HYBRID AND SWELLABLE MATERIALS FOR THE ADSORPTION OF ORGANIC DYE MOLECULES

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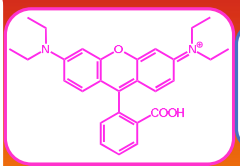
INTRODUCTION

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].

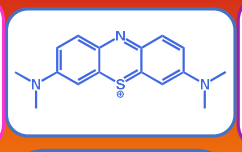
Different materials, for instance carbons, zeolite, clays, polymers are used to this purpose, but the class of hybrid organic-inorganic silica materials is deserving increasing interest for their peculiar adsorption performances [1]. Among the class of hybrid silicas, Swellable Organo-Modified Silicas (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 (tetrachloroethylene) [3, 4, 5].

DYE MOLECULES

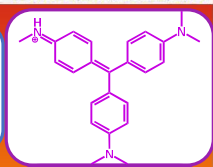
Dye molecules are one class of water pollutants released by industries, such as plastics, rubber, paper, cosmetics, food, leather and, in particular, textile, to colour their products. The global annual production of different colored dyes is estimated to be larger than 70 millions tons and 10% are released in water bodies [6]. The adverse effects of dyes on humans' health reported are acute toxicity, like skin irritation, mutagenicity and carcinogenicity. Moreover, dyes can interfere with photosynthetical processes in water bodies, reducing the penetration of light, and increasing the chemical oxygen demand (COD) up to 2-3 g/L [5]. Among the different classes of dye molecules, cationic dyes can be found, whose major and popular exponents are Rhodamine B, Methylene Blue and Crystal Violet [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.



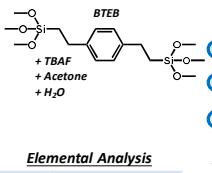
Methylene Blue (MB) is a cationic water-soluble azine dye molecule, containing a sulphur atom in the structure. This molecule is very popular in biological bacteria tests. MB has high solubility in water of about 44 g L^{-1} in water. MB is a weak acid with pK_a value of 3.8. At pH < 3 the indissociated form is prevalent, while at pH > 6 is completely protonated.



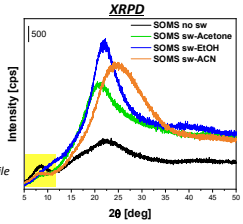
Crystal Violet (CrV) is a water-soluble triaryl methane dye, with a violet-blue colour. CrV is a weak acid (pK_{a1} 1.2, pK_{a2} 1.8) with good solubility (4 g L^{-1}) in water. CrV is a cation, in which the positive charge is shared by the 3 N atoms. At pH < 2, the other N atoms non-protonated, becomes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

SWELLABLE ORGANO-MODIFIED SILICA (SOMS)

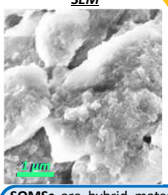
Synthesis



XRPD



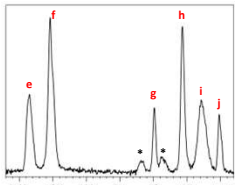
SEM



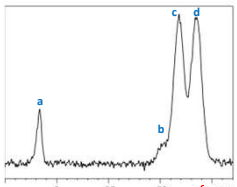
Elemental Analysis	
C %	50.02 ± 0.02 %
H %	6.0 ± 0.2 %
N %	0.07 ± 0.01 %

pH pzc	3.7

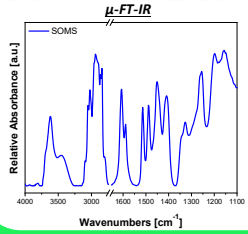
ssNMR ^{13}C-^{1}H CPMAS



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



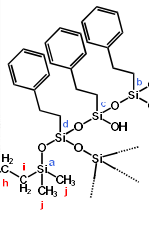
μ-FT-IR



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].

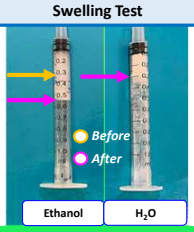
Highlight properties of SOMSs

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

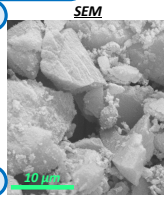


Solvent	Particle Diameter (DLS)	Swelling Ratio
Water	400 ± 100 nm	0.21 ± 0.01
Ethanol	230 ± 30 nm	5.0 ± 0.6
Acetonitrile	350 ± 70 nm	4.2 ± 0.3
Acetone	290 ± 30 nm	4.6 ± 0.1

Swelling Test



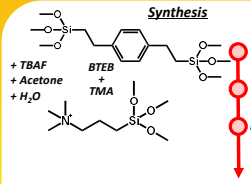
SEM



pH pzc	10.3
Swelling Ratio	3

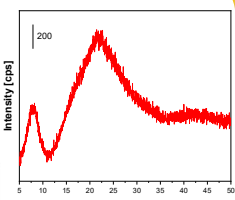
QUATERNARY AMINO MODIFIED SOMS (QA-SOMS)

