Surfactant-Modified Hierarchical Nanozeolites: Super-adsorbents for nitrate removal from contaminated water

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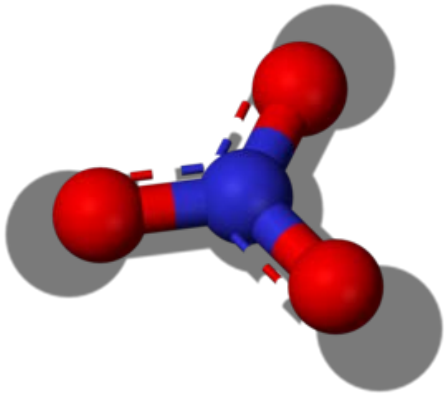
Nitrate contamination

- Essential for plants
- Very high solubility in water
- High content in aquatic environment:

1. Toxic for fauna and flora
2. Eutrophication
3. Dangerous for Biodiversity

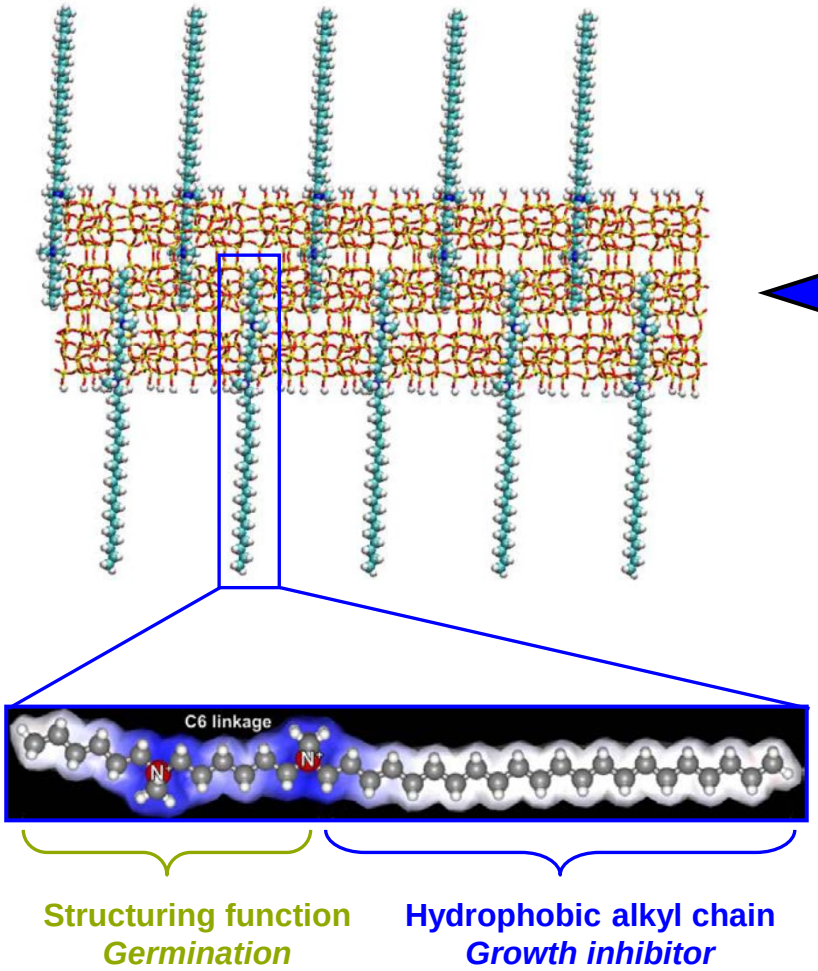


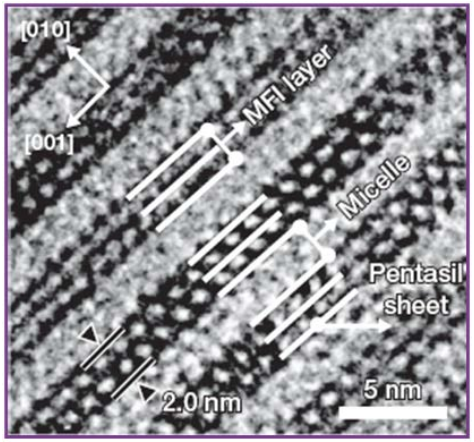
- Water for human consumption :

Limit value fixed by the world health organization: 50 mg/l

Aquat. Sci. **1989**, 46, 2.

