ELSEVIER 7th international Colloids Conference
18-21 June 2017
Sitges Barcelona Spain

Study of loading isothiazolinone-based biocide and release profiles from mesoporous silica matrices

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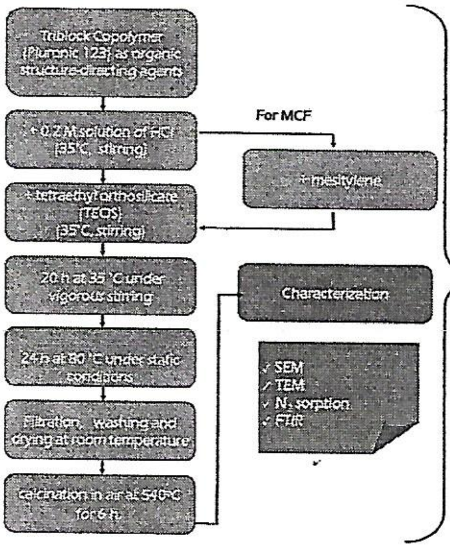
INTRODUCTION

Isothiazolinone and its derivatives are organic compounds used for the formulation of broad-spectrum biocides and preservatives such as antiseptic agents, bactericides, slimicides and fungicides. Isothiazolinone-based biocides have shown effective performance for microbial control in various industrial applications.
This preservative generally displays an excellent performance, but its effectiveness has to be checked when it is included in a particular product. Incompatibilities between constituents, thermal decomposition above 40ºC and instability in strong alkaline media (pH≥8) could affect its preservative properties.

Recent studies about biocide encapsulations by adsorption onto nanoporous inorganic materials indicate that this procedure could be appropriate for obtaining a long-term protection from fungal attack to environmentally exposed paints. The supported biocide could be released only on demand because adsorption interactions between the adsorbate molecules and the inorganic matrix render the biocide less resistant to leaching. In this study, mesoporous silica materials were proposed as new hosts for stabilizing isothiazolinone-based biocides. In the search of an enhancement of the CMIT/MIT stability, in this work the biocide encapsulation in SBA-15 and MCF mesoporous materials was proposed. The enhancement of the biocide stability was analyzed in terms of obtaining a delayed biocide degradation, minimizing the disadvantages associated with hydrolysis at high pHs and decomposition at temperatures above 40°C.

SYNTHESIS OF MATERIALS



Triblock Copolymer (Pluronic 123) as organic structure-directing agents

+ 0.2 M solution of HCl (35°C, stirring)

+ tetraethyl orthosilicate (TEOS) (35°C, stirring)

20 h at 35 °C under vigorous stirring

24 h at 80 °C under static conditions

Filtration, washing and drying at room temperature

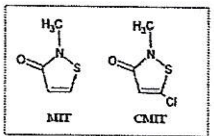
calcination in air at 540ºC for 6 h

For MCF

+ mesitylene

Characterization

- ✓ SEM
- ✓ TEM
- ✓ N_2 sorption
- ✓ FTIR

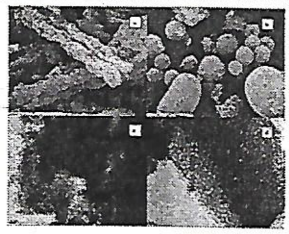


mixture to 1.5 % of
5-chloro-2-methyl-4-isothiazolin-3-one and
2-methyl-4 isothiazolin-3-one
in an approximate ratio of 3:1

BIOCIDE CHOSEN AS ADSORBATE FOR THIS STUDY

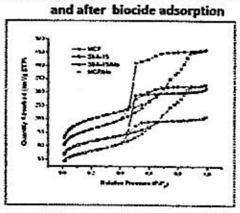
CHARACTERIZATION

SEM and TEM images of SBA-15 and MCF



SEM image showed that the SBA-15 sample consisted of rod-like sub-particles of relatively uniform size 1 μm in diameter and 14–16 μm in length (Fig. a). In the other side, a change in the morphology of the particles was attained by adding mesitylene to the synthesis mixture; the MCF sample exhibited spherical aggregates consisting of rounded particles of about 4-6 μm in size (Fig.b). TEM images confirmed the two-dimensional hexagonal structure (p6mm) of SBA-15-type materials and showed an ordered arrangement of cylindrical pores (Fig. c). In the case of MCF, the structural regularity was completely lost. TEM images show interconnected disordered, oval shaped pores (Fig.d).