Synthesis

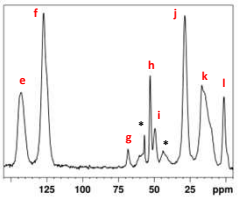


Elemental Analysis	
C %	42 ± 1 %
H %	5.9 ± 0.3 %
N %	0.68 ± 0.03 %

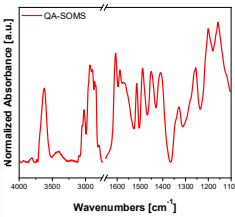
XRPD



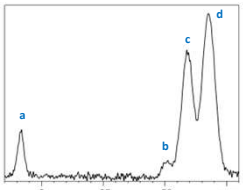
ssNMR ^{13}C-^{1}H CPMAS

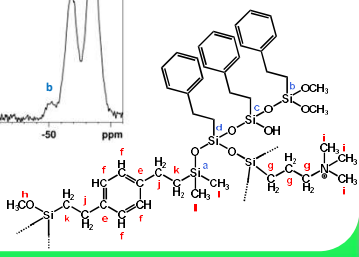


μ-FT-IR



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

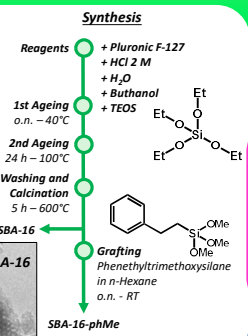


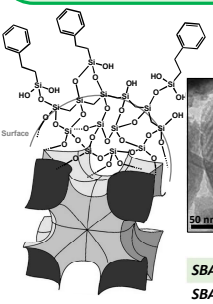


ORGANO-GRAFTED SILICA SBA-16

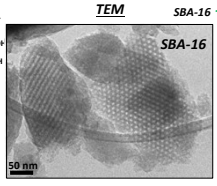
SBA-16 is a highly ordered mesoporous silica having large cubic structure of pores (> 100 Å). It is synthesized by sol-gel process in acid conditions of tetraethylorthosilicate (TEOS) in the presence of a non-ionic copolymer: Pluronic F-127, M_n > 12 kg/mol. This material can be functionalized with phenethyltrimethoxysilane to add a hydrophobic aromatic ring to the material (**SBA-16-phMe**).

Synthesis





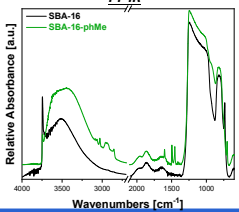
TEM



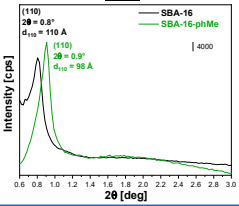
pH pzc	
SBA-16	2.57
SBA-16-phMe	2.91

Elemental Analysis (SBA-16-phMe)	
C %	6.02 ± 0.04 %
H %	1.6 ± 0.2 %
N %	0.11 ± 0.02 %

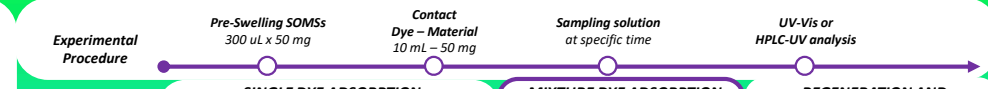
FT-IR



XRPD

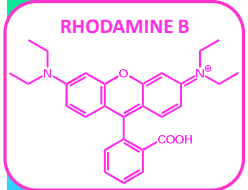


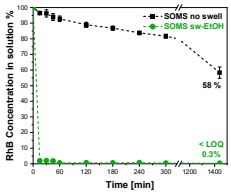
ADSORPTION OF DYES



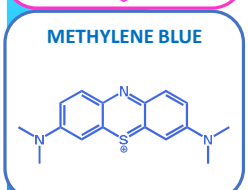
SINGLE DYE ADSORPTION

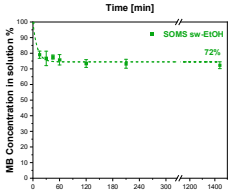
RHODAMINE B



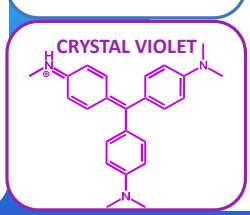


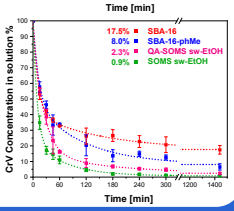
METHYLENE BLUE



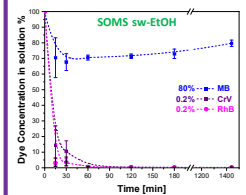


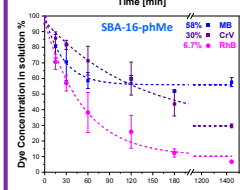
CRYSTAL VIOLET

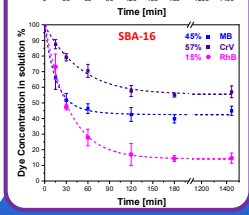




MIXTURE DYE ADSORPTION

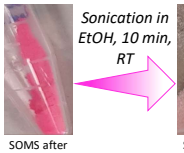


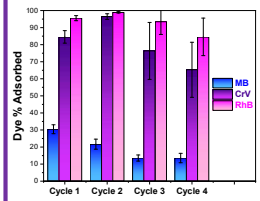




REGENERATION AND REUTILIZATION of SOMS

Regeneration Process





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**.