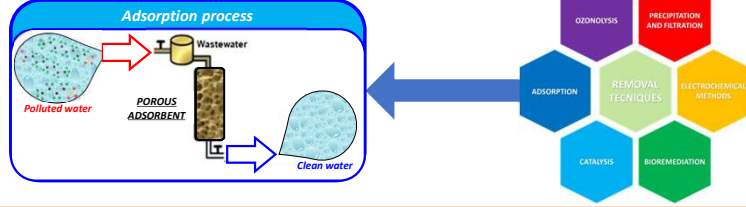


INTRODUCTION

Many anthropogenic activities unfortunately introduce pollutant species that deteriorate the quality of water, one of the essential life components. Various methods can be used to remove pollutants from water (e.g., filtration, precipitation, electrochemical methods, ozonolysis, bioremediation, catalysis, etc.), but adsorption onto solids (such as clays, zeolites, porous silicas) is considered an advantageous, cost-effective, and high-performance method [1]. For this purpose, interest was directed towards the study of an organic-inorganic hybrid silica material named Swellable Organically Modified Silica (**Silica-SOM**), 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 [2].

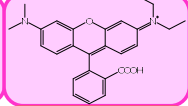


DYE MOLECULES

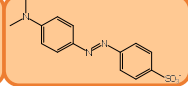
Among the most common water pollutants, organic dyes are a class of organic molecules widely used from textile, cosmetic, photographic, leather, paper, and plastics industries. Moreover, some organic dyes are also employed in food industry or as a fluorescent tracer and metal chelating reagents [5].

Rhodamine B (RhB) and **MethylOrange (MeOr)** are two of the most widely used organic dyes and deserve particular attention because of their toxicity and possible adverse effects on human health. Some carcinogenicity, reproductive and developmental toxicity, mutagenicity and teratogenicity, as well as neurotoxicity and chronic toxicity have also been reported for dye molecules and their metabolites. Furthermore, being an organic pigment, a dye molecule has a high capability to alter the environment and it can therefore significantly interfere with biological cycles related to photosynthetic processes [6].

Rhodamine B (RhB) is a water-soluble triaryl methane dye, belonging to the xantheno class. RhB is a weak acid (pKa 4.2) with good solubility (34 g L⁻¹) in water. At low pH values the organic part is a cation in which the positive charge is shared by the two N atoms. At pH > 4.2, the carboxylic group is predominantly deprotonated and the prevalent form of Rhodamine B is a Zwitterion.



MethylOrange (MeOr) is an anionic water-soluble azo-dye molecule. MeOr 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.

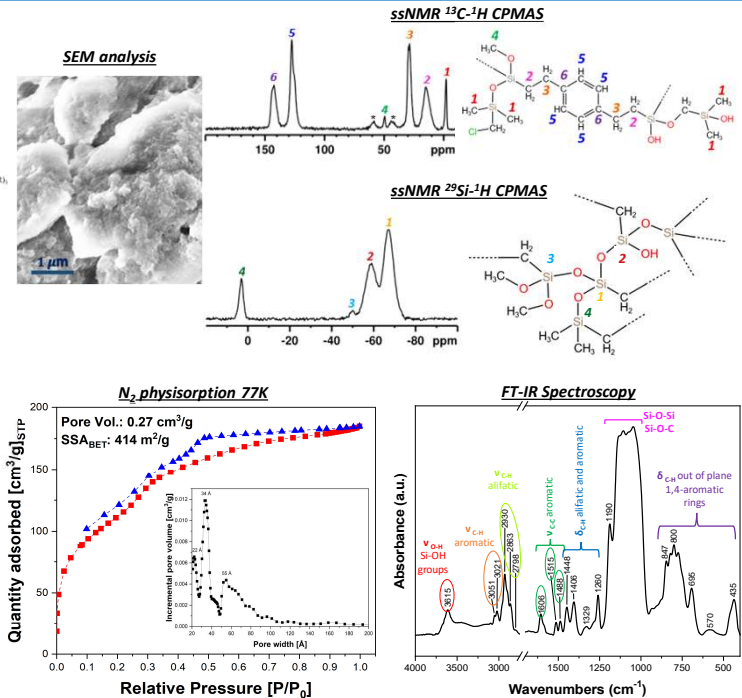
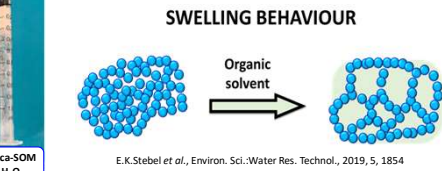
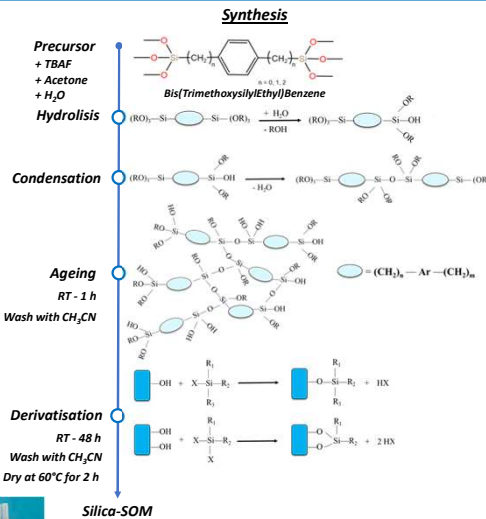


