SWELLABLE ORGANIC-INORGANIC SILICAS FOR THE REMOVAL OF DYES FROM WATER MEDIA

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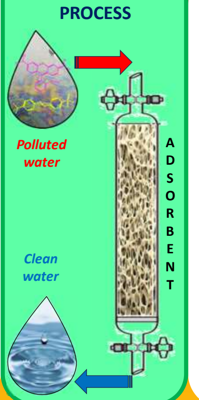
INTRODUCTION

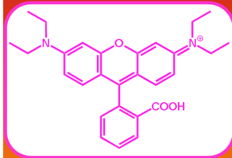
Organic dye molecules are used ubiquitously in industries, and are among the contaminants responsible for soil, air, and water pollution. The removal of organic dyes from wastewater can be made by physical, biological, and chemical methods, but the adsorption on solid sorbents is considered an efficient process and is becoming one of the standard treatments industrially used [1]. The widely used commercial adsorbents (for instance, carbons and silica-based materials) lack of affinity towards certain dyes or have low removal efficiency or are not easily regenerable and this is thus associated to the needing to study new materials with improved adsorption performance [2].
Different materials, for instance carbons, zeolite, clays, polymers are used to this purpose, but the class of hybrid organic-inorganic silica materials is deserving increasing interest for their peculiar adsorption performances [1]. Among the class of hybrid silicas, Swellable Organo-Modified Silicas (SOMS) possess the peculiar ability to swell, thus expanding their volume, when in contact with organic solvents, can be good candidates for the adsorption of dyes from water, considering that these materials have proven to be excellent adsorbents for perfluoroalkyl substances (PFAS) and other species, such as organic chlorinated solvents [3, 4, 5].

ADSORPTION PROCESS

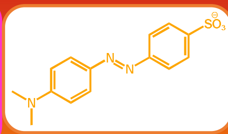


DYE MOLECULES

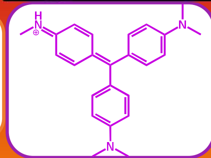
Dye molecules are one class of water pollutants released by industries, such as plastics, rubber, paper, cosmetics, food, leather and, in particular, textile, used for their product colorization. The global annual production of different colored dyes is estimated to be larger than 7·10^7 tons and 10% are released in water bodies [6]. Reported adverse effects of dyes on humans' health are acute toxicity, skin irritation, carcinogenicity and mutagenicity. Moreover, dyes can interfere with photosynthetical processes in water bodies, reducing penetration of light, and increasing the chemical oxygen demand (COD) up to 2-3 g/L [5]. Among the different classes of dye molecules, it can be found azo and triarylmethane dyes, whose major exponents are Methyl Orange and Rhodamine B [6].



Rhodamine B (RhB) is a water-soluble triaryl methane dye, belonging to the xanthene class. RhB is a weak acid (pK_a 4.2) with good solubility (34 g L^{-1}) in water. At low pH values RhB is a cation, in which the positive charge is shared by the two N atoms. At pH > 4.2, RhB is in its zwitterion form, in which the carboxylic group is deprotonated.



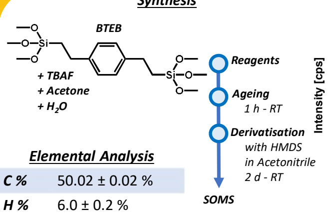
Methyl Orange (MO) is an anionic water-soluble azo-dye molecule. MO is an acid pH-indicator (pK_a 3.4) with a solubility of about 5 g L^{-1} in water. At pH values below 3, the molecule is protonated and red, while at pH above 4.4 occurs the deprotonation of N-atom and the molecule is negative and yellow colored.



Crystal Violet (CrV) is a water-soluble triaryl methane dye, with a violet-blue colour. CrV is a weak acid (pK_{a1} 1.2, pK_{a2} 1.8) with good solubility (4 g L^{-1}) in water. CrV is a cation, in which the positive charge is shared by the 3 N atoms. At pH < 2, the other N atoms non-protonated, becomes protonated.

