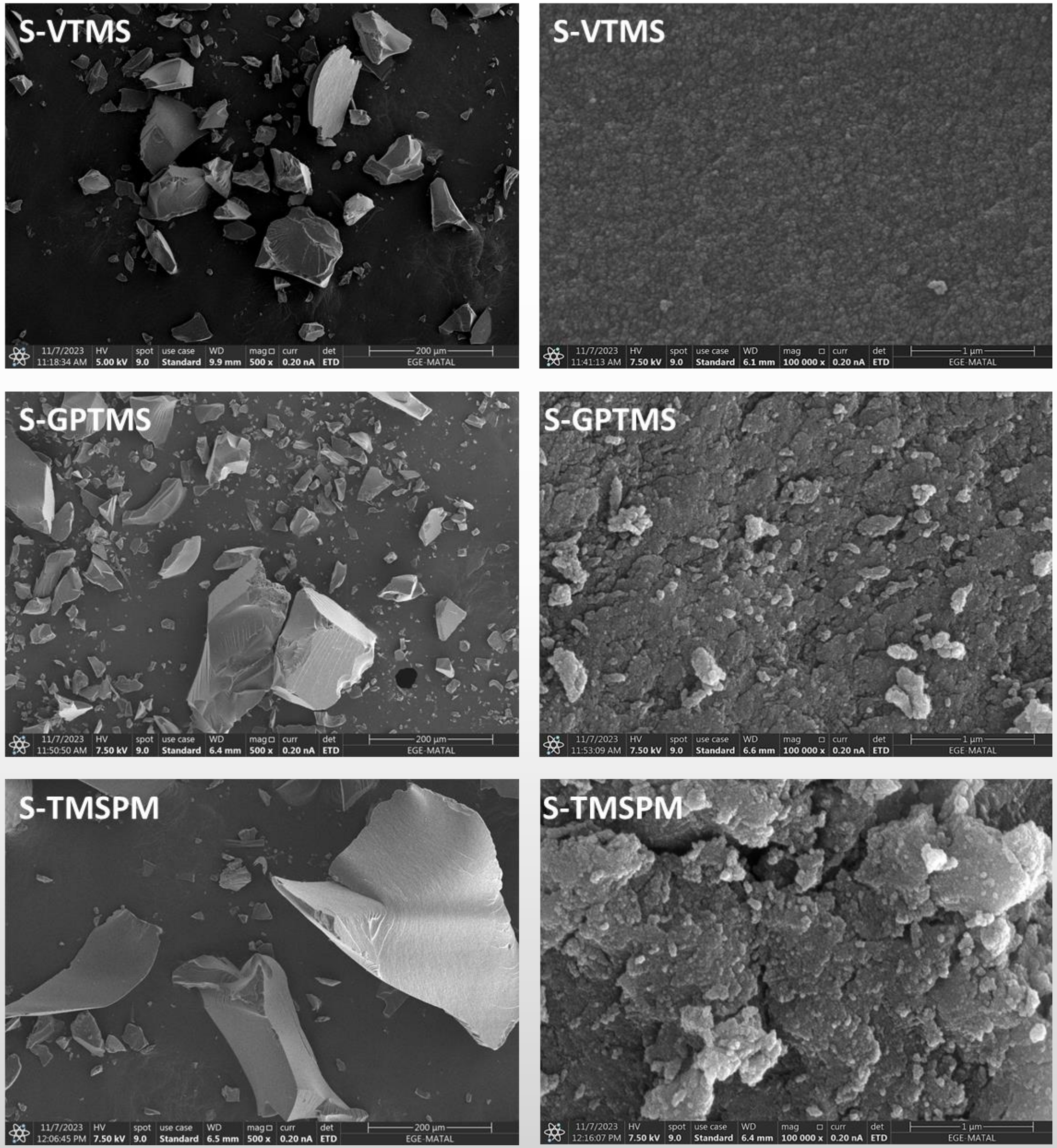
SEM



N_2 Porosimetry

Pore Properties	Sample ID		
	S-VTMS	S-GPTMS	S-TMSPM
BET Apparent Surface Area (m^2/g)	892	9.4	19.4
DR Micro Pore area (m^2/g)	54	4.86	13.1
BJH Total Pore Volume (cm^3/g)	1.02	0.0094	0.026
DR Micro Pore volume (cm^3/g)	0.32	0.0017	0.0046
BJH Avarage Pore Diameter (nm)	4.32	1.88	2.13
Bulk Density (g/cm^3)	0.094	0.173	0.156
Porosity (%)	96	92	93

