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# Encapsulation of mercaptobenzothiazole in silica nanocapsules and release study

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## INTRODUCTION

Micro or nanoencapsulation is a technique very used in the industries pharmaceutical, alimentary and textile. This technique allows protecting an active chemical substance by encapsulation through a physical barrier (capsule) and to control its release depending on the application (Nelson 2002).

2-Mercaptobenzothiazole (MBT) is an organic compound with corrosion inhibiting properties for different metallic materials. (Mohamed 2010)

Silica nanocapsules have been used as core material for several kinds of applications. We have encapsulated MBT in silica nanocapsules thought microemulsion oil in water, with a dynamic interaction in the water-oil interfaces (Chen 2008). Porous silica nanocapsules were obtained and the release of MBT was studied in the conditions that promote the corrosion phenomena.

## MATERIALS AND METHODS

***Materials*** Ammonia solution ($NH_4OH$) (25-28%), and ethyl ether (99.5%) were obtained from Riedel-de-Haën. Cetyltrimethylammonium bromide (CTAB) (99%), Tetraethoxysilane (TEOS) (99.9%) and 2-mercaptobenzothiazole (MBT) (97%) were purchased from Sigma-Aldrich. All chemicals were analytic grade and were used without further purification.

***Synthesis of silica nanocapsules with MBT*** Silica nanocapsules were prepared by using CTAB as cationic surfactant, ethyl ether as co-solvent and ammonia solution as catalyst. Firstly, a CTAB solution was prepared, 0.25 g in 35 ml of water, and 0.25 ml of ammonia solution (25-28%) was added. Then dissolves 0.1 g of MBT in 25 ml of ethyl ether and added to the aqueous solution, in order to form the microemulsion oil in water. With a vigorous agitation, 2.0 ml of TEOS were added to microemulsion. The mixture was vigorously stirred in a closed vessel for 24 h. A precipitate was obtained, filtered, washed with pure water and dried at 60 °C. The silica nanocapsules prepared, have been characterized by Scanning electron microscopy (SEM), Dynamic Light Scattering (DLS), Thermogravimetry (TG) and studies of MBT release were done by High Performance Liquid Chromatography (HPLC).

## RESULTS AND DISCUSSION

Silica nanocapsules were produced through microemulsion oil in water, using CTAB as surfactant and ethyl ether as co-solvent. TEOS was the silica precursor used to encapsulate MBT. The polymerization of TEOS is an exothermic reaction which increases the temperature in the reaction media. With this phenomenon, gasification of co-solvent occurs, from the center, inside of the nanocapsules to the outside, creating porosity in their structure (Chen 2008). The nanocapsules obtained were regular and have diameter around 150 nm. The encapsulation of MBT doesn't promote any structural change in the silica nanocapsules, as we can see in the figure 1.

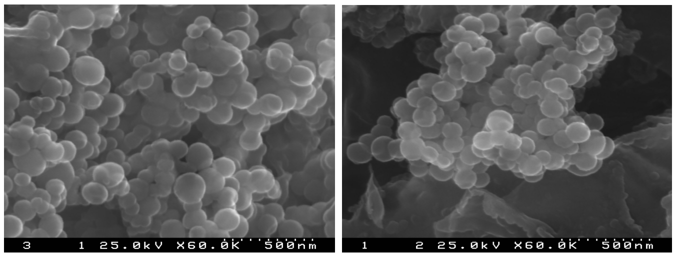

**Figure 1: SEM pictures of silica nanocapsules empty (left) and silica nanocapsules with MBT encapsulated (right).**

As we can see in the figure 2, silica nanocapsules have a narrow distribution of zeta potential value with a maximum at 34.2 mV, which indicates that these nanocapsules have a moderate stability.

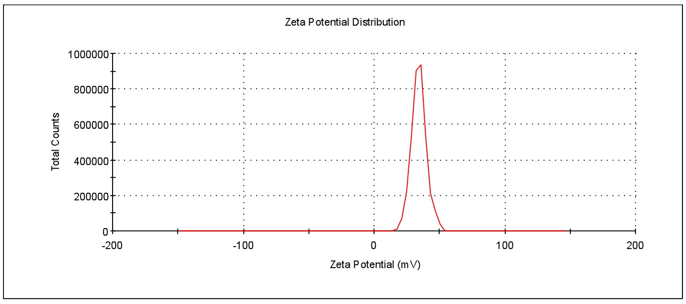


**Figure 2: Zeta potential of silica nanocapsules.**

According to zeta potential of silica nanocapsules, the probability to get some aggregates isn't very high, but when we make the study of size distribution of the nanocapsules we can see two distinct bands as we can see in figure 3, one centered in 100 nm corresponding to nanocapsules dispersed in solution. The other band corresponded to the clusters formed due to the relative stability of nanocapsules, as shown in the zeta potential.

