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ENCAPSULATION AND CONTROLLED RELEASE OF HCL IN PDMS CAPSULES

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Abstract. *Enhanced oil recovery methods (EOR) are applied to mitigate non-uniform oil sweep. Gel treatment in the injection wells is one of these methods. It consists in blocking off the high permeability path with a polymeric gel to divert subsequently injected water into less-permeable, oil-bearing pores. However, in this case, because the polymer is injected with its cross-linker the gelation time is not predictable. Therefore, it is not possible to control the depth that the chemicals will reach in the fracture before solidifying. Alternatively, microcapsules can be used to encapsulate the cross-linker or the polymer making it possible to completely fill the fracture before activating the gelation. It allows controlling the timing and location of the content release. The capsules features must make them mechanically stable and impermeable to the encapsulated material during storage. In this work, we propose the encapsulation of sodium silicate (Na-Si) gel activator, hydrochloric acid (HCl), making it possible to better control the gelation system to reach deeper locations of fractured reservoirs and, thus, improve oil recovery. Microcapsules with a polydimethylsiloxane PDMS shell are produced using a microfluidic device which combines co-flow and flow-focusing in coaxial glass-capillaries. Fluorescent dyes are used in the inner and middle phases to enable microcapsules characterization. HCl release in hypotonic media (water) evaluation is made through pH measurement. Due to the osmotic difference, capsules swell until burst. We discuss the effects of the mechanical properties of capsules on HCl release. Results show that the release time can be controlled by changing the eccentricity and stiffness of the capsules.*

Keywords: *EOR, PDMS, microcapsules, acid encapsulation*

1. INTRODUCTION

Water injection is one of the most studied and used methods in oil recovery. However, long-term water injection in naturally fractured reservoirs (NFR), which are common in carbonate rocks and represent significant amounts of oil and gas reserves, leads to reduced formation sweep since the injected water flows primarily through fractures (Hatzignatiou and Giske, 2018). There has been an increasing interest in fracture flow in recent years. In fractured reservoirs with high porous heterogeneity, the formation of highly permeable preferential paths yields early water breakthrough, excess of water production and, as a result, a low oil recovery efficiency. Thus, enhanced oil recovery methods (EOR) are applied to mitigate this non-uniform oil sweep. Gel treatment in the injection wells is one of these methods. It consists in blocking off the high permeability path with a polymeric gel to divert subsequently injected water into less-permeable, oil-bearing pores (Khamees and Flori, 2018). However, in this case, because the polymer is injected with its cross-linker the gelation time is not predictable. Therefore, it is not possible to control the depth that the chemicals will reach in the fracture before solidifying. Alternatively, microcapsules can be used to encapsulate the cross-linker or the polymer making it possible to completely fill the fracture before activating the gelation. It allows controlling the timing and location of the content release. The capsules features must make them mechanically stable and impermeable to the encapsulated material during storage (Amstad, 2017).

Sodium silicate (Na-Si) is one of the gels that can be used in injection wells. Its gelation can be activated by hydrochloric acid (HCl). HCl is widely used in various industries but requires careful handling due to its corrosiveness. Encapsulation offers a good alternative to mitigate the risks of exposure and equipment damage. The choice of encapsulating material significantly affects encapsulation efficiency and release kinetics (Luo et al. 2019; Yu et al., 2021, Xiao et al., 2022). Selecting the appropriate material depends on factors such as concentration, temperature, and duration of exposure.

Polydimethylsiloxane (PDMS) has gained attention as a promising material for encapsulating and delivering chemicals (Teixeira et al 2014; do Nascimento et al., 2017, Huang et al. 2015; Huang et al., 2018). PDMS possesses valuable characteristics, including flexibility, low glass temperature, resistance to oxidation, and water repellency. Its

excellent chemical resistance and adjustable mechanical properties make PDMS particularly suitable for encapsulating hydrochloric acid.

