HYBRID MATERIALS FOR THE ADSORPTION REMOVAL OF DYES FROM WATER

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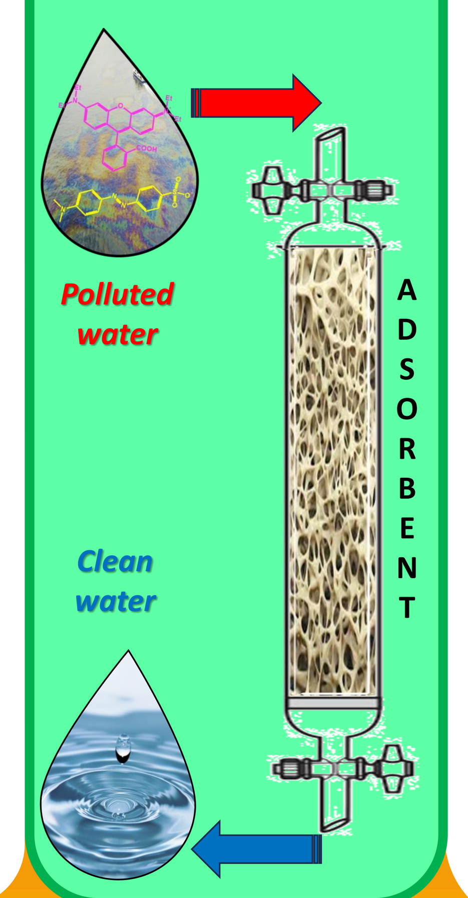
INTRODUCTION

The problem of environmental pollution is well-known by the scientific community. In last years, it is estimated that 7 x 10^5 tons of toxic wastewater containing dyes are produced every year. Dyes are known for their low biodegradability, high solubility in water and toxicity in the environment. Therefore, it is necessary to find a strategy for the removal of these pollutants from wastewater. The removal of organic molecules from water media through adsorption on solid sorbents deserved a lot of attention in the last years. [1]

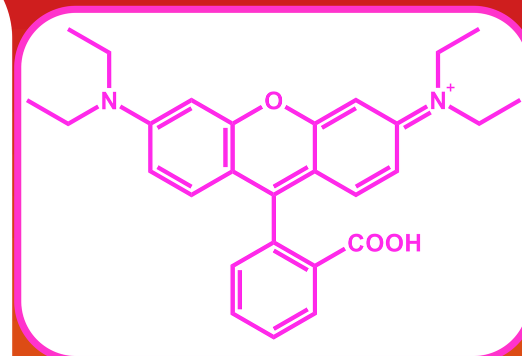
Briefly, **adsorption** can be considered the cumulation of molecules at the solid-liquid interface between the adsorbent and adsorbate [2]. An ideal adsorbent should remove in a short time high quantities of dyes and should be inexpensive, regenerable and reusable. Different materials, for instance 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 [3]. 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. The swelling property gives SOMS more enhanced adsorption performances towards organic moieties in water, including dyes, if compared to inorganic or organic-grafted silicas. [4]

ADSORPTION PROCESS

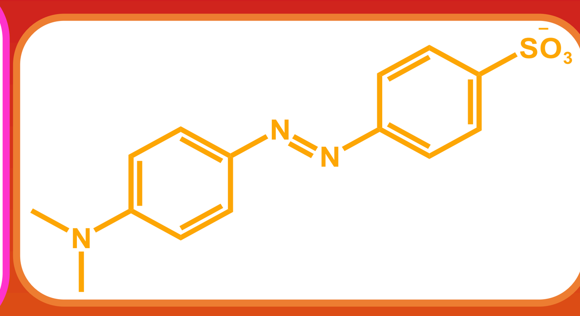


DYE MOLECULES

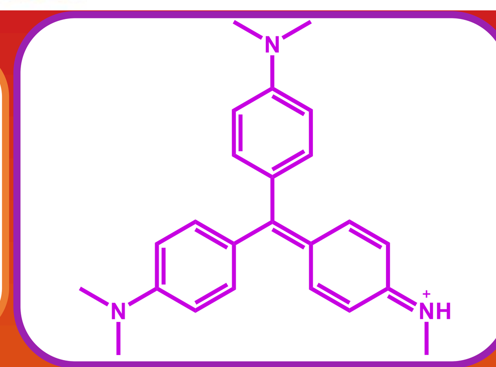
Among the water pollutants released by industries, dye molecules can be found. Dyes are used in different industries, such as plastics, rubber, paper, cosmetics, leather and, in particular, textile, to colour their products. The global annual production of different colored dyes is larger than 70 milions tons and 10% 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. 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 (paper, textile, paint, plastic, cosmetics) in large quantities [5].



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.