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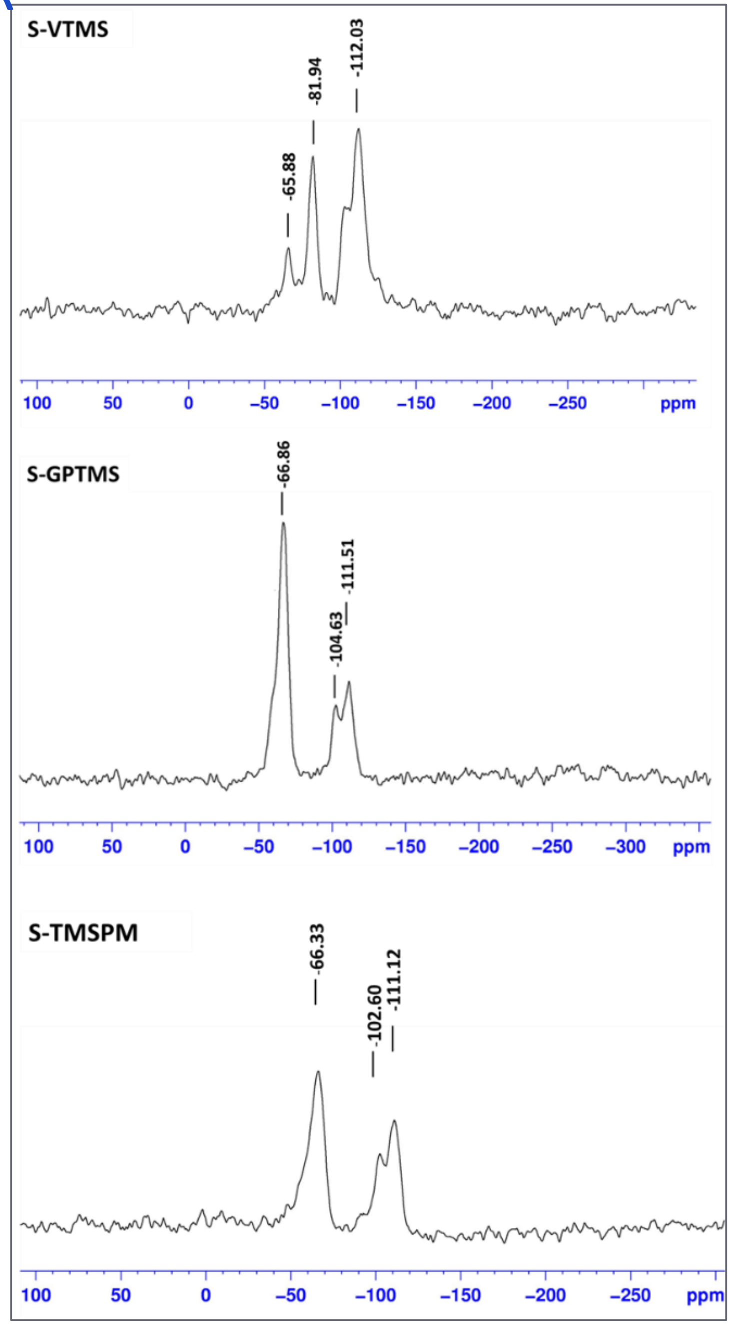
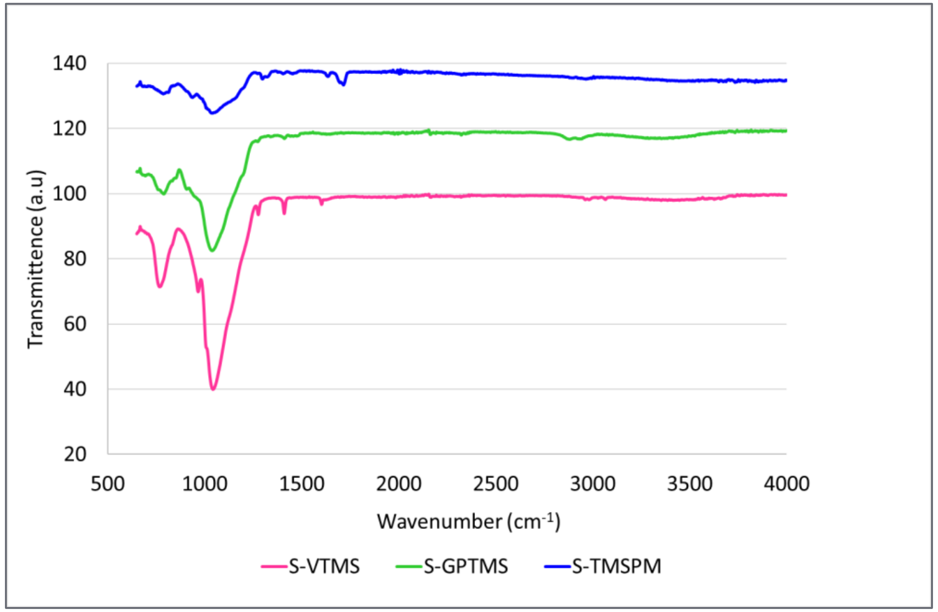
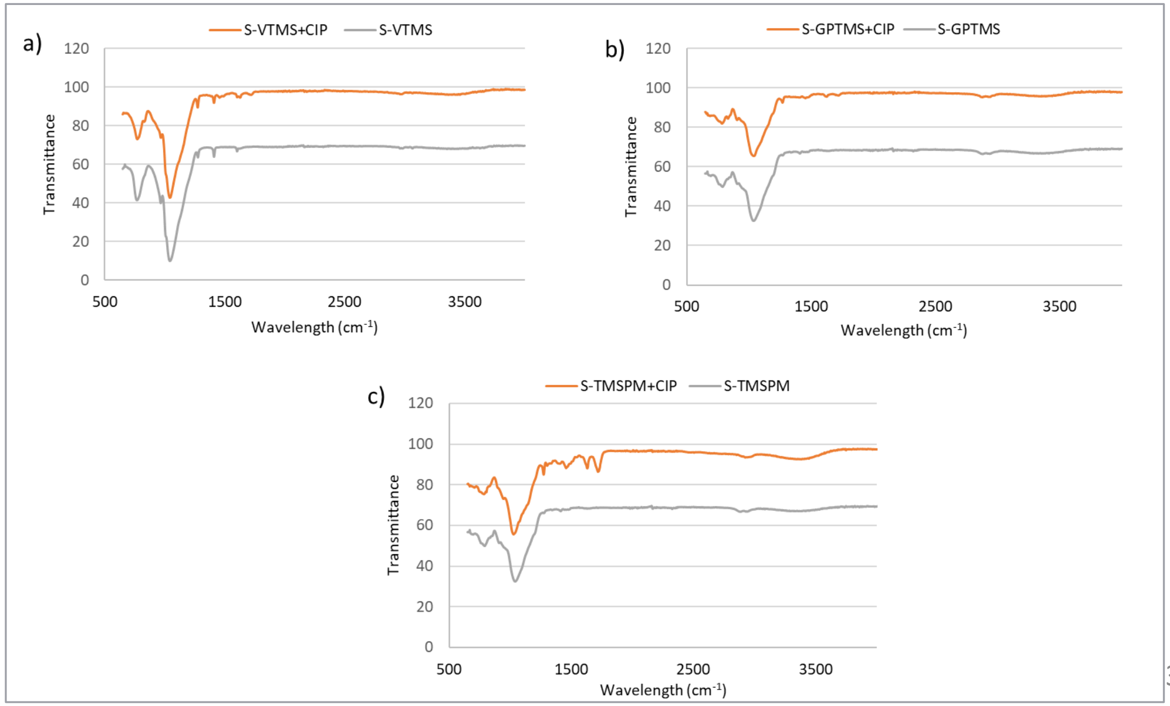
^{29} Si-NMR