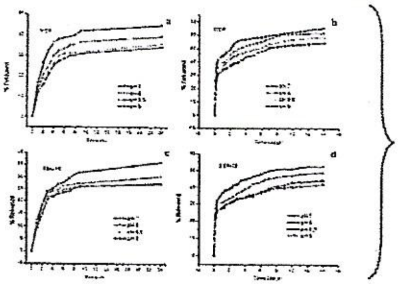
Nitrogen adsorption/desorption isotherms of SBA-15 and MCF before and after biocide adsorption



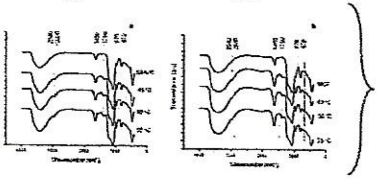
All the studied samples exhibit Type IV isotherms according to the IUPAC classification. The SBA-15 sample shows a type H1 hysteresis loop, which is associated with mesoporous materials consisting of well-defined cylindrical-like pore channels. A very sharp desorption branch was registered for MCF. Hysteresis loops of this type are given by more complex pore structures in which network effects are important. The very steep desorption branch observed can be attributed either to pore-blocking/percolation in a narrow range of pore necks or to cavitation-induced evaporation

Sample	S BET (m²/g)	Pore Vol. (cm³/g)	Pore size (nm)	% loaded
SBA-15	578	0.48	6.1	
MCF	713	0.71	13	
SBA-15/bio	247	0.34	5.55	18
MCF/bio	261	0.63	12.14	27

The textural characteristics of the synthetized solids are summarized in the Table. It could be noted that after biocide adsorption on both SBA-15 and MCF, a significant reduction in the surface area, pore volume and pore size occurred.



As it is shown in the figure, the release rate for both materials exhibits two steps, the first one is a fast delivery followed by a second stage where there is a slower delivery rate.
The retarded release observed as the pH increased could be explained on the basis of strong CMIT/MIT-mesoporous solid interactions as a result of van der Waals and electrostatic forces. Taking into account that the point of zero charge of both matrices is evidenced at very low pH values (which is about 4.3), the higher pH values of the leaching solution would favor a balance of negative charges on the surface of the siliceous materials. Then, as the alkalinity of the medium increases, there would be a greater availability of silanol groups that can interact with the positive ring and methyl group of both biocidal molecules (CMIT and MIT). The ring and methyl group of the biocide contribute to stabilize the negative charge of the silica surface.



The effective biocide loading was reflected in the IR spectra by the presence of the stretching vibrations bands of C–H at 2940, 2890 and 886 cm^{-1} and bending vibrations bands of C–H observed in the range 1450–1390cm-1. The band around 600 cm^{-1} is due to C–Cl stretching.
The figure corroborated the presence of biocide into SBA-15 and MCF. In all cases, the shoulder around 670 cm^{-1} corresponding to the C–Cl stretching appears in the FTIR spectra. This fact confirms the presence of CMIT into the siliceous material even at temperatures higher than the thermal decomposition temperature . Then, biocide encapsulation allows retarding the fast thermal decomposition above 40ºC.

CONCLUSIONS

Release tests in aqueous media indicated that the CMIT/MIT concentration in the leaching solution depends on the structural arrangement of siliceous material, being the highest obtained values when disordered matrices were used. Silicas presenting structural disordering seem to be the most effective matrices for fast release whereas ordered matrices were more suitable for biocide encapsulation. The stability of supported biocide in strong alkaline media and its sensitivity to temperatures higher than 40ºC were also studied. Results indicated that higher pH values of test solutions slightly delayed the biocide delivery. Additionally, test up to 55 ºC corroborated that biocide encapsulation allowed retarding the fast thermal decomposition of CMIT.