Various triggers can initiate the release of encapsulated content, such as pH, magnetic fields, stress, and temperature (Datta et al., 2014; Amstad, 2017; Xiao et al., 2022). Osmotically-driven controlled release systems have emerged as effective strategies for sustained and controlled delivery (Zhang et al., 2017; Zhang et al., 2019; Dave et al., 2006). Researchers have used microfluidic approaches to encapsulate enzymes within microcapsules, triggered to release by reducing osmotic pressure. The choice of polymeric materials affects mechanical stability, with higher molecular weight resulting in increased stability (Zhang et al., 2017). Additionally, microcapsules with inhomogeneous shell thickness can release their cargo through controlled osmotic shock, with increased eccentricity leading to a higher fraction of ruptured capsules (Zhang et al., 2019).

This work focuses on the microfluidic production of PDMS microcapsules for encapsulating hydrochloric acid. By varying the capsule's stiffness and eccentricity, we investigate the impact on release kinetics when osmotic shock is applied. This study provides valuable insights into optimizing acid encapsulation processes. These insights highlight the potential use of these microcapsules as alternative tools for gel treatment purposes.

2. MATERIALS AND METHODS

2.1 Microcapsules production

HCl encapsulation was achieved using W/O/W templates created through microfluidics techniques, as shown below in Figure 1. To fabricate these templates, we employed three-dimensional coaxial microfluidic devices consisting of two cylindrical glass capillaries with inner diameter (ID) of 0.58 mm and outer diameter (OD) of 1 mm (World Precision Instruments Inc., USA). These capillaries were inserted into opposite ends of a square capillary with an ID of 1.05 mm (Atlantic International Technology Inc., USA), which was assembled on a glass slide. Both cylindrical capillaries were coaxially aligned at a distance of 225 µm.

For the injection capillary, we treated it with a commercial rain repellent called Glass Shield (Inove Pack do Brasil, Brazil) for a minimum of 60 min. This treatment rendered the surface hydrophobic. On the other hand, the collection capillary was treated with a solution of polyelectrolytes, comprising 1 wt.% poly (acrylamide-co-diallydimethyl-ammonium chloride) (Sigma-Aldrich, USA) and 2 mol/L NaCl, to create a hydrophilic surface.

To achieve the desired dimensions, we tapered the tips of the injection cylindrical capillary to an inner diameter of approximately 20 µm using a micropipette puller (model P-1000, Sutter Instrument Co., USA) and then we sanded it to a final diameter of 150 µm.

During the production process, the inner phase flowed through the injection capillary, while the middle and outer phases flowed in opposite directions through the interstices between the cylindrical and square capillaries. This arrangement allowed the formation of double emulsion templates inside the collection capillary. To regulate the flow rates, syringe pumps (model Pump 11, Harvard Apparatus, USA) were employed.

The inner phase was a 4000 mOsmol/kg HCl solution in water (2M) dyed with methylene blue, the middle phase was Polydimethylsiloxane (PDMS) (Sylgard 184 from Dow Corning base and curing agent) dyed with Oilglo 22 and the outer phase was 10 wt.% polyvinyl alcohol (PVA) solution in water. Capsules were collected in an isotonic sucrose solution that kept them stable over time.