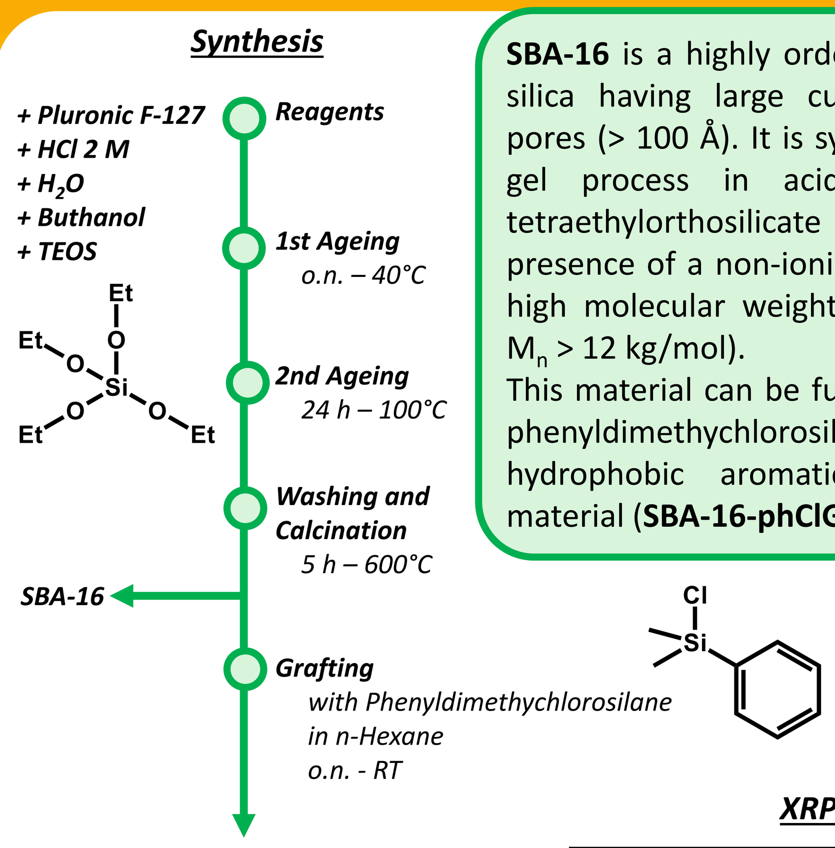


MethylOrange (MO) is an anionic water-soluble azo-dye molecule. MO is an acid pH-indicator (pK_a 3.4) with a solubility of about 5 g L^{-1} in water. At pH values below 3, the molecule is protonated and red, while at pH above 4.4 occurs the deprotonation of N-atom and the molecule is negative and yellow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



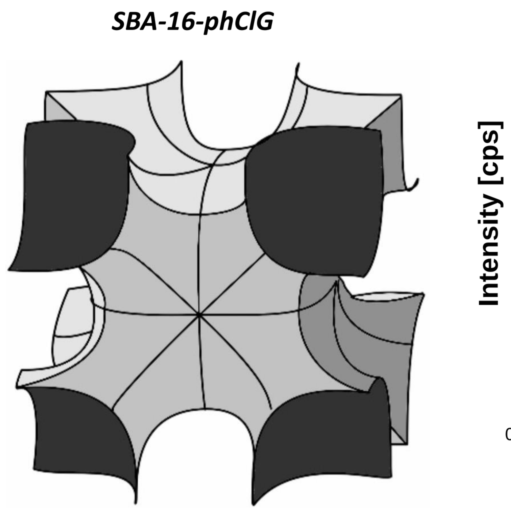
Crystal Violet (CrV) is a water-soluble triaryl methane dye, with a violet-blue colour. CrV is a weak acid (pK_{a1} 1.2, pK_{a2} 1.8) with good solubility (4 g L^{-1}) in water. CrV is a cation, in which the positive charge is shared by the 3 N atoms. At pH < 2, the other N atoms non-protonated, becomes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

