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Long-lasting isothiazolinone-based biocide obtained by encapsulation in micron-sized mesoporous matrices

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ABSTRACT

The use of mesoporous silica materials as new hosts for stabilizing isothiazolinone-based biocides was investigated. Two types of porous matrices were synthesized: SBA-15 mesoporous silica and mesocellular siliceous foam (MCF). The physicochemical properties of the silicas (structure, textural properties) were evaluated by SEM, TEM, XRD and adsorption/desorption of N_2 in order to determine their ability to encapsulate, stabilize and subsequently release a commercial biocide used for latex preservation (CMIT/MIT). CMIT/MIT consists of an aqueous solution of the active ingredients CMIT (5-chloro-2-methyl-4-isothiazolin-3-one) and MIT (2-methyl-4-isothiazolin-3-one), present in a CMIT/MIT: 3/1 wt ratio. It was observed that the biocide can be encapsulated in both silica frameworks without suffering structural damage. The SBA-15 support exhibits a lower adsorption capacity of biocide molecules than MCF, which may be attributed to both agreater MCF pore volume and pore size. MCF has less hindered diffusion causedby a short channel length, which facilitates the biocide access to the pores ofthe matrix. The long pore length of SBA-15 makes the diffusion of CMIT/MIT mixture more difficult. Biocide release tests in aqueous media indicated that the CMIT/MIT concentration in the leaching solution depends on the matrix nature, the smaller values being obtained when the ordered matrix was used. Additionally, biocide delivery could be delayed by increasing the working pH from 7 to 9. Results showed that biocide encapsulation allows maintaining a long-lasting release, even under alkaline conditions (pH 9), at which the hydrolysis of non-supported CMIT occur. Several release tests at different temperature (318, 323 and 328 K), were carried out for 20 days at pH 7. The biocide loading after the tests was reflected in the IR spectra, and it has been corroborated that biocide encapsulation allows retarding the fast thermal decomposition of CMIT.

1. Introduction

Isothiazolinones are a class of broad spectrum biocides used to control the growth of microorganisms such as bacteria, fungi and yeast, and are generally employed for preserving different industrial formulations. Compared to other biocides, isothiazolinones are very effective, fast-acting compounds for the inhibition of microbial growth and metabolism, aside from being capable of controlling biofilm development. These biocides are frequently used for the control of microbial growth in different industrial arrangements, such as cooling water systems, industrial water treatment, oil extraction systems, fuel storage tanks, pulp and paper mills, wood preservation, antifouling agents, coating industry, personal-care and cosmetic industry, etc. [1–3].

In the coating industry, isothiazolinones are included in waterborne formulations such as paints for walls, printing inks, adhesives, and sealants [4]. At first, during the manufacturing process, a fast biocide action is necessary to reduce the great amount of microorganisms present in the raw materials and industrial water. Then, in the storage and transport stage, the biocide action must continue because the acidic metabolic products of the remaining microorganisms could reduce the pH, destabilizing the film-forming material emulsion. This fact causes, in turn, different drawbacks, mainly malfunction of additives, odor generation and poor film adhesion.

The commercial formulation most frequently used in the coating industry for providing wet state protection is a 1.5 wt% aqueous solution containing both 5-chloro-2-methyl-4-isothiazolin-3-one (CMIT) and 2-methyl-4-isothiazolin-3-one (MIT) in a CMIT/MIT = 3 wt ratio [5]. The MIT and CMIT structure is shown in Fig. 1.

The mechanism proposed for CMIT/MIT is based on its electrophilic characteristics, which allow it to react with critical enzymes, inhibiting growth and metabolism, leading to irreversible cell damage occurring

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Nomenclature

C_e	Equilibrium liquid phase concentration (mg/mL)	1/n	Freundlich constant
C_0	Initial biocide concentration (mg/mL)	q_e	Equilibrium solid phase concentration (mg/g)
ΔG°ads	Gibbs free energy of adsorption (kJ/mol)	*R*	Universal gas constant (8.314 J/(mol K))
ΔH°ads	Enthalpy of adsorption (kJ/mol)	R^2	Regression correlation coefficient
Kc	Equilibrium constant for the adsorption process	ΔS°_{ads}	Entropy of adsorption (J/mol K)
k_F	Freundlich constant, (mg/g (mL/mg)$^{1/n}$	*T*	Temperature (K)
		T	Time (h)
		V	Volume of solution (mL)

after several hours. Therefore, CMIT/MIT is effective against aerobic and anaerobic microorganisms because the key enzymes involved in the inhibition process are present in both species [6].

Despite its effectiveness as a successful preservative, CMIT/MIT is a strong sensitizer, producing skin irritation and allergies [7–9], and could pose ecotoxicological risks [1]. Consequently, its use has been restricted by EU legislation to limited concentrations depending on the product type to be preserved [10,11].

This preservative generally displays excellent performance, but its effectiveness has to be checked when it is included in a particular product. Incompatibilities between constituents, thermal sensitivity above 313 K, and instability in strong alkaline media (pH ≥ 8) would be the reasons for the decrease of its preservative properties [12].