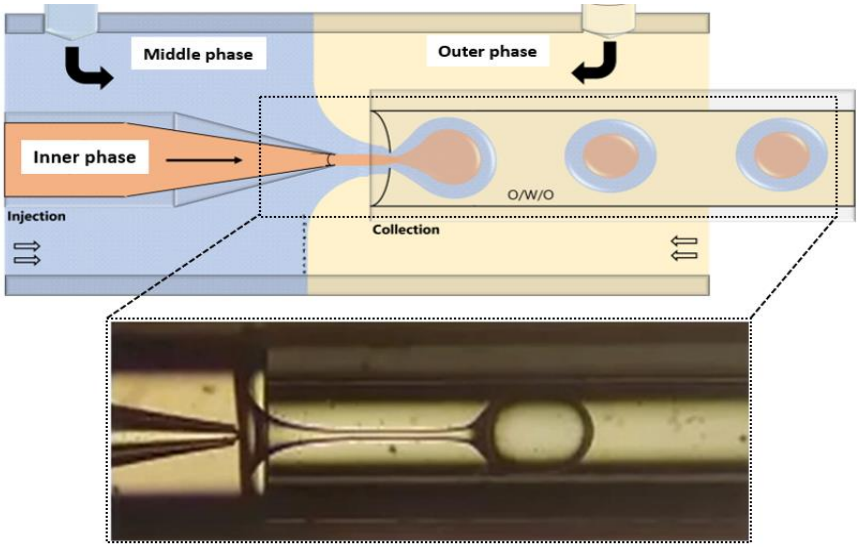

Figure 1. PDMS microcapsules production: Schematic view (top) and microscope image (bottom).

There are two protocols to PDMS reticulation, one for thick capsules and another for thin capsules. In the first case, after thick capsules production, they are left to rest for approximately 24 h, after that, they run through a thermal treatment, which consists of being taken into the oven and kept at 60 °C for 1 h. They are then taken to the refrigerator, where they are stored before being characterized or used in any test. Now, for the thin capsules production, they immediately run through a thermal treatment, this time, kept at 60 °C for 40 min into the oven, they are taken to the refrigerator after that.

2.2 Characterization

It is essential to have information about microcapsules geometry to understand how they behave in the phenomenon of releasing their internal phase. Once the microcapsules have been produced, heat treated and stored, the next step is to characterize them. This procedure is performed under a confocal microscope.

Both microcapsule shell (PDMS) and its internal content (HCl) are stained with a fluorophore agent. The graph in Figure 2 shows the curves of intensity as a function of wavelength for Oilglo 22 fluorophores and Methylene blue, in which we noticed that the absorption and emission ranges of each occurs at different wavelengths, which guarantees that we can observe each region of the microcapsules separately.

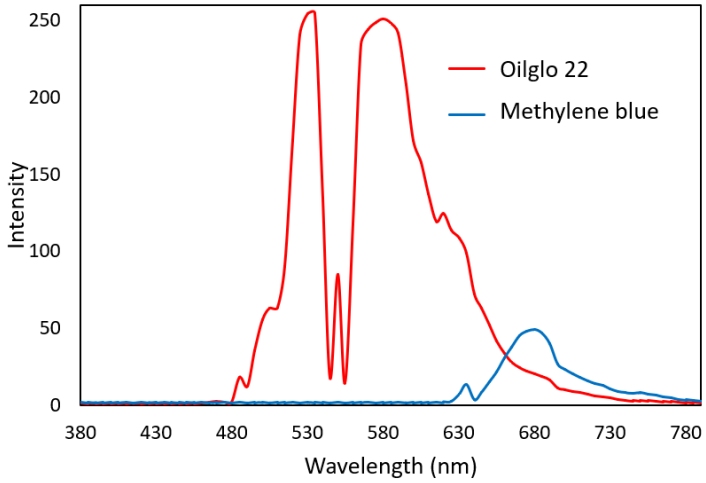

Figure 2. Curve of intensity as a function of wavelength.

The interest is to obtain the geometric dimensions of the microcapsules. The microcapsules are removed from the vials where they are stored with a pipette and placed in the Kline plate cavities, as shown in Figure 3. Taken to the confocal microscope, the sample is illuminated by a laser system and a series of images are acquired for further analysis. Figure 4 shows an example how each microcapsule is characterized using the ImageJ program.