Hierarchical nanozeolites with higher external surface

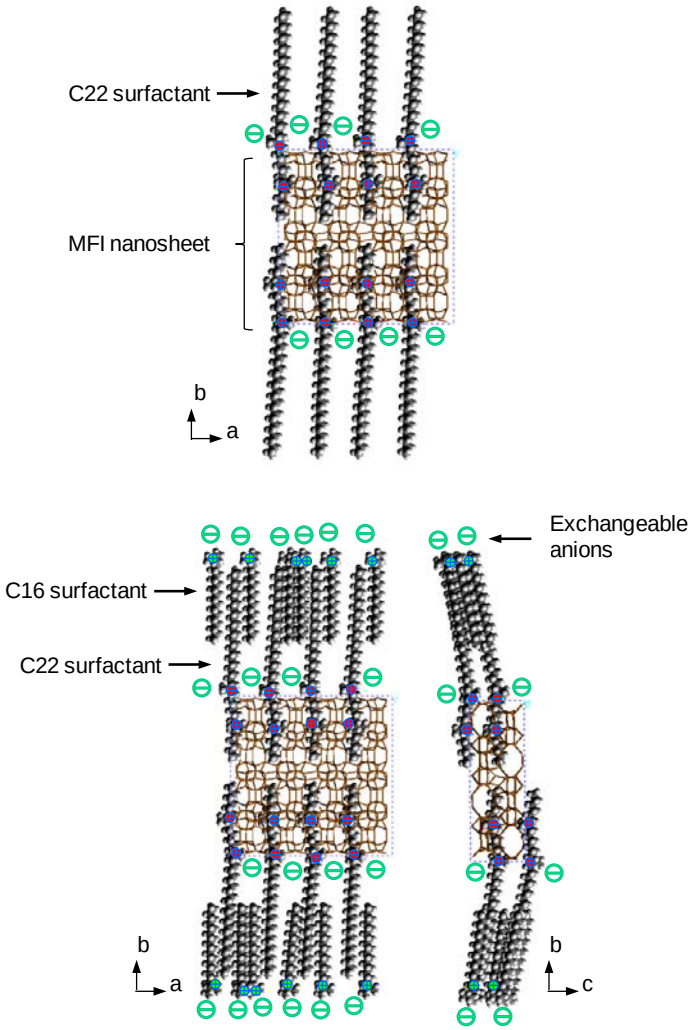


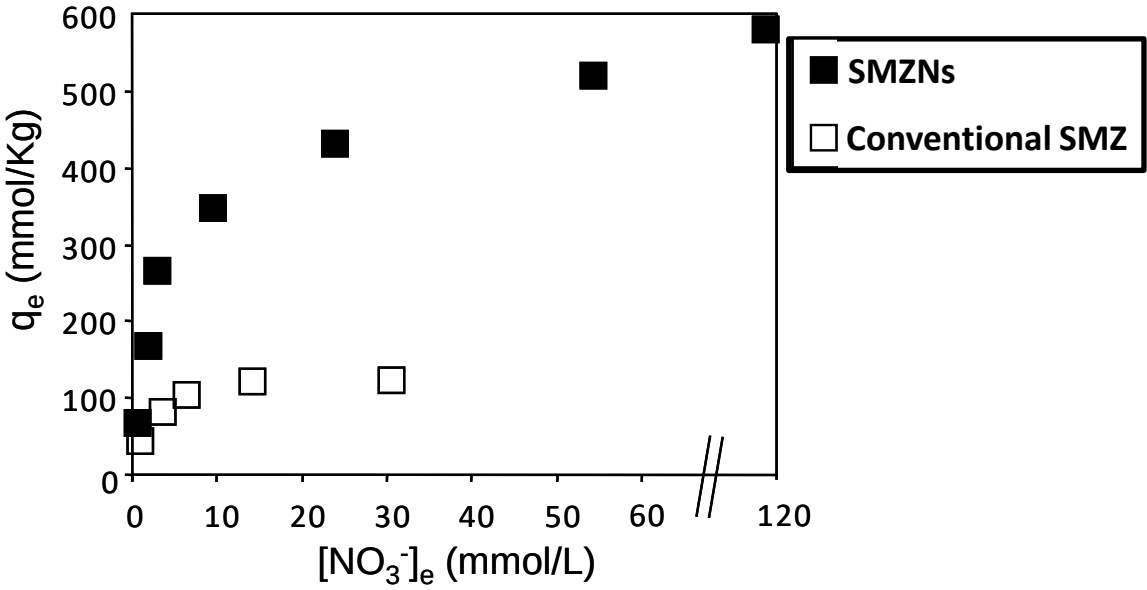


- Micro/mesoporous material
- Thickness ≈ 2 nm along *b*-axis

Nature **2009**, 461, 246
Chem. Mater. **2011**, 23, 5131
Science **2011**, 334, 72