In addition, during the storage and transport steps, the paint could be subjected to high temperatures, leading to the biocide decomposition and consequently to the loss of its killing power. Without biocide in the wet state of paint, the bacteria degrade organic materials (polymer and cellulosic additives act as nutrients) generating gases (hydrogen chloride, nitrogen oxides, sulfur oxides) that could cause rapid pressure buildup in closed systems or cans. Then, maintaining the biocide release beyond 313 K is an additional challenge. Kazeminski et al. [12,13], monitored the aqueous degradation of isothiazolinones as a function of temperature and pH. They found that the half-life for the first-order decomposition of isothiazolinones was 4.6 days at 313 K and 0.48 days at 333 K. As a function of pH, at 297 K the half-lives were 46 days at pH = 8.5, and 3.41 days at pH = 9.62.

Recent studies about biocide encapsulations by adsorption onto nanoporous inorganic materials indicate that this procedure could be appropriate for obtaining a longer-term protection from microbiological attack [14–16]. The supported biocide could be slowly released because adsorption interactions between the adsorbate molecules and the inorganic framework render the biocide more resistant to leaching [17–20]. In this way, biocide encapsulation could be an environmentally friendly option because the incorporation of high initial biocide concentrations to ensure long-term preservation would be avoided [14–22].

Mesoporous silica nanocarriers can offer many advantages as vehicles for controlled release, such as high surface area, well-defined and tunable pore size. The most often used mesoporous silica-based vehicles have been the SBA series [23–25]. In particular, SBA-15 is a mesoporous material presenting unidirectional cylindrical pores and pore volume of about 1 g/cm^3. These properties favor adsorption processes and the development of slow release formulations [26–31]. On the other hand, mesocellular siliceous foam (MCF) is a mesoporous material that consists of uniform cells and windows [32]. The uniform windows interconnect the spherical cells forming a continuous three-dimensional (3D) pore system [33]. It is known that the particle size and morphology of the siliceous matrices, as well as the size, volume and geometry of the pores, are all important parameters determining the release rate of the incorporated molecules [34,35].

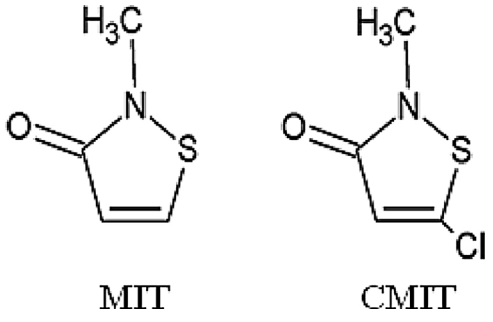

Fig. 1. Methylisothiazolinone (MIT) and chloromethylisothiazolinone. Chloromethylisothiazolinone (CMIT) structure.

In the search for an enhancement of CMIT/MIT stability, in this paper the biocide encapsulation in mesoporous materials SBA-15 and MCF synthesized at our laboratory is proposed. The improvement of the biocide stability was analyzed in terms of obtaining a delayed biocide degradation, minimizing the disadvantages associated with hydrolysis at high pH values and decomposition at temperatures above 313 K.

2. Experimental

2.1. Chemicals

The chemicals used in this study include triblock copolymer poly (ethylene oxide)-poly(propylene oxide)-poly(ethyleneoxide) (Pluronic P123, MW: 5800, Aldrich), tetraethyl orthosilicate (TEOS, 98%, Aldrich), hydrochloric acid (HCl, 37%, Anedra), mesitylene (MES, 98%, Aldrich) and a commercial aqueous biocide for latex preservation composed of a mixture of 5-chloro-2-methyl-2H-isothiazol-3-one and 2-methyl-2H-isothiazol-3-one (Rohm and Haas).

2.2. Synthesis of materials

SBA-15 mesoporous silica was prepared according to the methodology described by Zhao [36]. In a typical preparation, 4 g of Pluronic P123 block copolymer was dissolved in 4 mL of 2 M HCl aqueous solution under stirring at 35 °C. Then, 8 g of TEOS was added dropwise to the mixture, under stirring. The stirring was continued for 20 h. Subsequently, the reacting mixture was heated to 80 °C for 24 h. The molar composition used was 1TEOS:5HCl:0.018PEO:184H_2O. The solid material obtained was washed with water, dried at 120 °C, and calcined for 6 h at 540 °C. MCF was obtained employing a procedure similar to that previously described for obtaining the SBA-15, differing in the addition of mesitylene to the synthesis mixture [33]. The molar composition of the gel was 1TEOS:1.15MES:5HCl:0.018PEO:184H_2O.

2.3. Characterization

In order to determine the morphology and particle size of the materials, a Philips 505 scanning electron microscope (SEM) was used. Transmission electron microscopy (TEM) was performed with a JEOL100CX instrument operated at 100 kV. For the preparation of SEM samples, a small amount of sample was placed on carbon tape and sputter coated with gold. For the preparation of TEM samples, a small amount of the sample was suspended in hexane before being deposited on specific grids (400 mesh copper grid covered with an ultrathin carbon membrane of 2–3 nm thickness).

The X-ray diffraction (XRD) measurements were carried out on a