SWELLABLE ORGANO-MODIFIED SILICA (SOMS)

Synthesis

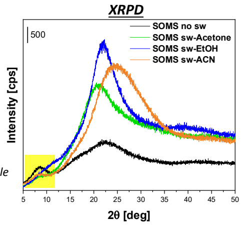


Elemental Analysis

C %	50.02 ± 0.02 %
H %	6.0 ± 0.2 %
N %	0.07 ± 0.01 %

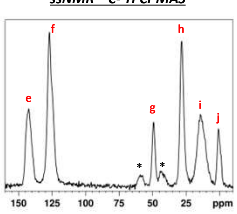
pH pzc 3.7

XRPD

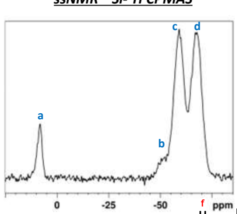


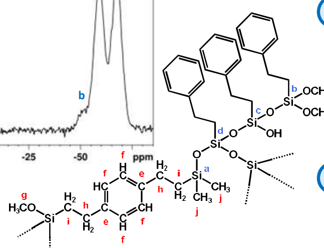
SEM

ssNMR ^{13}C-^{1}H CPMAS

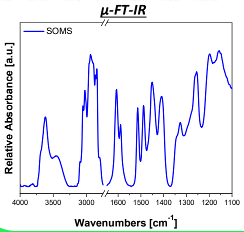


ssNMR ^{29}Si-^{1}H CPMAS





µ-FT-IR

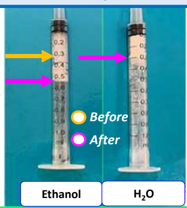


SOMSs are hybrid materials consisting of organic units linked to an inorganic matrix by a covalent silicon-carbon bond. It is synthesized by a sol-gel synthesis of a particular bridged polysiloxane precursor (bis(trimethoxysilylethyl)benzene - BTEB), using tetrabuthylammonium fluoride (TBAF) as a basic catalyst. Then, the material is derivatized with hexamethyldisilazane (HMDS) to prevent further condensation and to achieve the property of swelling [4].

Highlight properties of SOMSs

- Porous, hydrophobic and flexible structure
- Highly cross-linked solid
- High Swelling Ratio (SwR) with organic solvents
- Do not expand in water

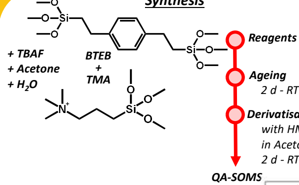
Swelling Test



Solvent	Particle Diameter (DLS)	Swelling Ratio
Water	400 ± 100 nm	0.21 ± 0.01
Ethanol	230 ± 30 nm	5.0 ± 0.6
Acetonitrile	350 ± 70 nm	4.2 ± 0.3
Acetone	290 ± 30 nm	4.6 ± 0.1

QUATERNARY AMINO MODIFIED SOMS (QA-SOMS)