FTIR



FTIR after antibiotic adsorption



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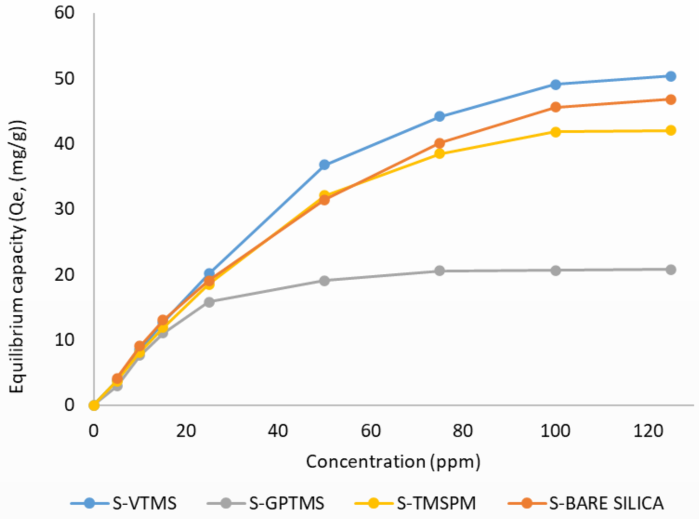
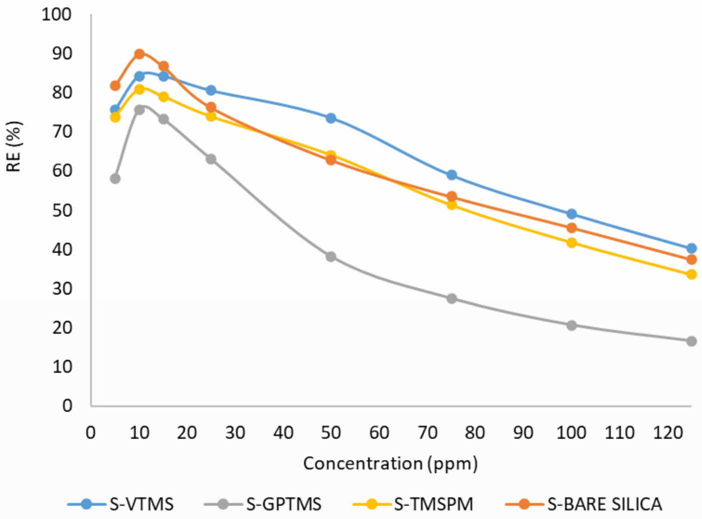
Antibiotic Adsorption Study

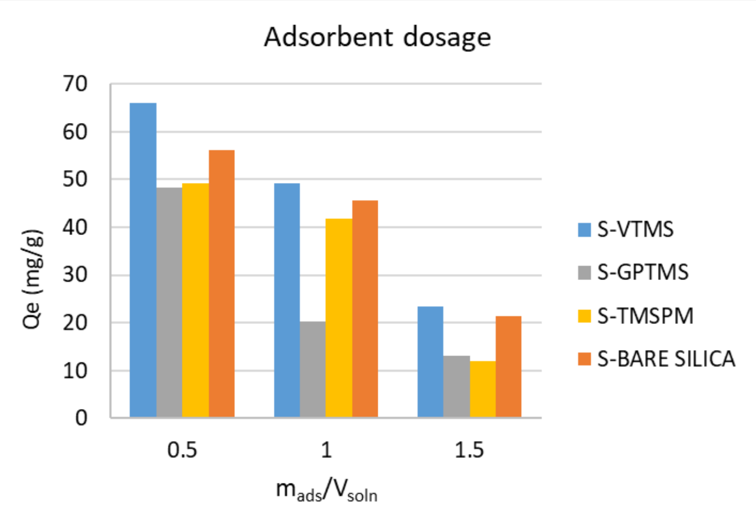
a)