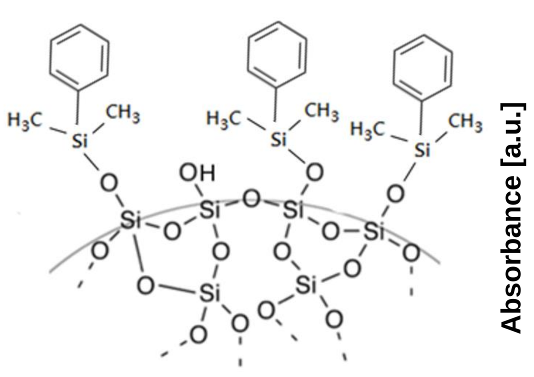
ORGANO-GRAFTED SILICA SBA-16

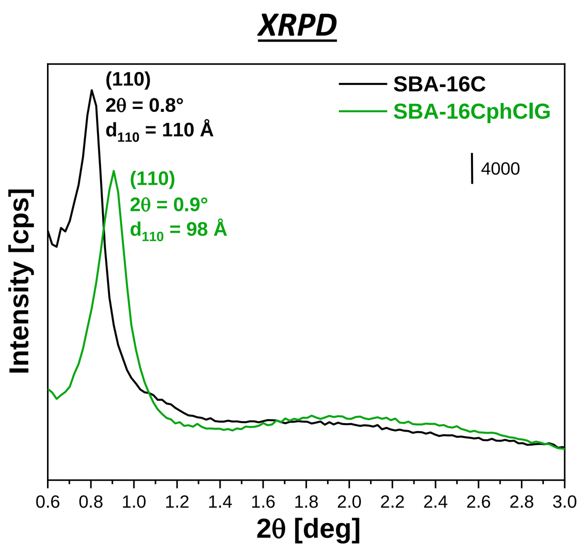


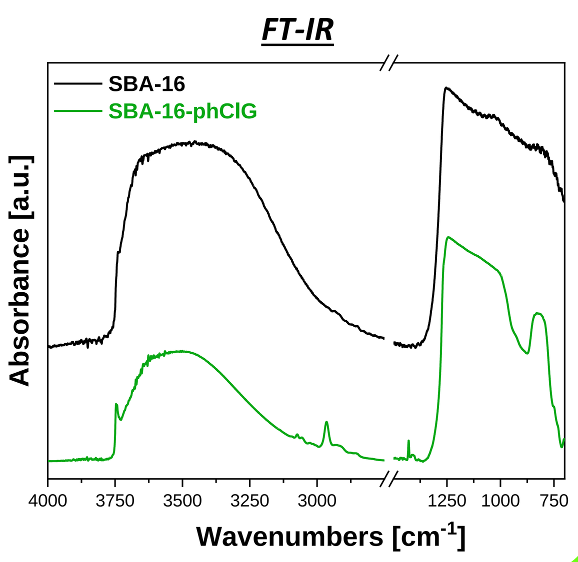
SBA-16 is a highly ordered mesoporous silica having large cubic structure of pores (> 100 Å). It is synthesized by sol-gel process in acid conditions of tetraethylorthosilicate (TEOS) in the presence of a non-ionic copolymer with high molecular weight (Pluronic F-127, M_n > 12 kg/mol).
This material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

SBA-16-phClG









pH pzc	3.95 (SBA-16)
	1.99 (SBA-16-phClG)

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 basic catalyst. Then, the material is derivatized with 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 (N-trimethoxysilylpropyl-N,N,N-trimethylammoniumchloride, TMA) [6].

Highlight properties of SOMSs

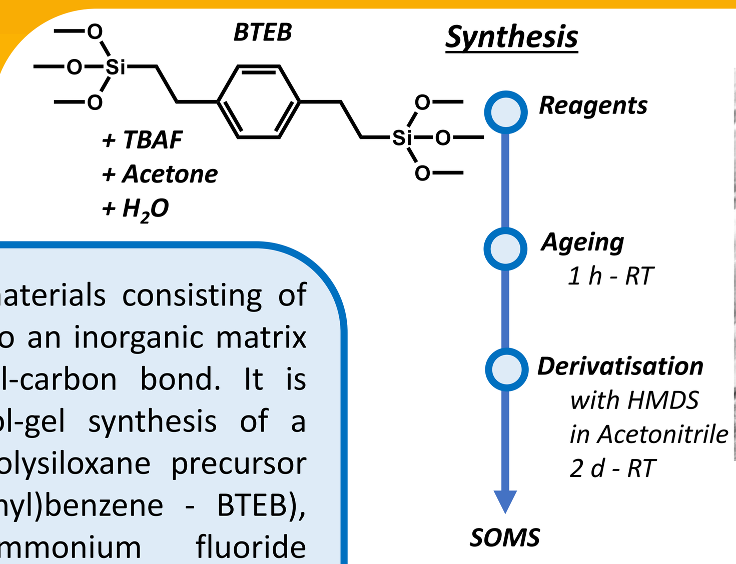
Porous, hydrophobic and flexible structure

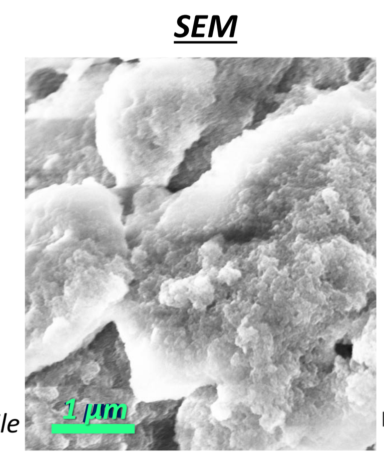
Highly cross-linked solid

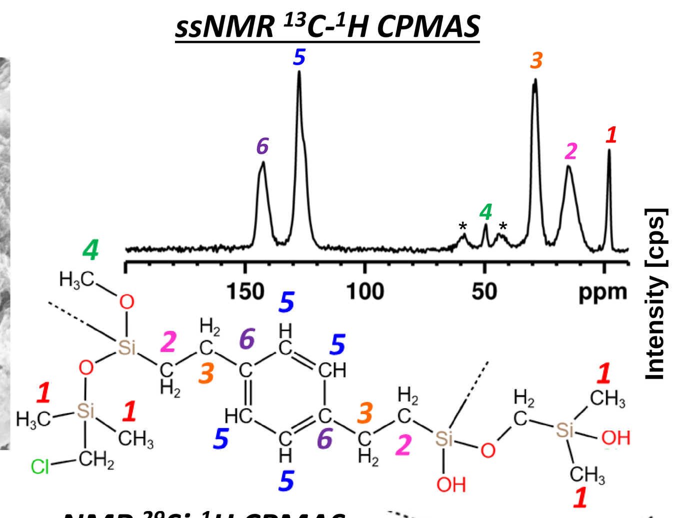
High Swelling Ratio (SwR) with organic solvents