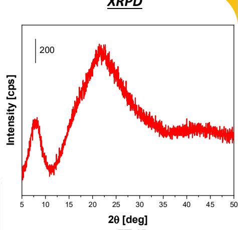
Synthesis



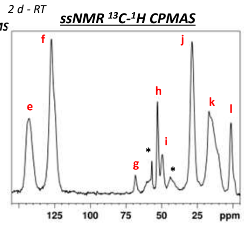
Elemental Analysis

C %	42 ± 1 %
H %	5.9 ± 0.3 %
N %	0.68 ± 0.03 %

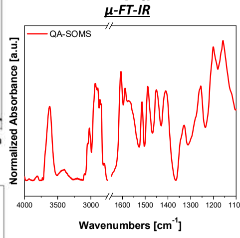
XRPD



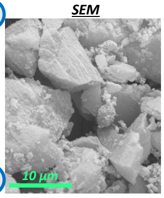
ssNMR ^{13}C-^{1}H CPMAS



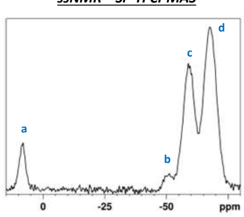
µ-FT-IR



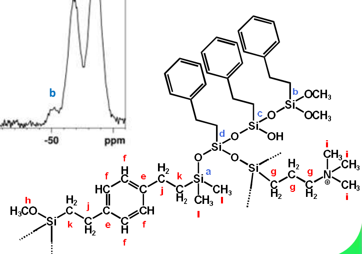
SEM



ssNMR ^{29}Si-^{1}H CPMAS

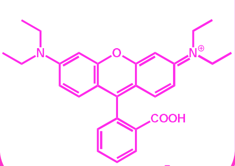


pH pzc	10.3
Swelling Ratio	3

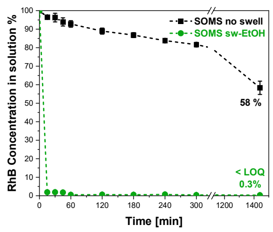


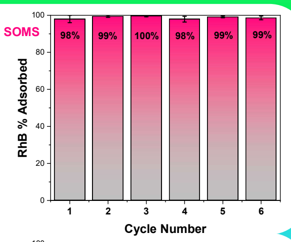
ADSORPTION OF DYES

RHODAMINE B

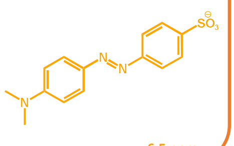


5 ppm

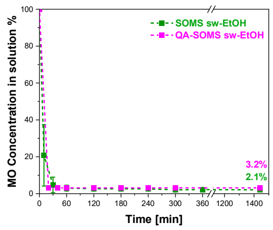


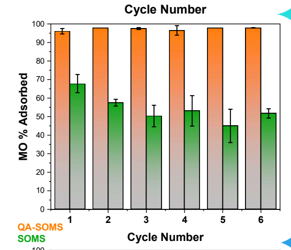


METHYL ORANGE

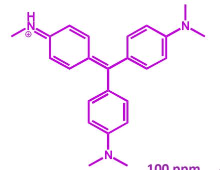


6.5 ppm

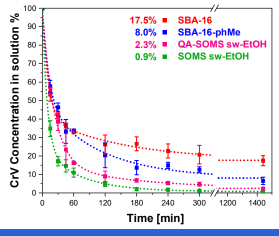


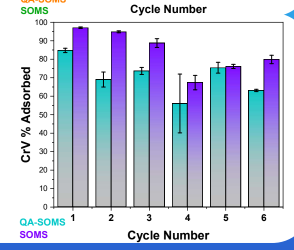


CRYSTAL VIOLET

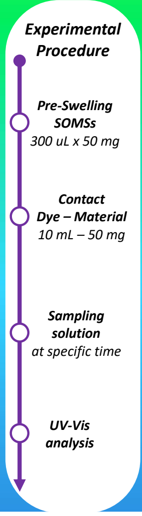


100 ppm

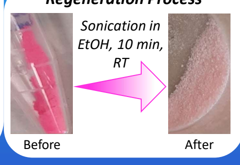




Experimental Procedure



Regeneration Process



CONCLUSIONS

The adsorption performance of SOMS and QA-SOMS against different soluble organic dye pollutants in the aqueous phase (RhB, MO and CrV) was studied. The samples showed very promising removal capacities: in less than 1 hour of contact more than 97% of the dyes was removed. Adsorption cycles were carried out, after desorption of the pollutant in alcohol solution by sonication. These tests showed that both SOMS and QA-SOMS are fully regenerable and reusable under the studied conditions.

FUTURE PERSPECTIVES

- ❑ Further optimization of SOMS and QA-SOMS synthesis
- ❑ Characterization of the swollen form of SOMS
- ❑ Adsorption of mixtures of dyes
- ❑ ss-NMR to understand adsorbent-adsorbate interactions

REFERENCES

[1] Agarwala, R. et al., *ChemBioEng Rev.*, 10 (326-335), **2023**.
[2] Xiang, W. et al., *Separation and Purification Tech.*, 330 (125268), **2024**
[3] Miglio, V. et al., *J. Phys. Chem. C*, 128, 5 (2179–2189), **2024**.
[4] Stebel, E. K. et al., *Environ. Sci.: Water Res. Technol.*, 5 (11), **2019**.
[5] Maccarino, L. et al., *Microporous Mesoporous Mater.*, 375 (113178), **2024**.
[6] Oladoye, P. O. et al., *Results in Engineering*, 16 (100678), **2022**.