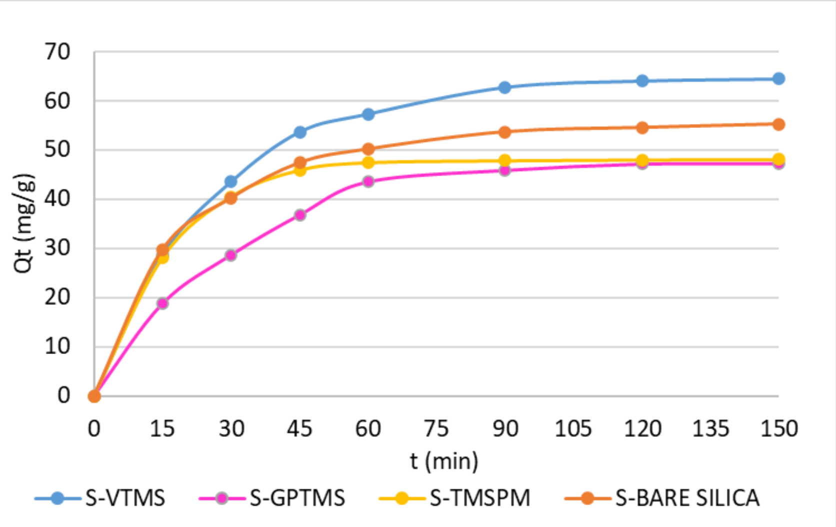


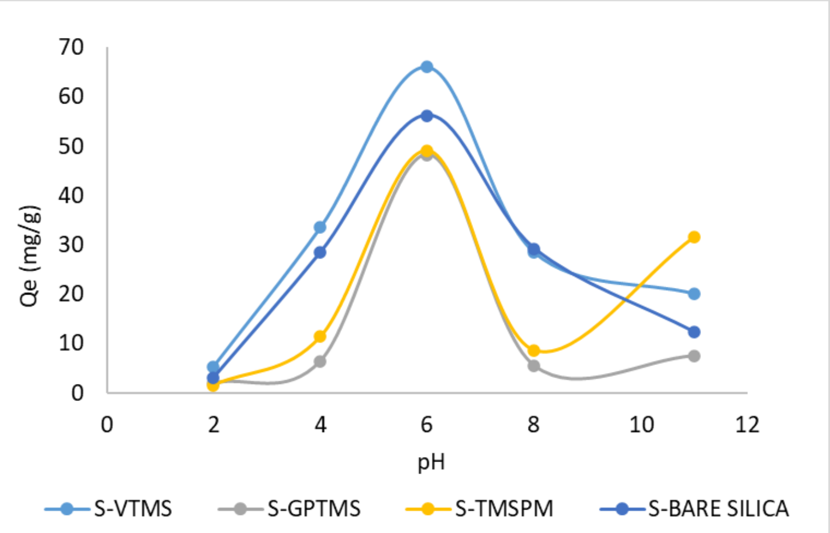
b)