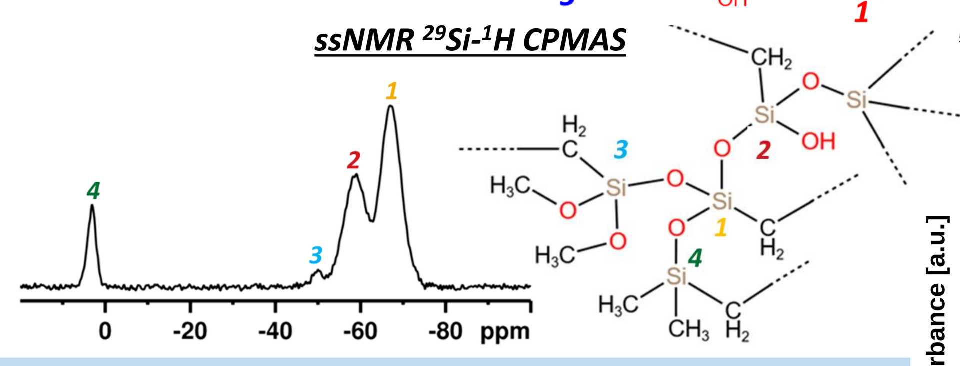
Do not expand in water

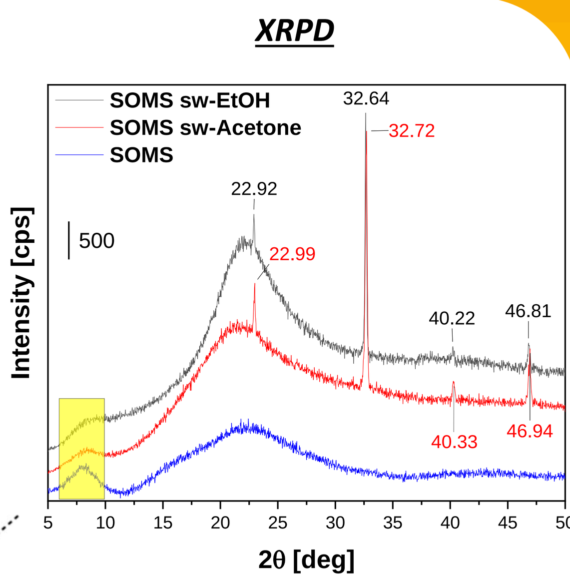
Swelling Test

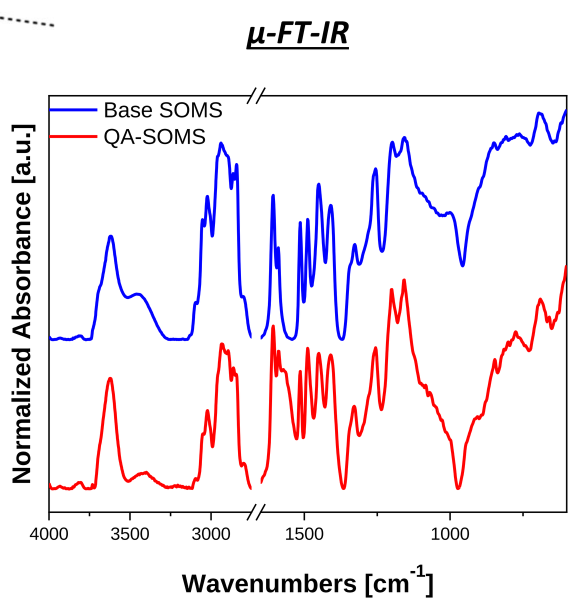








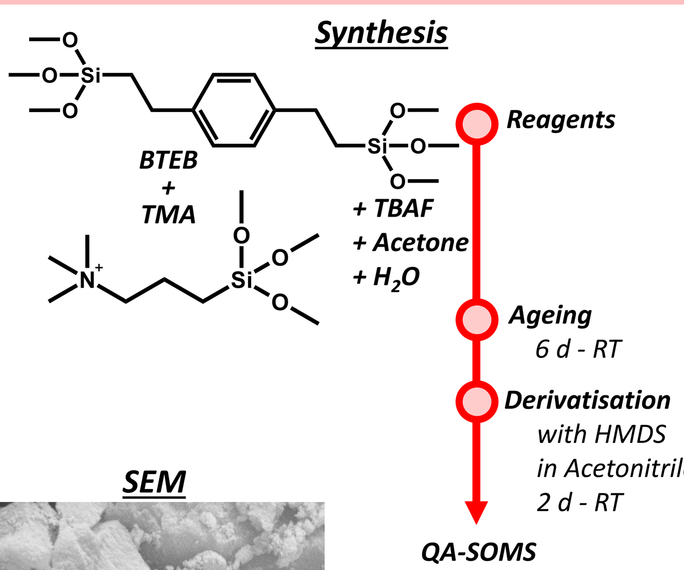


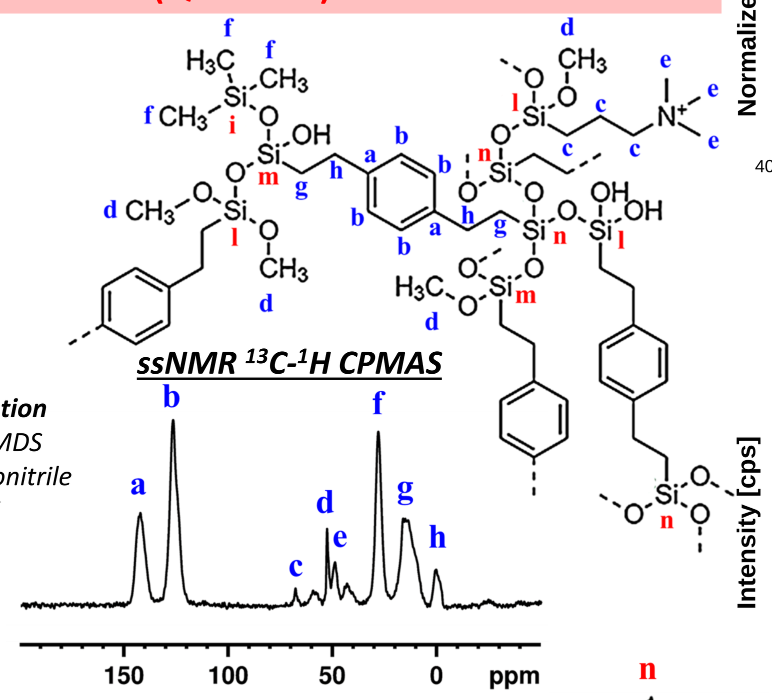


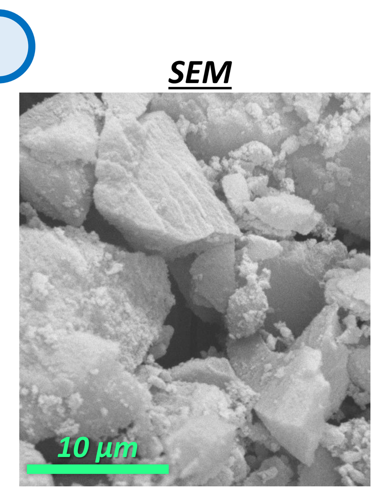
pH pzc	3.7
C %	49.84±0.08 %
N %	0.12±0.02 %
SwR	2.09

Base SOMS

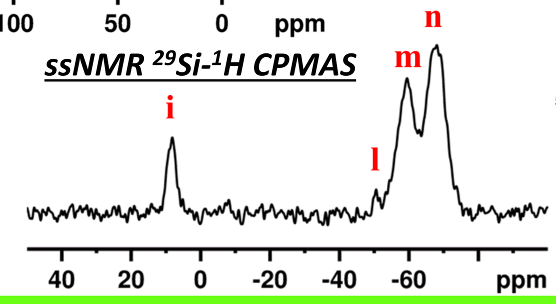
Quaternary-Amine-SOMS (QA-SOMS)