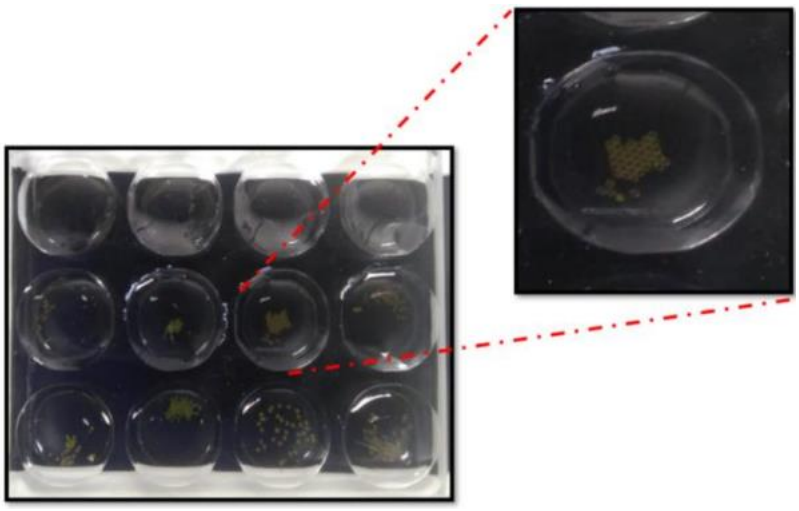

Figure 3. Kline plate with microcapsules to be taken under the confocal microscope.

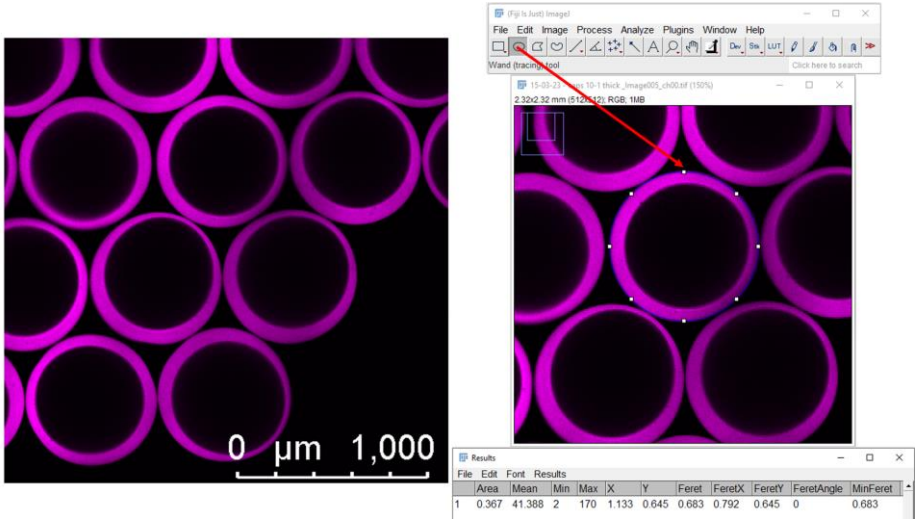

Figure 4. Microcapsules characterization: Image obtained by confocal (left); characterization through ImageJ (right).

Many works have been developed showing the potential of using microcapsules for release control. The characteristics of the microcapsules can be adjusted by controlling the flow rates of the phases and the geometry of the capillary device. Michelon et al. (2020) studied the production of gellan microcapsules through various microfluidic devices with different geometries, and were able to manipulate the thickness and size of the membranes by changing the flow rates of the internal, medium and continuous phases.

The relevant properties for the study of microcapsules behavior in the delivery of the internal content are the outer diameter D_0, the core diameter D_i, the average shell thickness t, the minimum shell thickness t_{min} and the shell eccentricity parameter, given by the ratio t_{min}/t.

Eccentricity is an important feature of microcapsules to be explored that may favor the rupture of its shell. In this way, through the manufacture of eccentric microcapsules, a high tension point (weak spot) is formed in the membrane, configuring the eccentricity as a way of controlling the time in which the microcapsule releases its internal content. Figure 5 below presents a simplified schematic of the geometry of a concentric and an eccentric microcapsule.

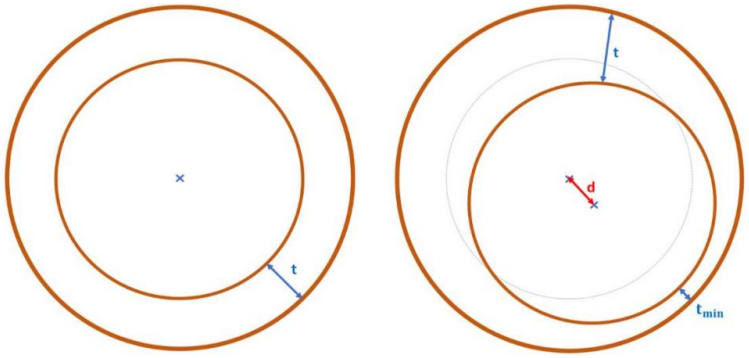

Figure 5. Scheme showing the geometry of concentric and eccentric microcapsules.