Adsorption Parameters







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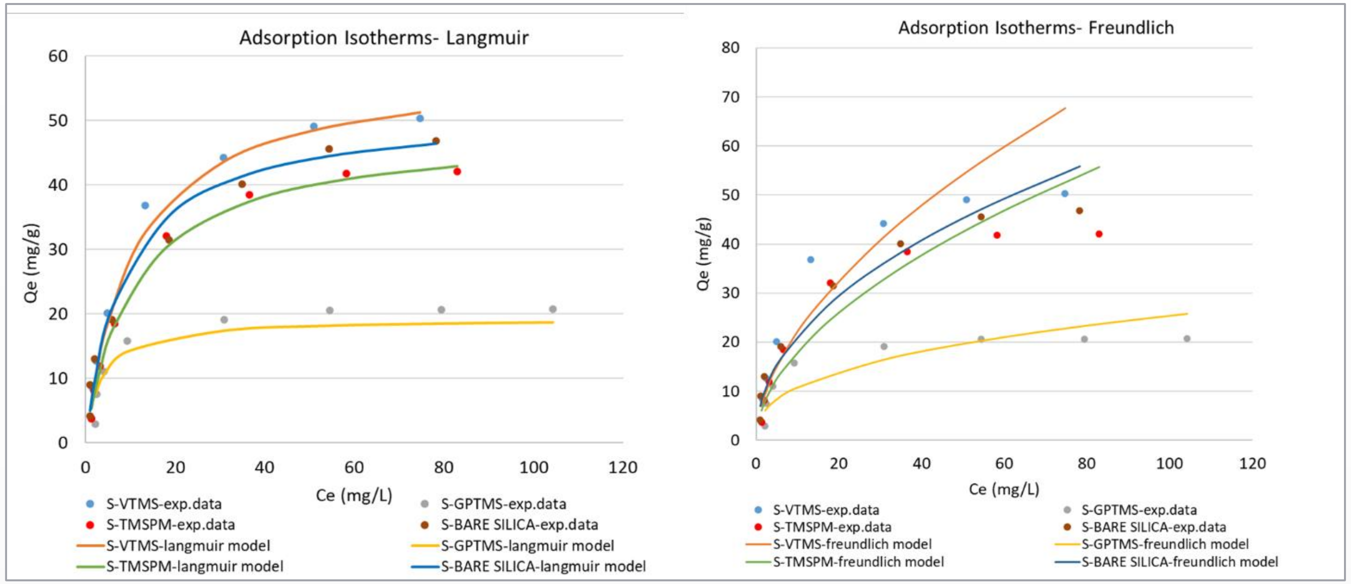
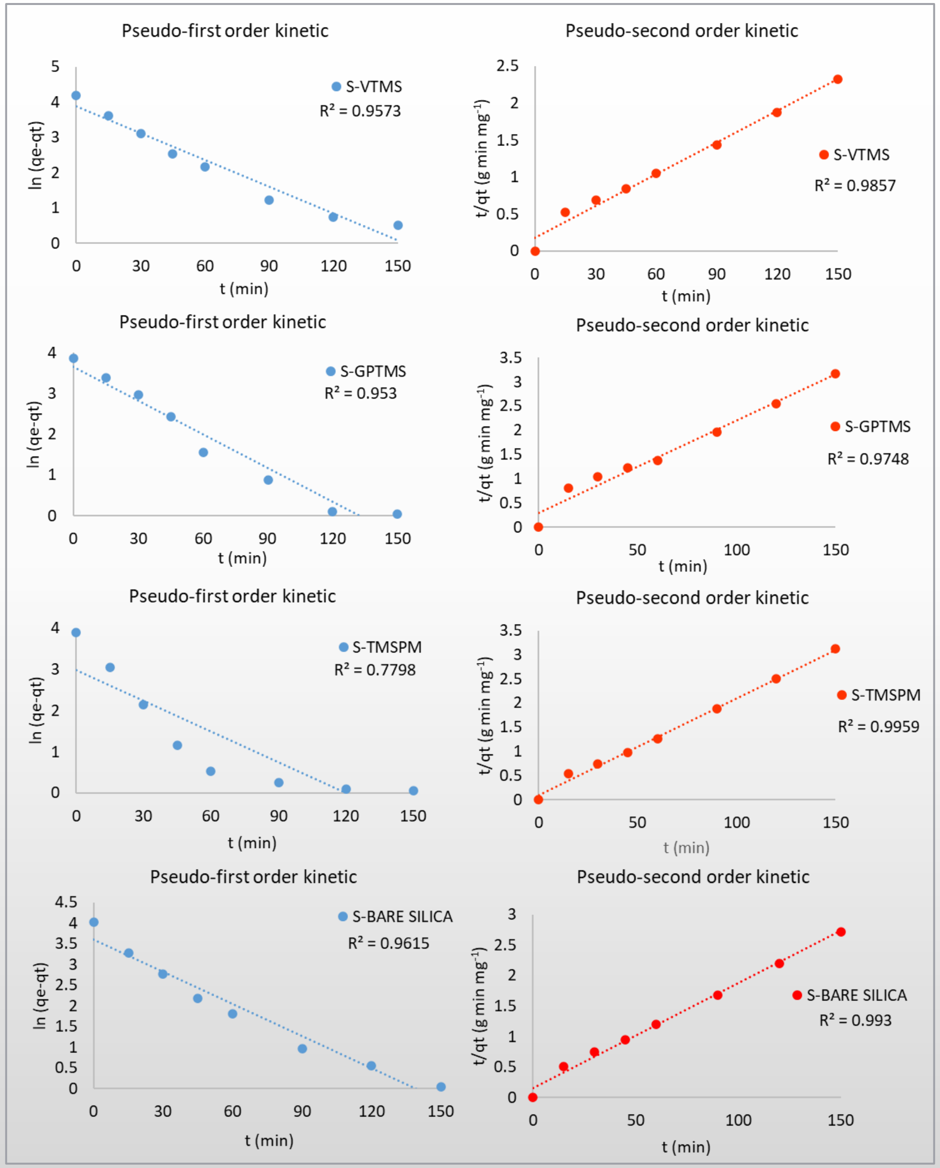
Equilibrium and Kinetic Sorption Studies





Isotherm Models

Sample ID	$q_{e,exp}$ (mg/g)	Langmuir Parameters q_m (mg/g)	Langmuir Parameters K_L (L/mg)	Langmuir Parameters R^2	Freundlich Parameters $q_{e,the}$ (mg/g)	Freundlich Parameters n	Freundlich Parameters K_F (mg/g)	Freundlich Parameters R^2
S-VTMS	50.33	58.47	0.095	0.987	67.71	1.803	6.192	0.883
S-GPTMS	20.72	19.26	0.297	0.977	25.78	2.701	4.617	0.722
S-TMSPM	42.03	48.54	0.092	0.994	55.74	1.869	5.243	0.907
S-BARE SILICA	46.77	51.54	0.116	0.992	55.89	2.134	7.253	0.916

