SWELLABLE ORGANO-MODIFIED SILICAS AS NOVEL ADSORBENTS FOR ORGANIC DYES FROM WATER BODIES

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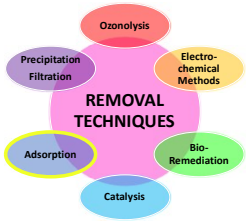
INTRODUCTION

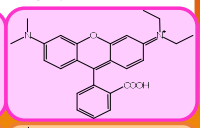
Many anthropogenic industrial activities are depleting the quality of water, one of the essential life components, introducing in it different types of pollutants. Various **removal techniques** are employed to restore the quality of water (e.g., filtration, precipitation, electrochemical methods, ozonolysis, bioremediation, catalysis, etc.), but adsorption is currently the best wastewater treatment technique, considering its versatility in removing different classes of pollutants, easiness, lower costs than traditional methods – 5–200 US$ per 1,000 L of water – and high removal capacities of about 99.9% [1]. Briefly, **adsorption** can be considered the cumulation of molecules at the solid-liquid interface between the adsorbent and adsorbate [2]. For this purpose, interest was directed towards the study of hybrid materials named Swellable Organo-Modified Silicas (**SOMSs**), which possesses the unique property of swelling, *i.e.*, expanding their structure and, consequently, their porous volume more than 1.5 times their dried volume, under appropriate conditions, being potentially capable of storing significant amounts of pollutants [3].



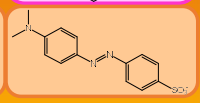
DYE MOLECULES

Among the water pollutants released by industries, dye molecules can be found. Dyes are used in different industries, such as plastics, rubber, paper, cosmetics, leather and, in particular, textile, to colour their products. The global annual production of different colored dyes is larger than 700,000 tons and 10-15% are released in water bodies. 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 [4]. Among the different classes of dye molecules, it can be found azo and triarylmethane dyes, whose major exponents are Methyl Orange and Rhodamine B, which are used in several industries in large quantities [5].

Rhodamine B (RhB) is a water-soluble triaryl methane dye, belonging to the xanthene class. RhB is a weak acid (pKa 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.



MethylOrange (MO) is an anionic water-soluble azo-dye molecule. MO is an acid pH-indicator (pKa 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.



SWELLABLE ORGANO-MODIFIED SILICAS

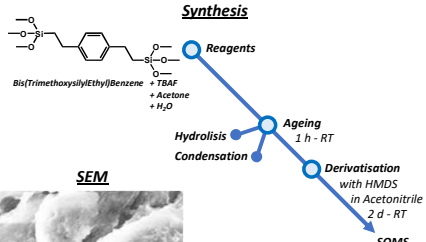
SOMSs are hybrid materials consisting of organic units linked to an inorganic matrix by a covalent metal-carbon bond. It is synthesized by a sol-gel synthesis of a particular bridged polysiloxane precursor (bis(trimethoxysilylethyl)benzene - BTEB), using tetrabuthylammonium fluoride (TBAF) as a catalyst. Then, the material is derivatized with disilazane (hexamethyldisilazane – HMDS) to prevent further condensation and to achieve the property of swelling [6].
QA-SOMS is the quaternary-amino functionalized form of SOMS, in which a positively charged group is added in the structure [6].

Highlight properties of SOMSs

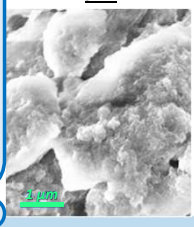
- Porous, hydrophobic and flexible structure
- Highly cross-linked solid
- Swelling with organic solvents
- Do not expand in water

Swelling Test

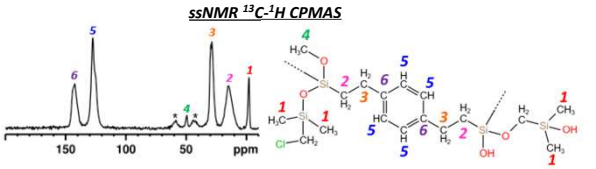
Synthesis



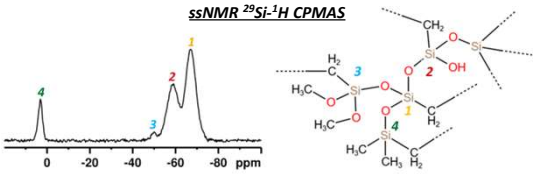
SEM



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

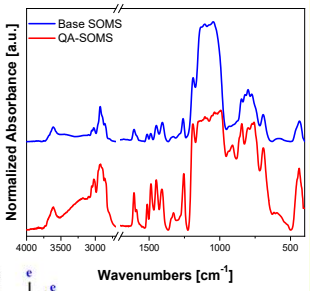


ssNMR ^{29}Si-^{1}H CPMAS



SOMS	
pH pzc	3.7
C %	49.84±0.08 %
N %	0.12±0.02 %

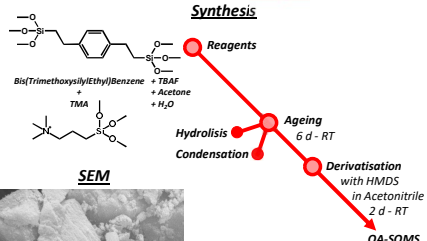
FT-IR



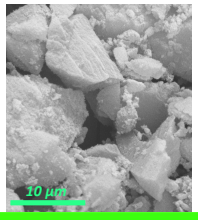
Base SOMS

Quaternary-Amine-SOMS (QA-SOMS)