SWELLABLE ORGANICALLY MODIFIED SILICA (Silica-SOM)

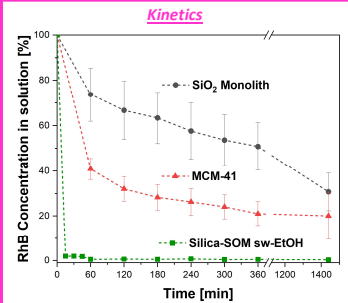
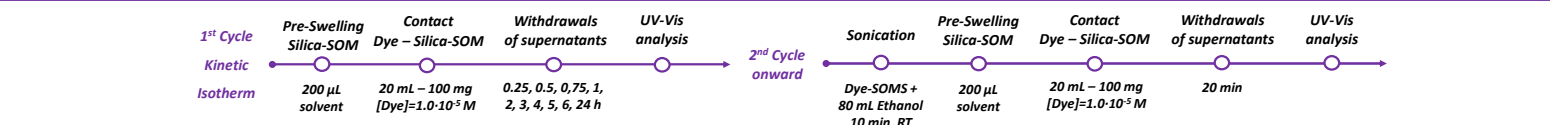
Silica-SOM is a hybrid material consisting of organic units linked to an inorganic matrix by a covalent metal-carbon bond. It is synthesized by polycondensation of a bridged polysiloxane precursor (bis(trimethoxysilyl)ethyl)benzene, using tetrabutylammonium fluoride as a catalyst [3]. Then, the material is derivatized with a chlorosilane or a disilazane to prevent further condensation and to achieve the property of swelling [4].

Highlight properties of Silica-SOM:

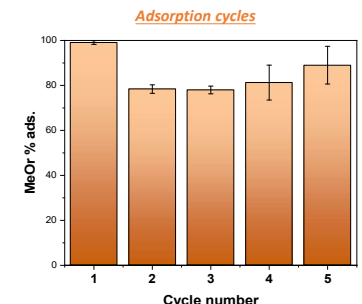
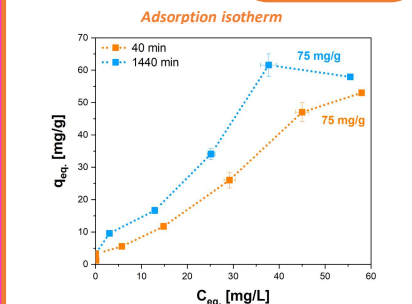
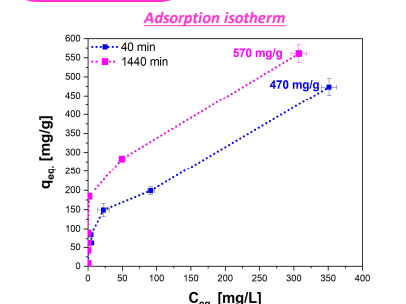
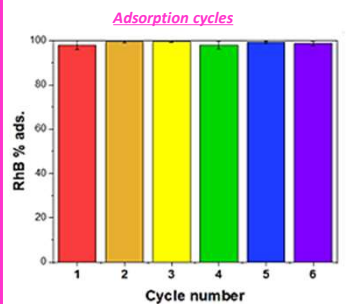
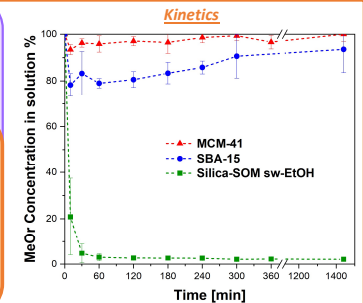
- Porous, hydrophobic and flexible structure
- Highly cross-linked solid
- Matrix expands in contact with organic compounds
- Surface negatively charged at pH > 3.7
- Do not expand in water



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



To study the **adsorption kinetics**, Silica-SOM was firstly pre-swollen with ethanol, then placed in contact with a Rhodamine B solution or a Methylorange solution. Samples were taken at increasing times from the beginning of contact, then analyzed by UV-Vis spectroscopy. The kinetics follows a pseudo-second order model ($R^2 > 0.99999$) for both the target molecules. To study the **reutilizability** of Silica-SOM adsorption-desorption cycles were performed. The desorption process consists in a sonication of Silica-SOM after adsorption in about 80 mL of ethanol for 10 min at room temperature. For RhB, after 6 cycles, Silica-SOM does not show any losses in adsorption performance, while for MeOr, after 5 cycles, it can be seen a decrease in the quantity adsorbed from about 100% to 80% from the second cycle onward. The **maximum adsorption capacity** of the material has also been investigated and calculated using the Langmuir monolayer adsorption model. For RhB it resulted to be ranging from 470 mg/g in 40 min of contact to 570 mg/g in 24 hours of contact, while for MeOr was 75 mg/g at any time.



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