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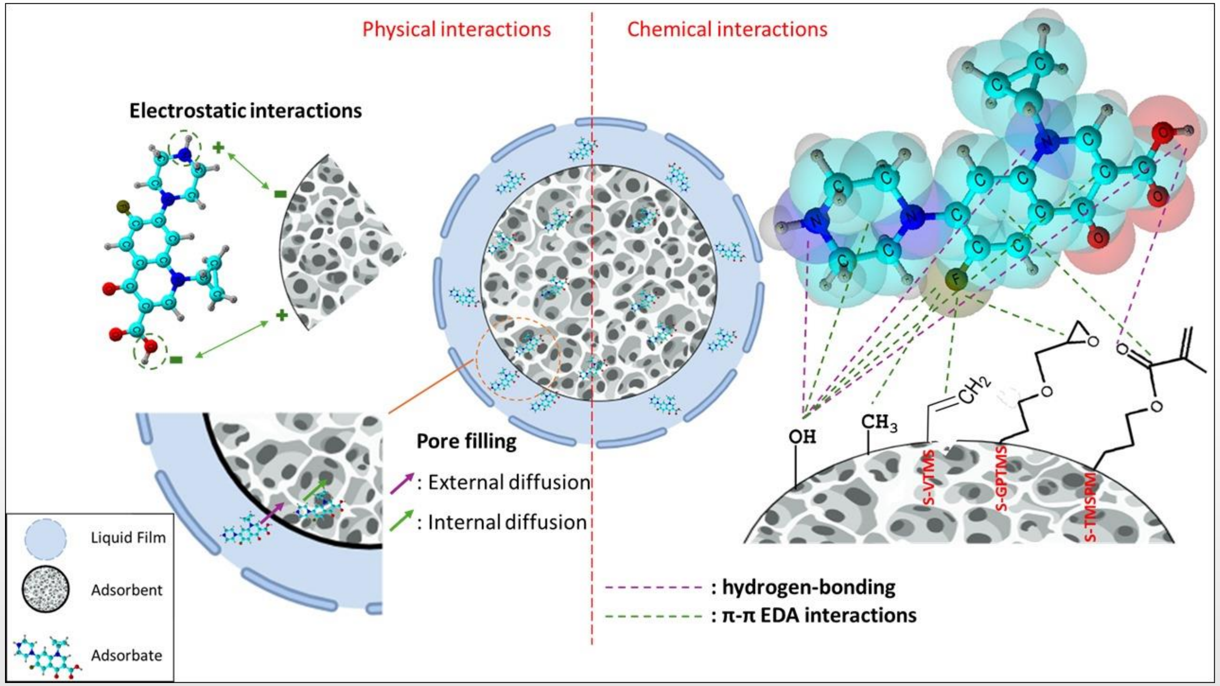
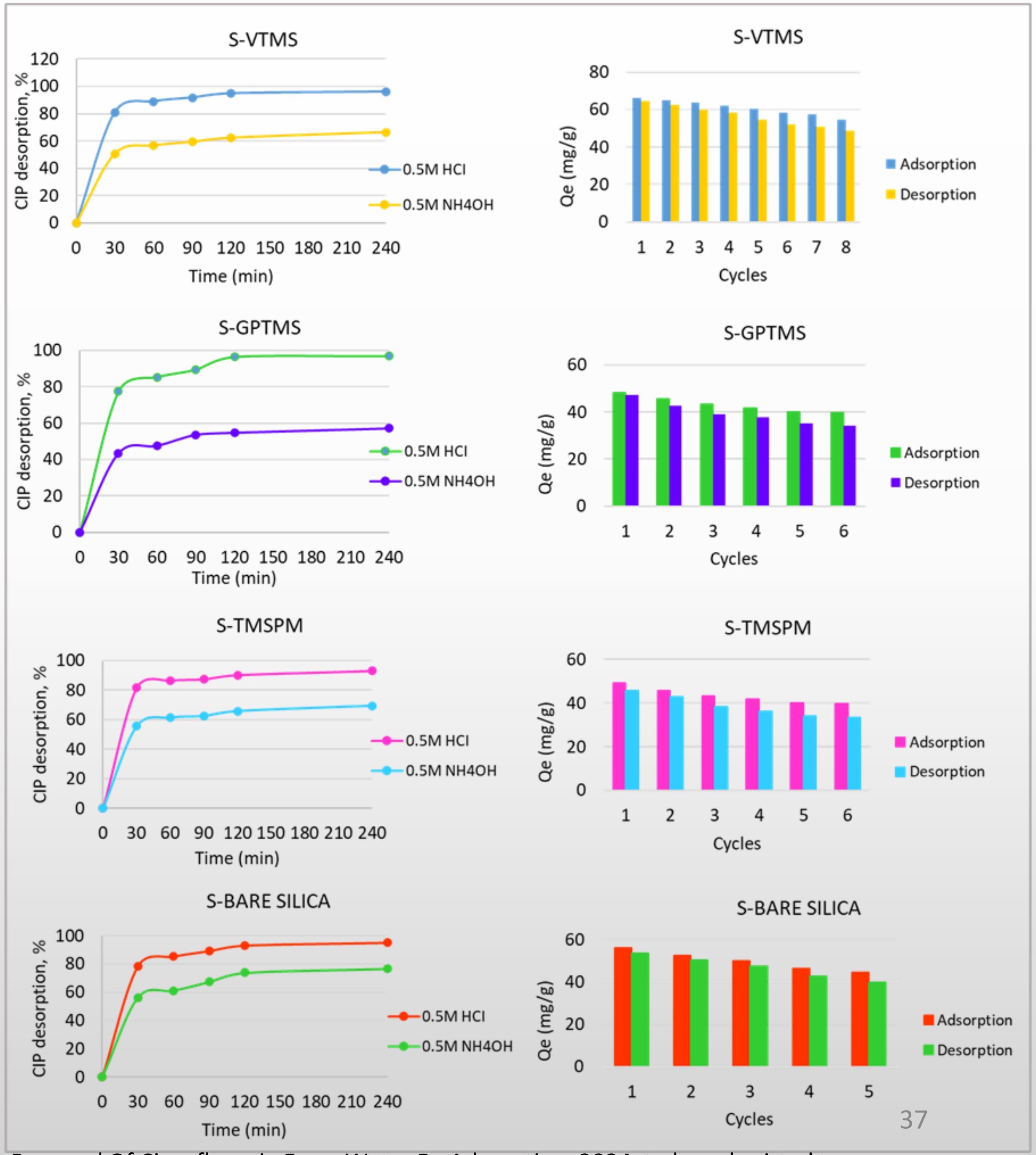
Regeneration and reusability