Surfactant-modified MFI nanosheets: a high capacity anion-exchanger





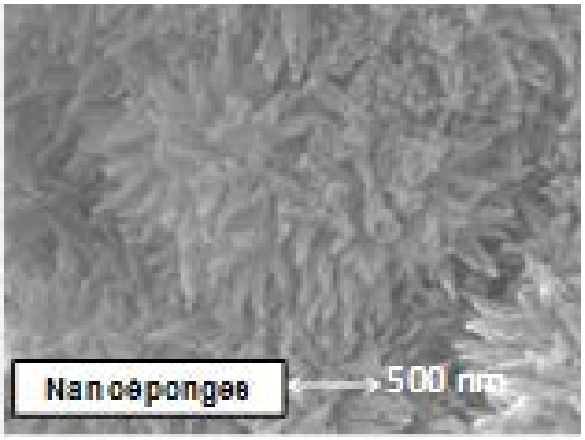
- More efficient anionic exchange capacity
- Higher removal rates and adsorption kinetics than the conventional SMZ

Synthesis and characterization of MFI-type nanosponge zeolite

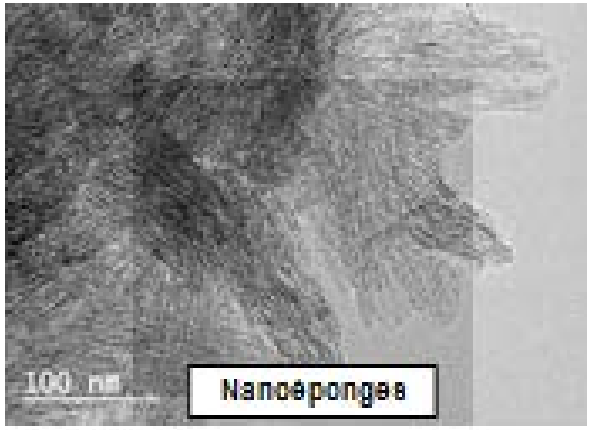
Dual-porogenic organic compound : C_{18}-$\overset{+}{N}(C_1)_2C_6\overset{+}{N}(C_1)_2C_6\overset{+}{N}(C_1)_2C_{18}$

Molar composition of the gel : $1SiO_2: 0{,}025Al_2O_3: 0{,}22Na_2O: 8ETOH: 0{,}05C_{18}N_3C_{18}: 71H_2O$