2.3 Controlled release experiments

The process chosen for the rupture of the microcapsule's membrane was the osmotic pressure difference. Osmosis is defined as the passage of solvent from a hypotonic medium to a hypertonic medium through a semipermeable membrane. The pressure that the more concentrated solution exerts to prevent osmosis is known as the osmotic pressure. If the microcapsules are exposed to an osmotic pressure gradient, due to the tendency to have a pressure equilibrium, the solvent migrates to the more concentrated medium. This will be the internal content release mechanism. Placed in a hypotonic medium, the microcapsules absorb solvent and swell until they break their shell. In this work, the hypotonic medium is water (Milli-Q) and the internal content is HCl acid.

We calculate the percentage of HCl, in volume percentage (% v/v), released when they are dispersed in 15 mL of milli-Q water. Then, we can measure the sample's pH and finally calculate how much HCl is being delivered, as shown in Figure 6.

The microcapsules were placed on a Kline plate to be visualized in the confocal microscope, and thus, from some images, be counted. Then, microcapsules were placed in 15 mL of Milli-Q water in a falcon tube already placed together with the stirring bar on the stirring plate with rotation of 750 rpm. The temperature of the experiment was kept constant, about 23 °C. Each capsule system was performed in triplicate.

During a week at least, twice a day, the pH (Oakton pHmeter) was measured in each falcon tube, in order to calculate the volume of HCl released, according to the initial calibration.

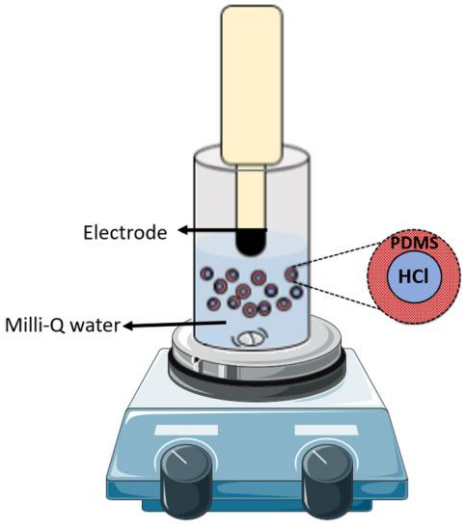

Figure 6. pH measurement scheme.

The pH meter electrode was introduced carefully in order to avoid the vortex formed by the stirring bar, and thus, prevent capsules getting stuck in the electrode. Before being used in each falcon tube, the electrode was properly cleaned and dried to avoid sample contamination.

3. RESULTS

Batches of PDMS microcapsules with different stiffness, shell thickness and eccentricity were used to explore the effect of these variables on the osmotic pressure acting on HCl release. We studied 10:1, 15:1, 20:1 PDMS-crosslinker rigidity ratios for each batch with similar physical proprieties (size, shell thickness, eccentricity). Table 1 and Table 2 below, respectively for thin and thick capsules, shows the PDMS capsules systems used in pH tests to study the release dynamics.

Table 1. System of thin PDMS capsules used in pH tests

Stiffness	**D_o (mm)**	**D_i (mm)**	**t (mm)**	**t_{min} (mm)**	**$2t/D_i$**	**t_{min}/t**
10:1	0.686 ± 0.005	0.628 ± 0.007	0.027 ± 0.003	0.022	0.086	0.826
15:1	0.705 ± 0.012	0.653 ± 0.011	0.026 ± 0.005	0.019	0.079	0.740
20:1	0.667 ± 0.010	0.608 ± 0.009	0.028 ± 0.006	0.021	0.091	0.718