Adsorption Mechanisms





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CONCLUSION

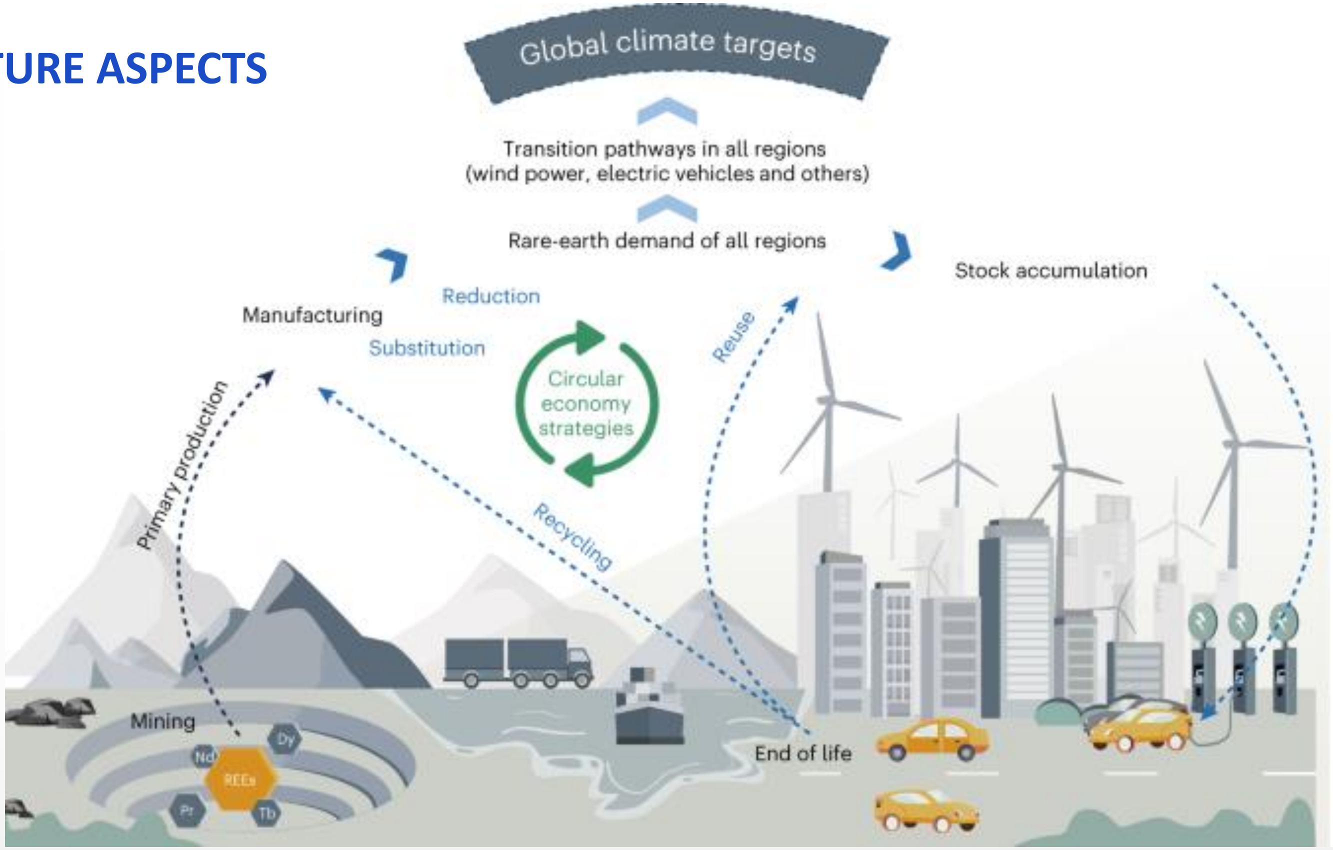
Organically modified silica aerogel-like nanomaterials containing vinyl, methyl, epoxide and methacrylate moities have found to be effective in many applications such as:

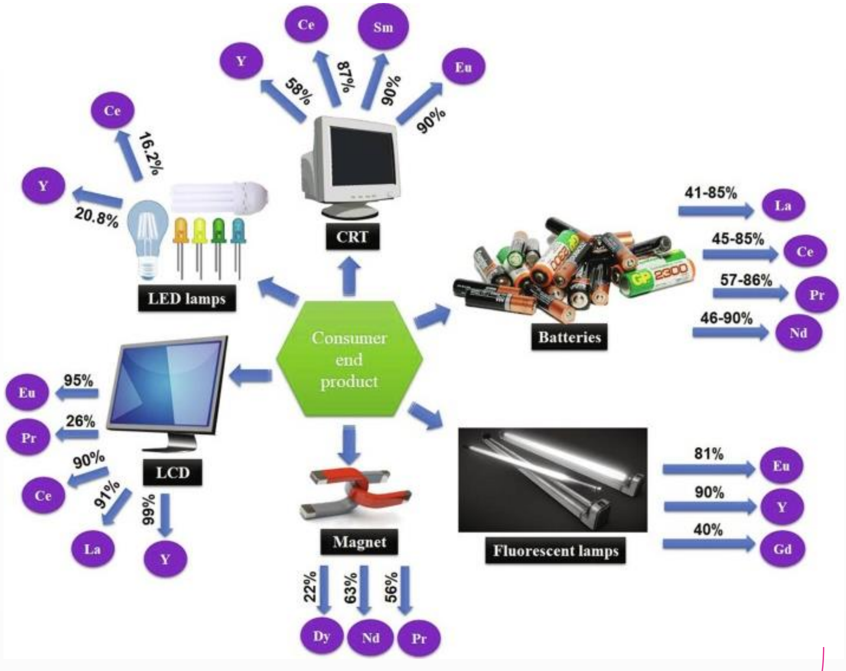
- Thermal insulation
- Oil/Organic Solvent Removal
- Pharmaceutically active compounds Removal
- Self Cleaning Surfaces
- Bacteria-repelling Surfaces