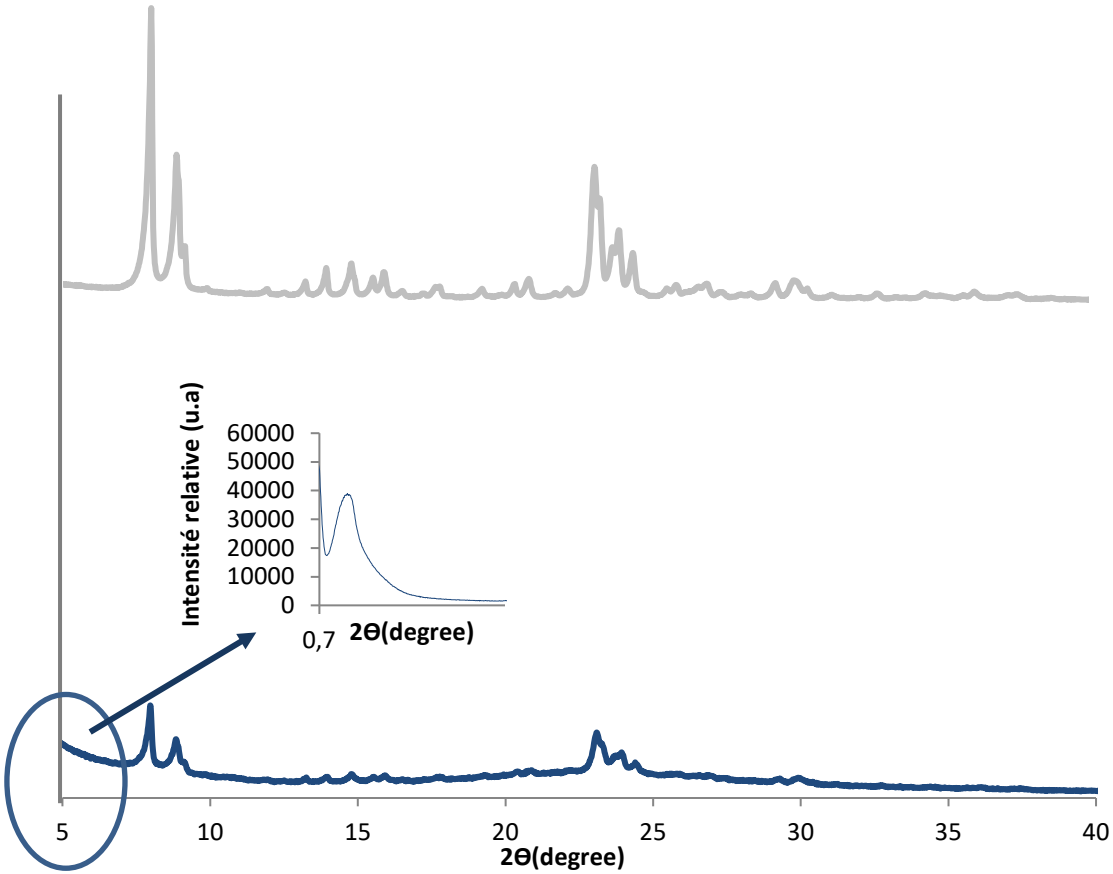
Synthesis conditions : 150 °C, 5 days, mechanical stirring at 30 rpm



SEM image of ZSM-5 nanosponges.



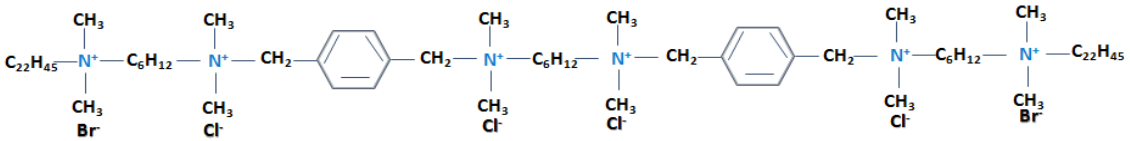
TEM image of ZSM-5 nanosponges



Synthesis and characterization of *BEA-type nanosponge zeolite

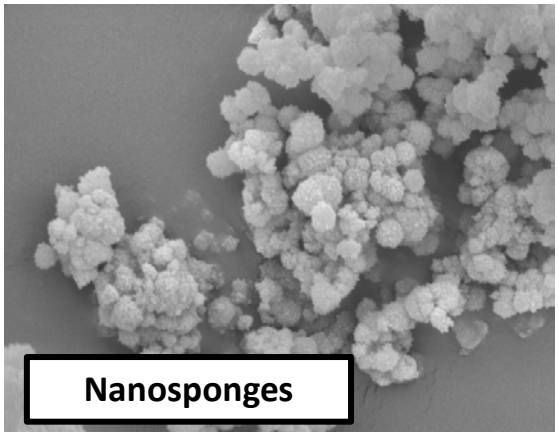
Dual-porogenic organic compound :

N_6-Di*Phe*

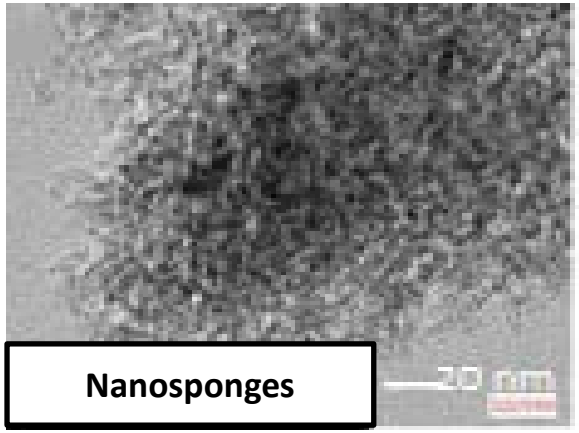


Molar composition of the gel : $1SiO_2 : 0{,}22Na_2O : 0{,}025Al_2O_3 : 0{,}05N_6\text{-DiPhe} : 8ETOH : 71H_2O$