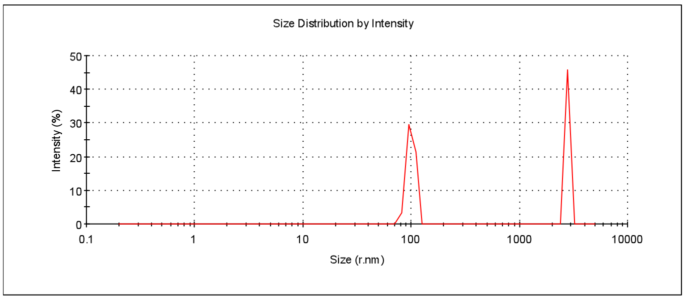


**Figure 3: Size distribution of silica nanocapsules.**

Thermal stability of encapsulated MBT has been established by thermogravimetric analysis. The TGA profile indicates a comparable stability of $SiO_2$ and $SiO_2$_MBT (Figure 4). As figure 4 shows, $SiO_2$ prepared has an excellent thermal stability. The curve corresponding to SiO2_MBT shows a weight loss of about 30-35% between 200-600 ºC corresponding to degradation of MBT in prepared material. Thus, we conclude that this will be the approximate amount of MBT encapsulated.

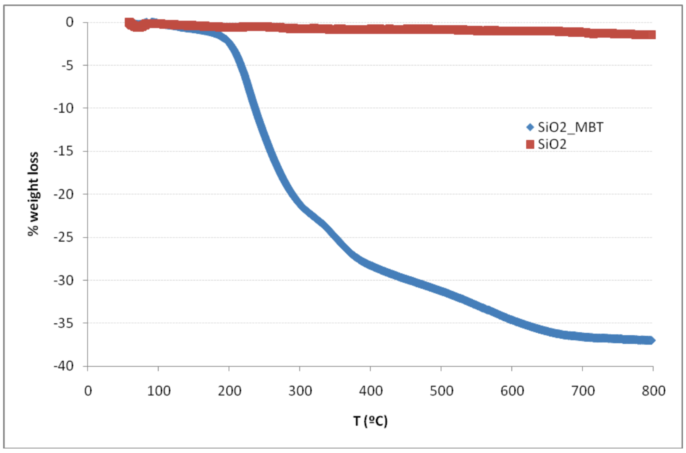


**Figure 4: Thermogravimetric curves of $SiO_2$ and $SiO_2$_MBT.**

The release of the MBT from the dispersed nanocapsules was monitored by HPLC at different pH's (figure 5) and at different concentrations of NaCl (figures 6).

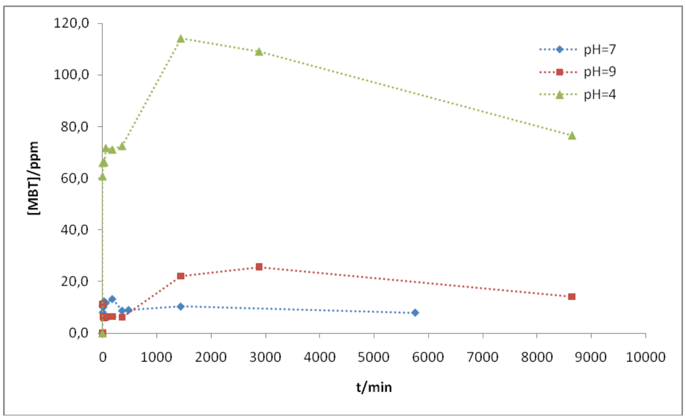


**Figure 5: Release of MBT from $SiO_2$ at [NaCl] = 0.05M and different pH's.**

Figure 5 shows that the release of the MBT is higher in alkaline or acid conditions, since in a neutral medium the amount released over time is too small, being the acid conditions the most favored. From minute 2000 or 3000 the amount of MBT in solution tends to decrease, probably due to interaction of MBT with NaCl.

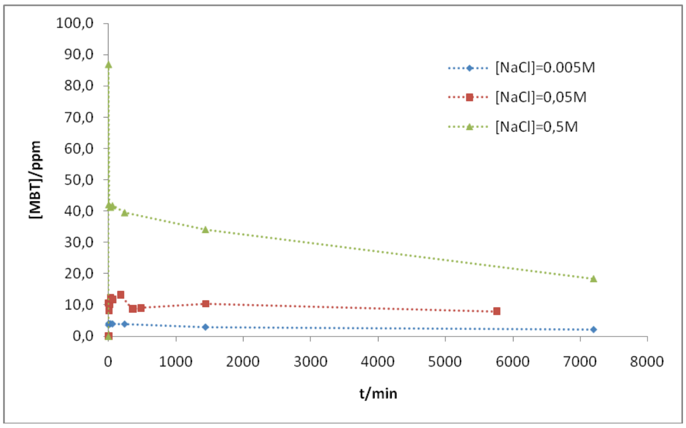


**Figure 6: Release of MBT from $SiO_2$ at pH=7 different concentrations of NaCl.**

Figure 6, shows the release of MTB with the concentration of NaCl. The curves show that the higher is the NaCl concentration, the greater the amount of MBT released. Moreover, as the amount of MBT released is greater, is also higher the interaction with NaCl, verifying a decrease in the amount of MBT in solution over time.

## CONCLUSIONS

$SiO_2$ nanocapsules were successfully prepared with the encapsulation of MBT. These nanocapsules have a regular shape and a diameter of approximately 150 nm and are thermally stable.
Studies of the release of MBT showed that the most suitable conditions for their release are the acidic pH and a higher concentration of NaCl. However the interaction of MBT with NaCl becomes more evident, making their amount in solution will decrease over time.

## REFERENCES


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