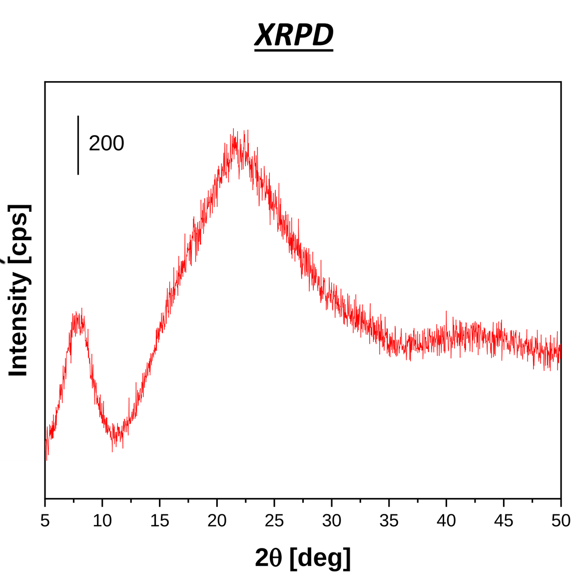






pH pzc	10.3
C %	47.8±0.3 %
N %	0.84±0.05 %
SwR	3

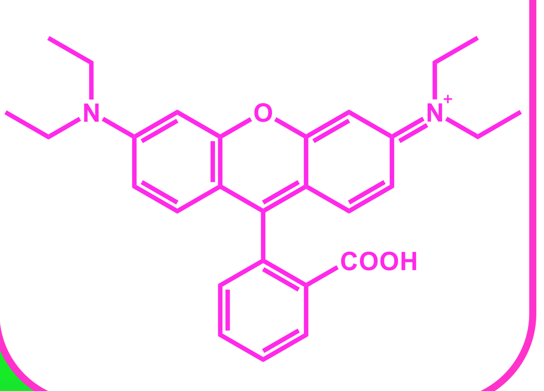


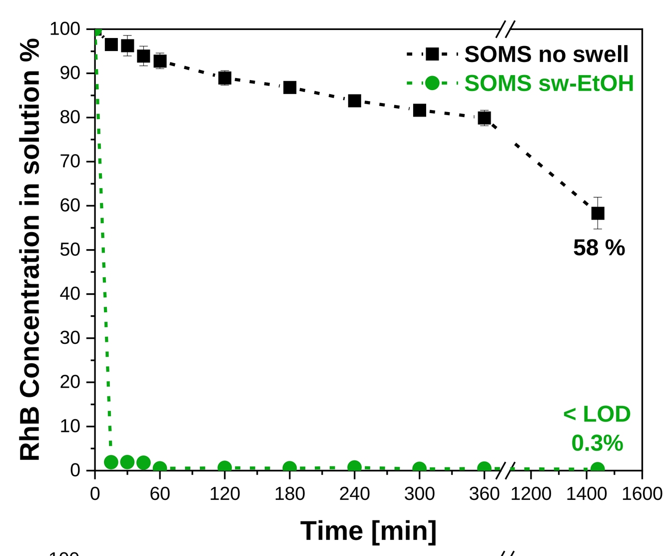


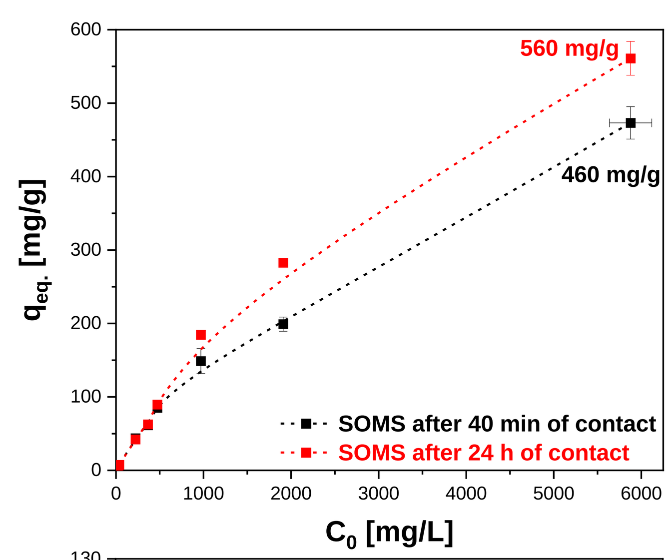
ADSORPTION OF DYES

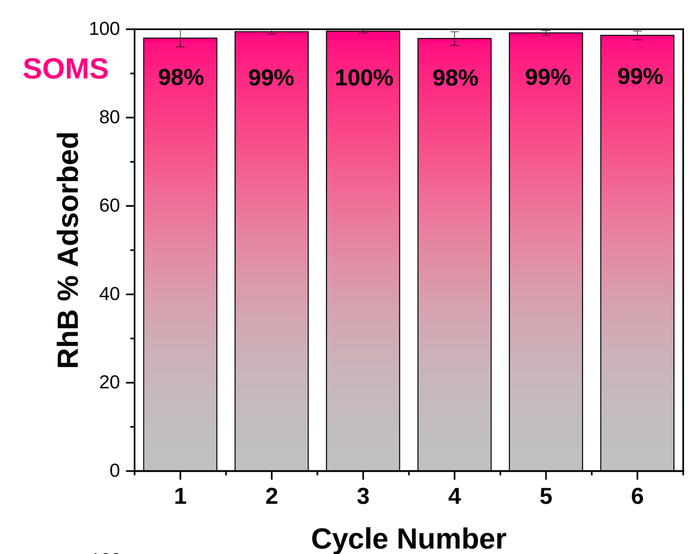
ADS. KINETICS | ADS. ISOTHERM | ADS. CYCLES