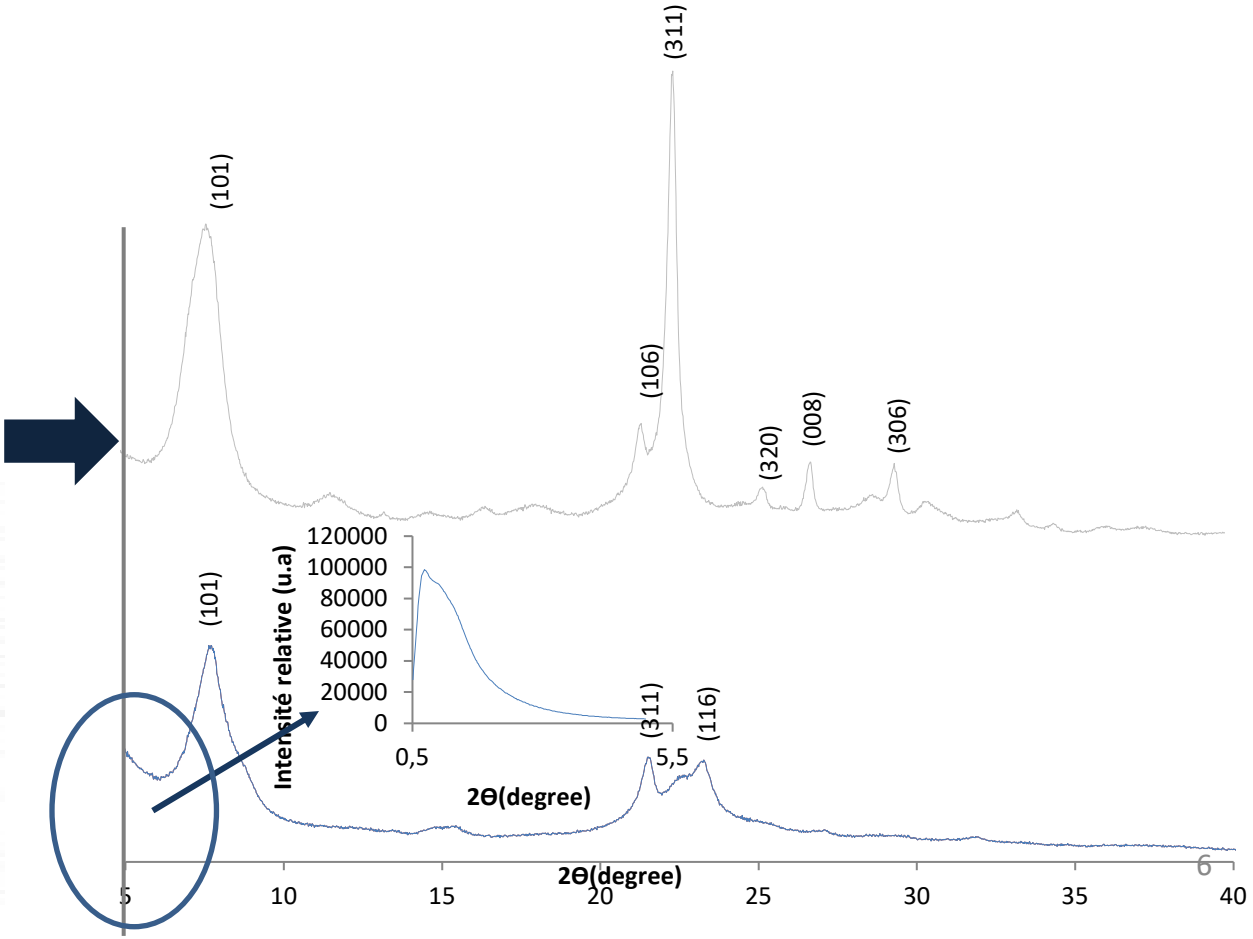
Synthesis conditions : 140 °C, 4 days, mechanical stirring at 30 rpm