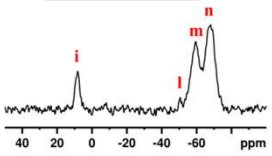
Synthesis



SEM



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



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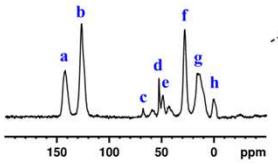
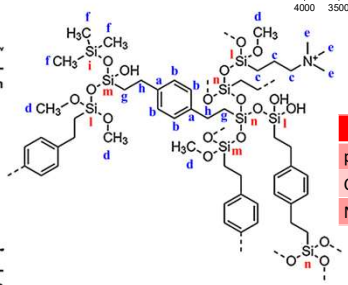
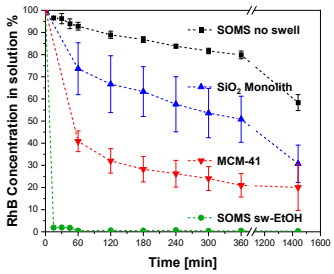




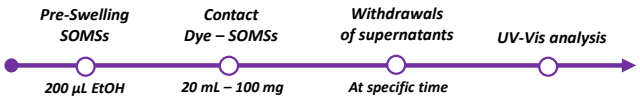
QA-SOMS	
pH pzc	10.3
C %	47.8±0.3 %
N %	0.84±0.05 %

ADSORPTION OF RHODAMINE B AND METHYLORANGE: KINETIC, ISOTHERM AND MATERIAL REUTILIZATION

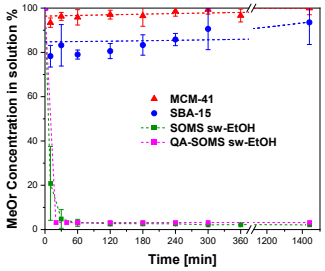
Kinetics



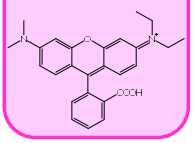
Experimental Procedure



Kinetics

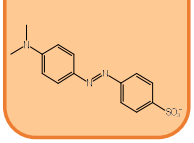


RHODAMINE B ADSORPTION

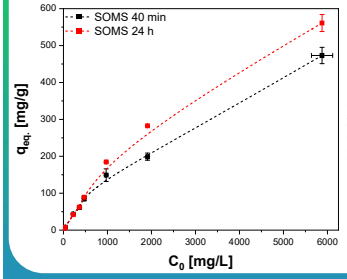


	q_{max} 40 min	q_{max} 24 h
SOMS ads. RhB	0.981 mmol/g	1.190 mmol/g
SOMS ads. MO	0.229 mmol/g	0.229 mmol/g
QA-SOMS ads. MO	0.293 mmol/g	0.438 mmol/g

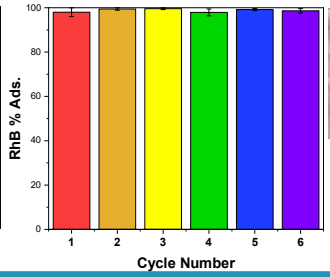
METHYLORANGE ADSORPTION



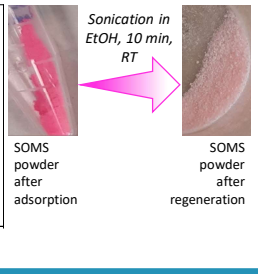
Adsorption isotherm



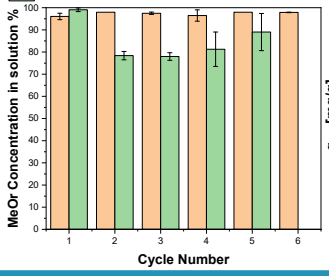
Adsorption cycles



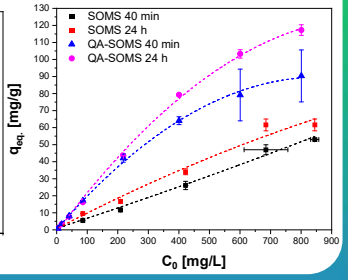
Regeneration Process



Adsorption cycles



Adsorption isotherm



References

[1] Gupta, V. K. et al., *RSC Adv.*, 2 (16), 6380, **2012**.
[2] Ali, I. et al., J. Environmental Management, 113 (170–183), **2012**.
[3] C. M. Burkett et al., J. Non-Crystalline Solids, 351 (40–42), **2005**.
[4] AL-Kazragi et al., Internat. J. of Phytoremediation, 1-30, **2023**.
[5] Su, Y. et al., Desalination and Water Treatm., 52 (31–33), **2014**.
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