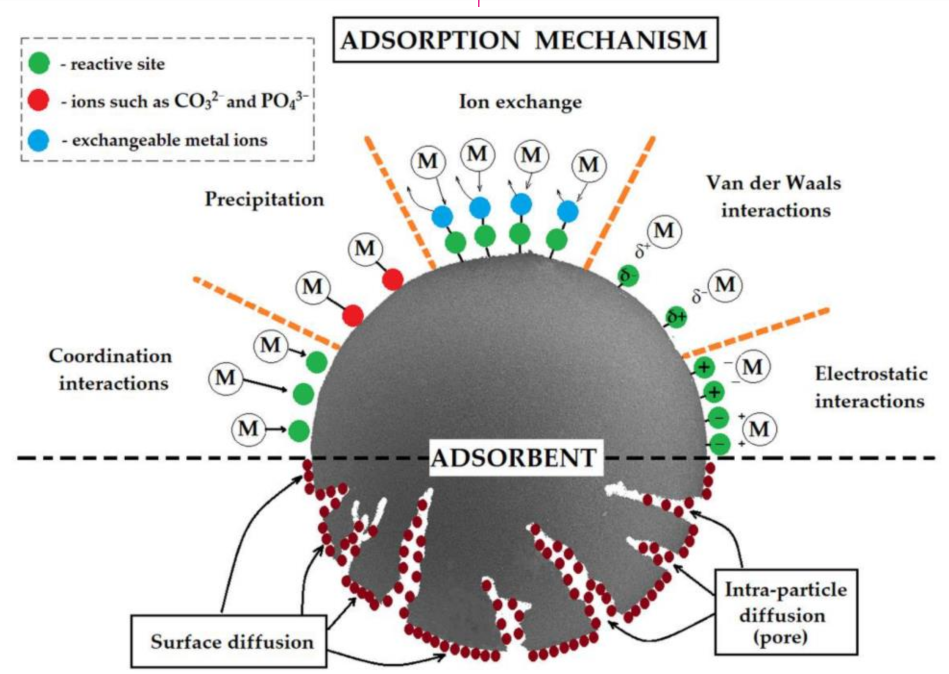
Advanced structure-sensitive techniques such as ^{29}Si-NMR, SANS, and SAXS, in addition to basic techniques such as FTIR, N_2 porosimetry or SEM is crucial

- in establishing structure-activity relationship of these materials
- in deliberately tailoring the porous network and surface chemistry of the silica based nanomaterials for better design for any target application.

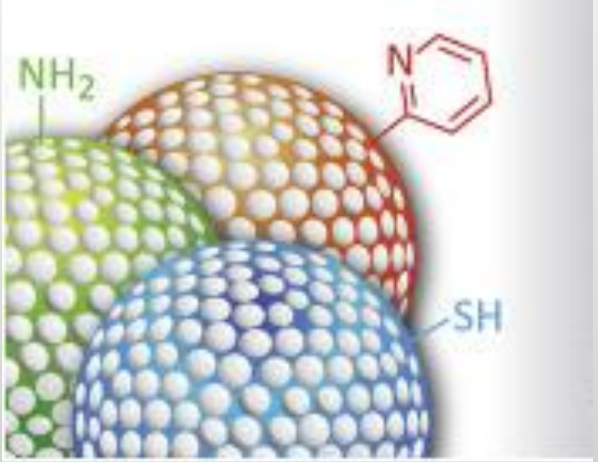
FUTURE ASPECTS

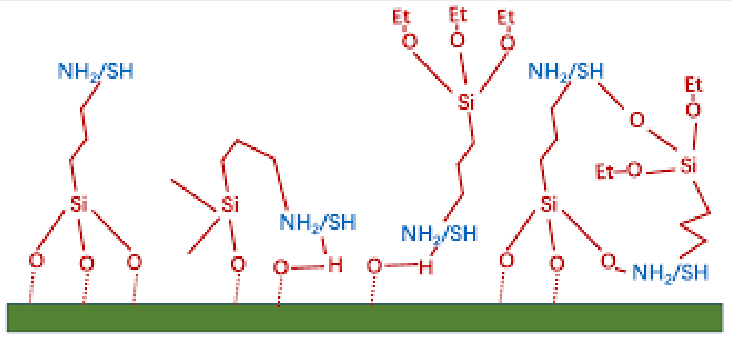






Amine, thiol funcitonal silica aerogel adsorbents





THANK YOU!