RHODAMINE B ADSORPTION

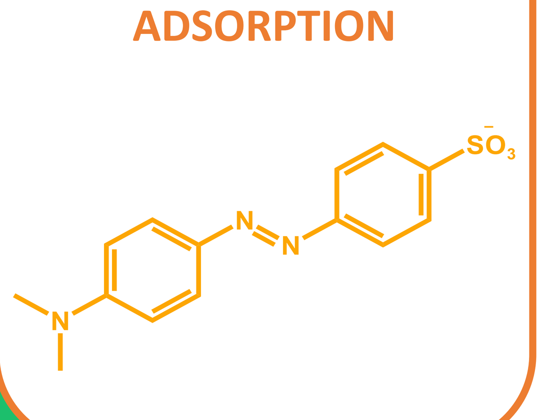


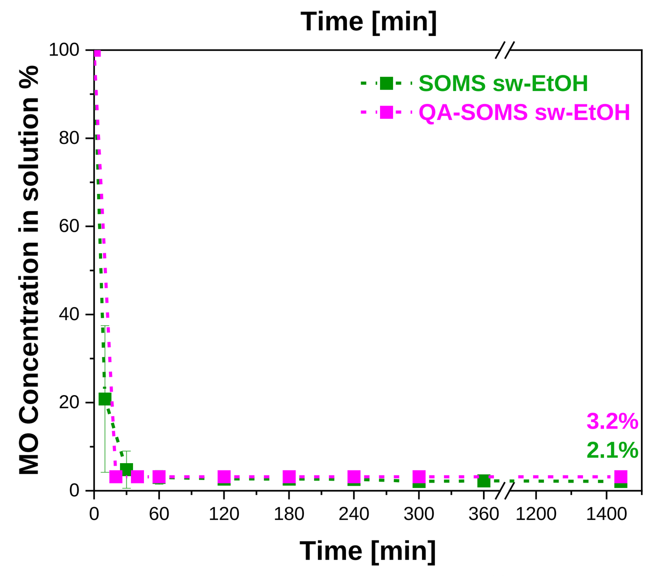


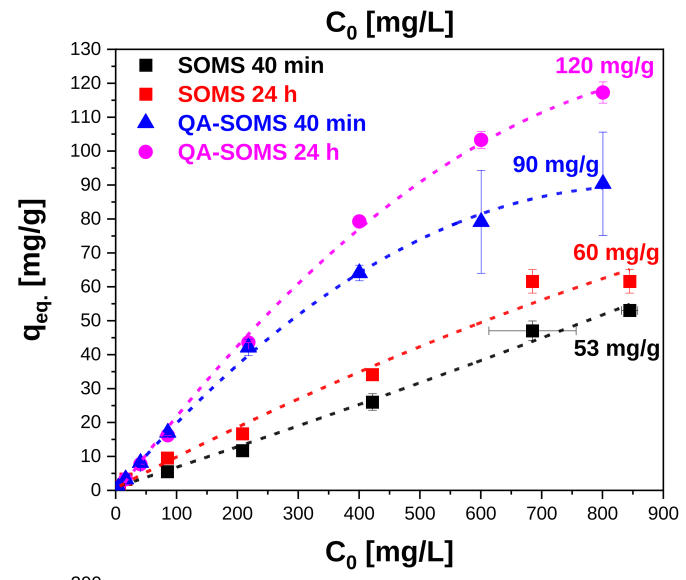


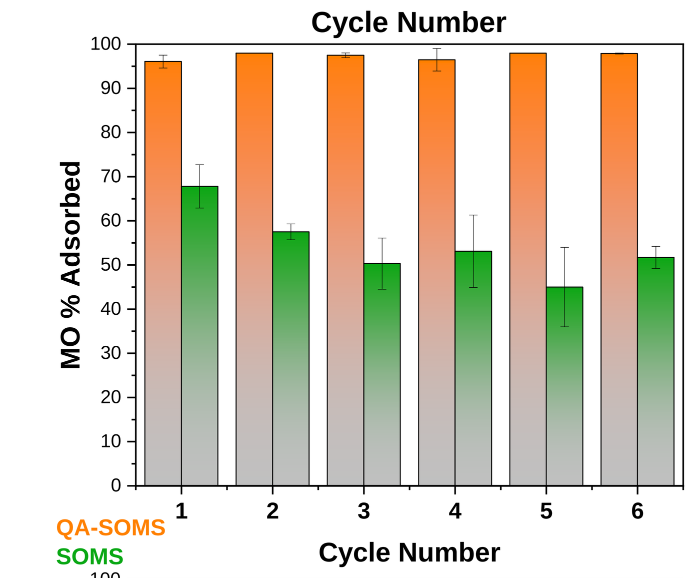


METHYLORANGE ADSORPTION

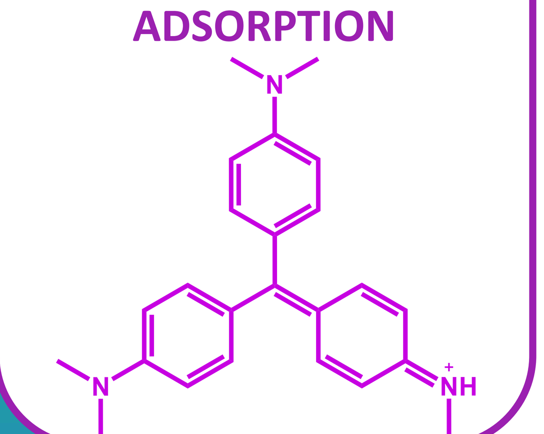


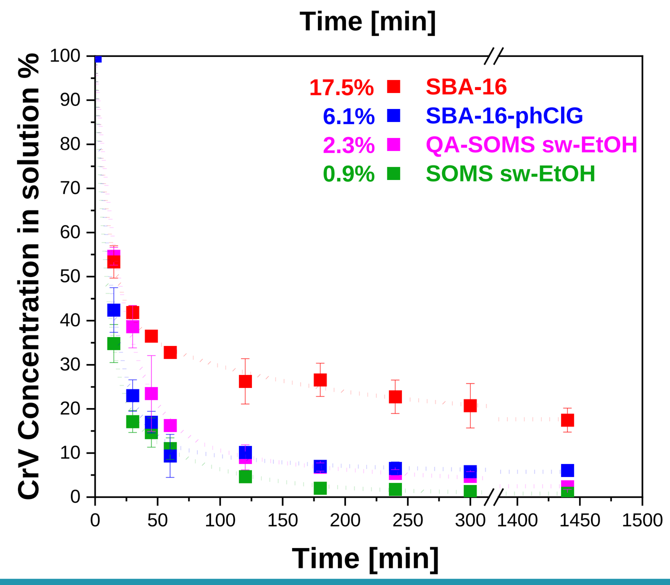


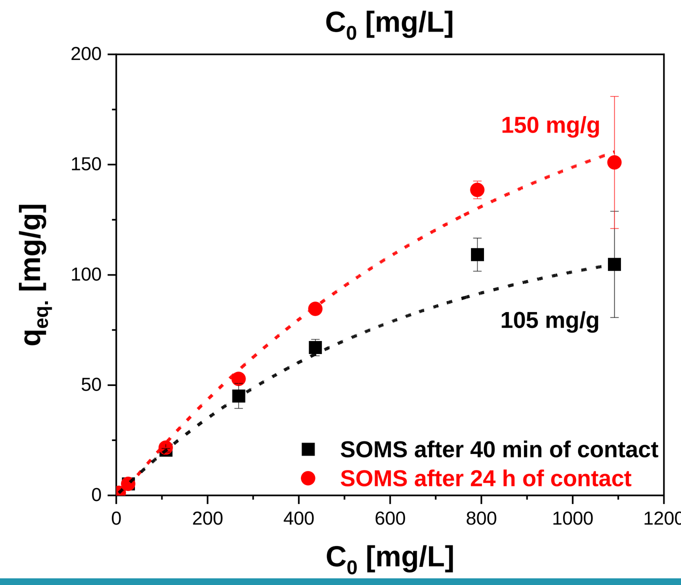