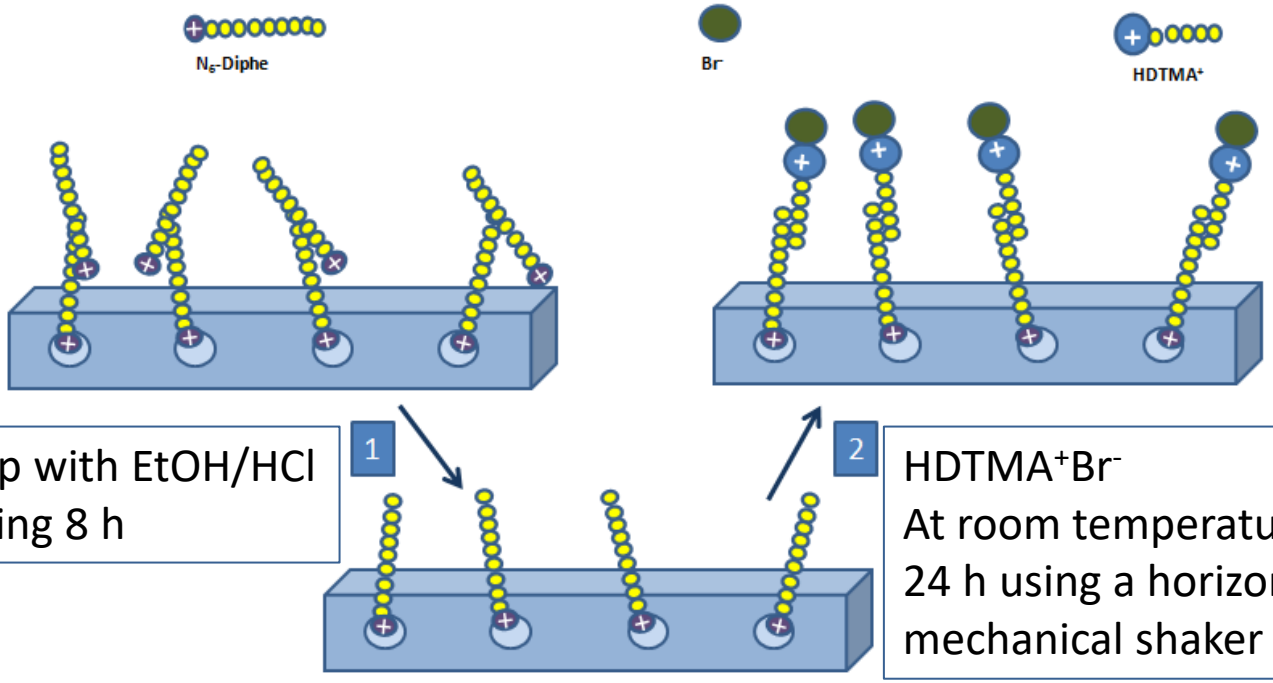
*SEM image of *BEA nanosponges*



*TEM image of *BEA nanosponges*



Schematic representation of the surface modification of hierarchical zeolites in order to obtain the SMZ_{NS} materials



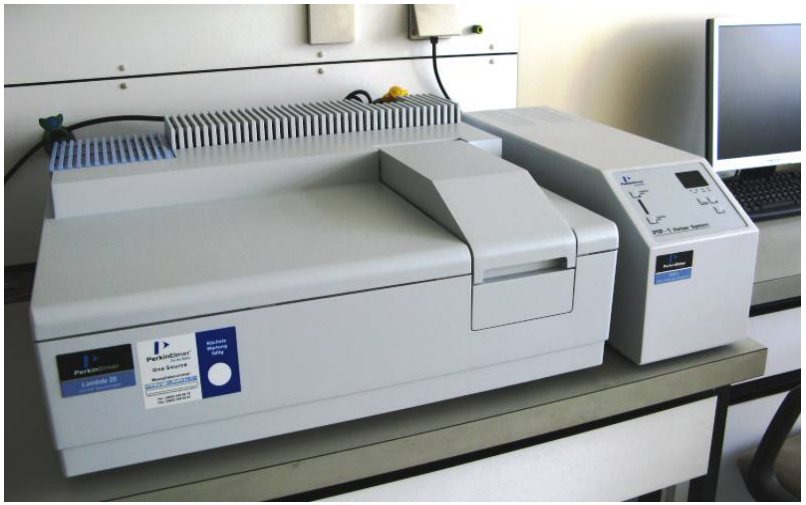
Washing step with EtOH/HCl
At 80 °C during 8 h

$HDTMA^+Br^-$
At room temperature during 24 h using a horizontal mechanical shaker

Chem. Commun. **2011,** *47*, 902-904.

Determination of the nitrate uptake

Samples were removed by filtration, the supernatants were diluted and analyzed by UV-Vis spectrophotometry to determined the concentration of nitrate.



- Nitrate Concentrations
- Contact time
- pH
- Adsorption kinetic

λ = 220 nm

Determination of the number of exchangeable sites (Br^-, Cl^-)

Material type	XRF results	
	Cl %	Br %
ZSM-5 Nanosponges as synthesized	-	0,00213
ZSM-5 Nanosponges (HCl /ETOH)	0,586	-
ZSM-5 Nanosponges-HDTMA	0,0513	1,86

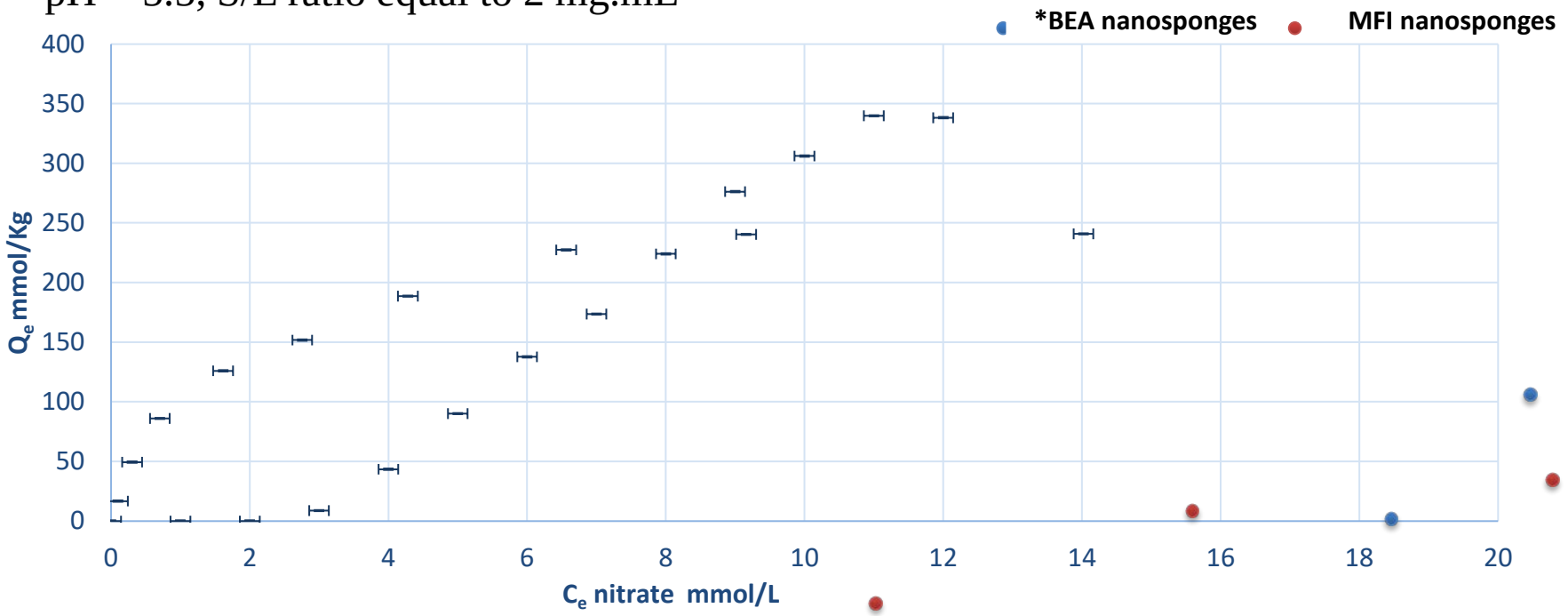
Increase of the number of exchangeable site after treatment with $HDTMA^+$