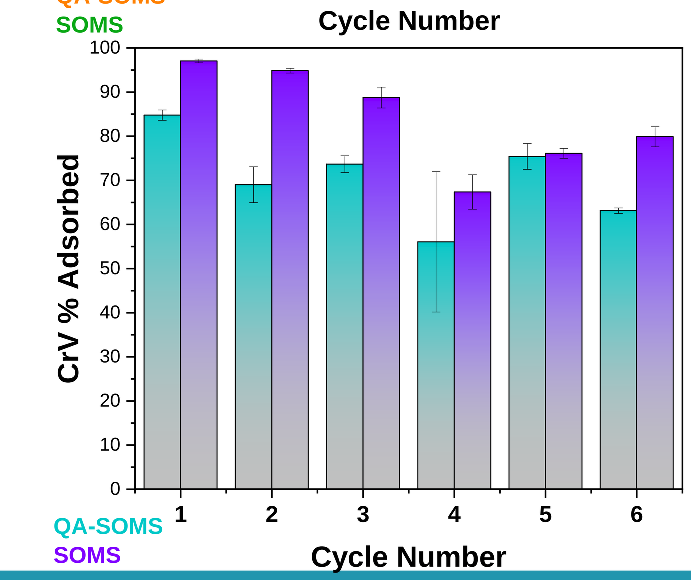


CRYSTAL VIOLET ADSORPTION

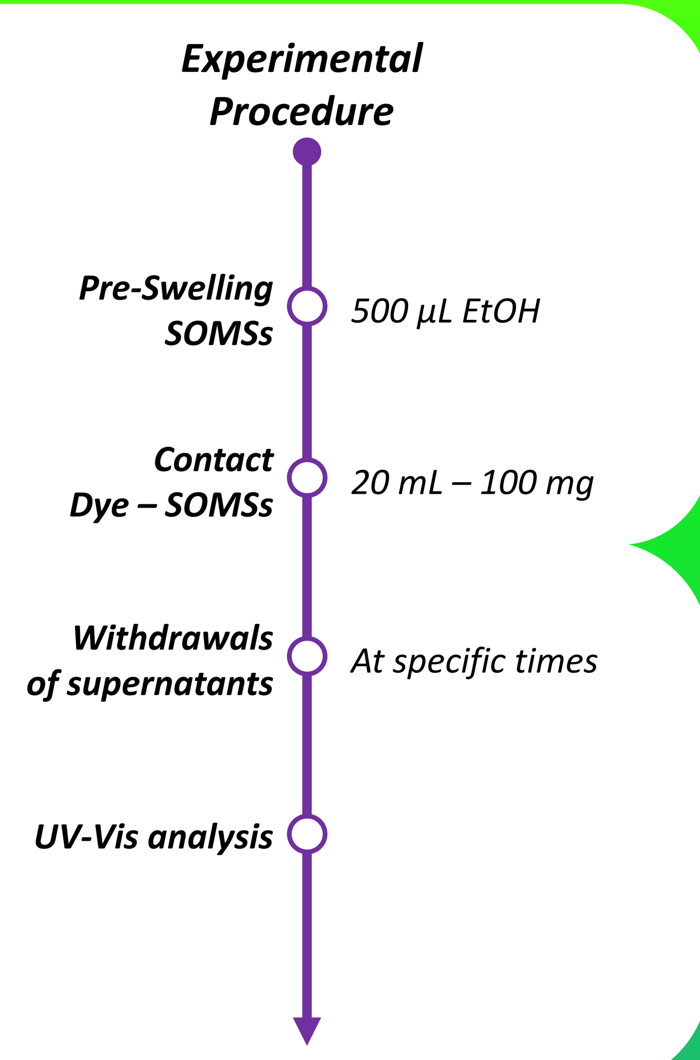




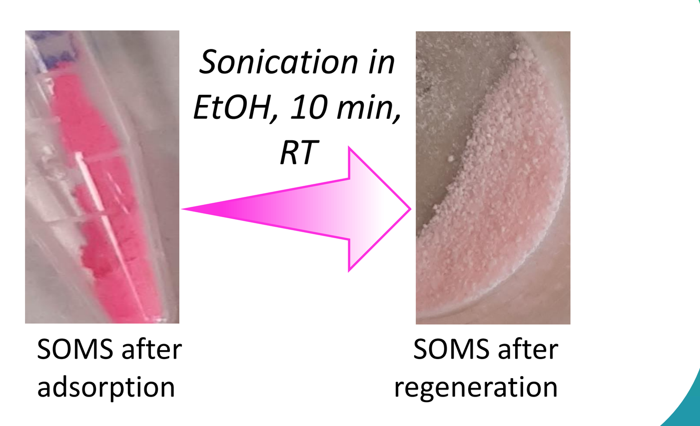




Experimental Procedure



Regeneration Process



References

[1] J. Guo et al., *Separation and Purification Technology*, 330 (125480), **2024**.

[2] Ali, I. et al., *J. Environmental Management*, 113 (170–183), **2012**.

[3] R. Agarwala et al., *ChemBioEng Rev.*, 10 (326-335), **2023**.

[4] V. Miglio et al., *J. Phys. Chem. C*, 128, 5 (2179–2189), **2024**.

[5] Benkhaya, S. et al., *Inorg. Chem. Comm.*, 115 (107891), **2020**.

[6] Stebel, E. K. et al., *Environ. Sci.: Water Res. Technol.*, 5 (11), **2019**.