$246*10^{-4}$ mmol $[NO_3^-]$/Kg SMZNS
For modified **ZSM-5 nanosponges**

$352*10^{-4}$ mmol $[NO_3^-]$/Kg SMZNS
For modified **ZSM-5 nanosponges**

Nitrate adsorption isotherme on zeolite nanosponges

pH = 5.5, S/L ratio equal to 2 mg.mL^{-1}



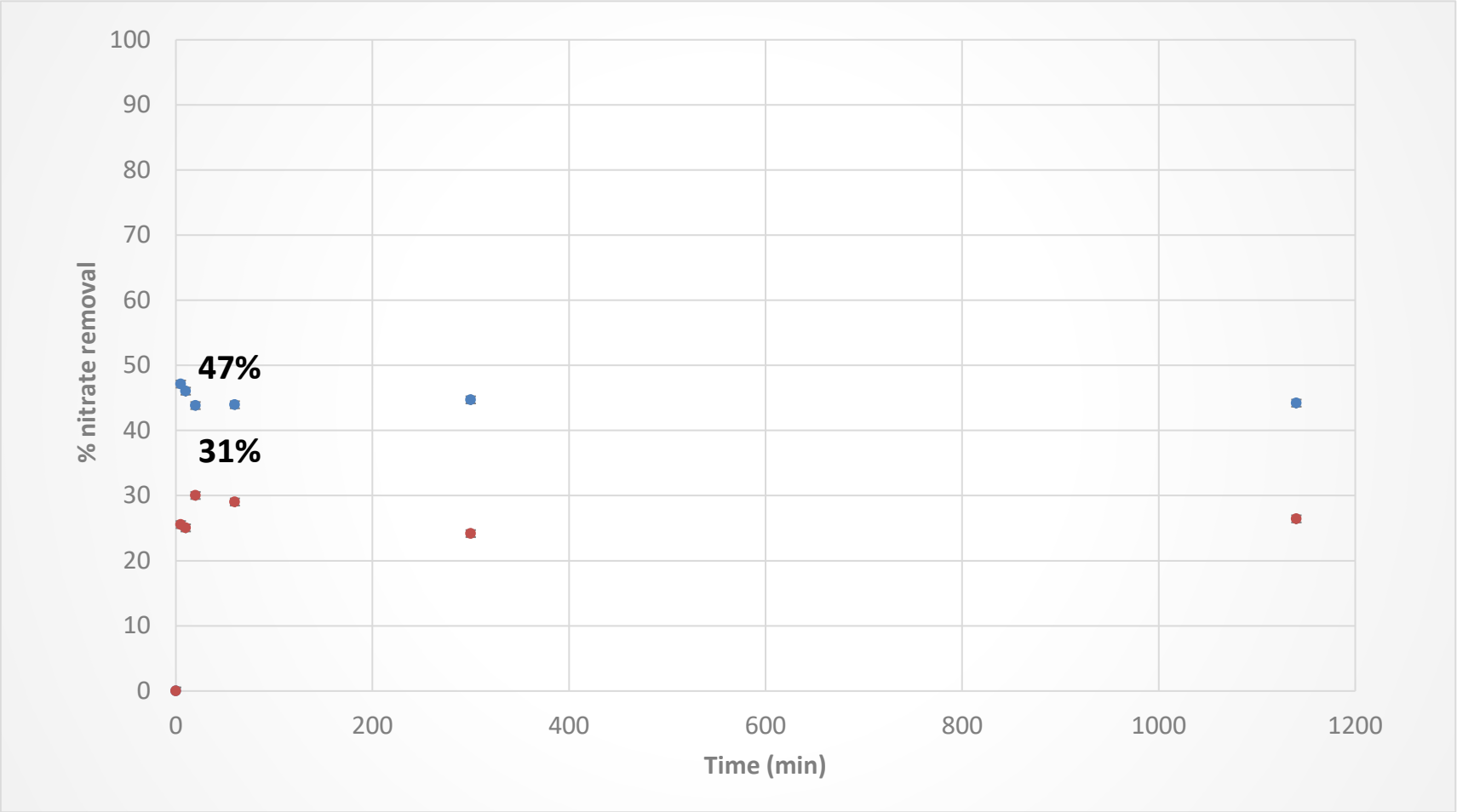
*BEA	Expected capacity deduced from XRF	Real capacity deduced from isotherm
	352 mmol/Kg	**340 mmol/Kg**

MFI	Expected capacity deduced from XRF	Real capacity deduced from isotherm
	246 mmol/Kg	**228 mmol/Kg**

Higher adsorption capacity for SMZNS

Clinoptilolite
90-135 mmol/Kg

Kinetic of nitrate uptake on modified zeolite nanosponges



The removal kinetics for hierarchical zeolites are very fast and higher than conventional zeolite

Clinoptilolite
15% (5-10 min)

Conclusion

- Surfactant modified hierarchical zeolites: higher nitrate uptake than conventional zeolites
- Higher nitrate removal kinetic than conventional zeolites
- High-performance materials for industry

Acknowledgments

This work was supported by the ANR

Thank you