Table 2. System of thick PDMS capsules used in pH tests

Stiffness	D_o (mm)	D_i (mm)	t (mm)	t_{min} (mm)	$2t/D_i$	t_{min}/t
10:1	0.683 ± 0.008	0.568 ± 0.007	0.058 ± 0.005	0.037	0.203	0.641
15:1	0.741 ± 0.012	0.616 ± 0.013	0.063 ± 0.006	0.039	0.204	0.630
20:1	0.687 ± 0.012	0.564 ± 0.011	0.062 ± 0.006	0.048	0.218	0.775

According to the tables, a capsule is considered thin if the ratio between two times its thickness and the inner diameter is below 0.1 ($2t/D_i < 0.1$), or thick, if $2t/D_i \geq 0.1$.

Each rigidity is separated as follows: 10:1 (black), 15:1 (red), 20:1 (blue).

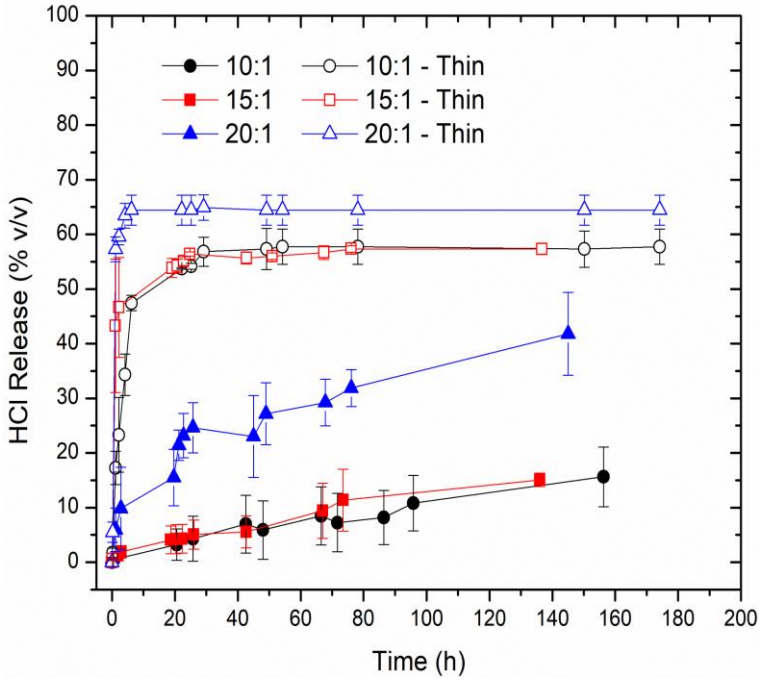

Figure 7. Shell thickness effect for several stiffness ratios.

We investigated how the capsule shell thickness affects release dynamics. As shown above in Figure 7, we compare thin capsules with other systems. The release profile of this type of capsule indicates a much faster delivery, as its release plateau was reached after just over twenty hours, during which about 60% of the total HCl available in the capsules was delivered.

In relation to the systems studied, 20:1 capsules are those with the lowest amount of crosslinker, therefore, they are the less rigid. On the other hand, as expected, 10:1 capsules are the most rigid because they have a higher amount of crosslinker. Results show that, for the same time interval, the most rigid capsules release less their internal content in comparison with the less rigid ones, that means, less rigid capsule is more susceptible to deliver due to the low crosslinking bonds of the its shell.

An important observation is that the release doesn't stabilize at the end for the most rigid capsules indicating that it would be needed longer periods to release its internal content, differently for less rigid capsules that reach a plateau earlier.

Another investigated parameter was the eccentricity of the capsule. Table 3 below shows the PDMS eccentric capsules 10:1 system used in pH tests to study the release dynamics.

Table 3. System of PDMS eccentric capsules 10:1 used in pH tests

Stiffness	D_o (mm)	D_i (mm)	t (mm)	t_{min} (mm)	$2t/D_i$	t_{min}/t
10:1	0.730 ± 0.014	0.569 ± 0.017	0.081 ± 0.008	0.036	0.283	0.450

We also consider a capsule to be eccentric only if $t_{min}/t < 0.5$.

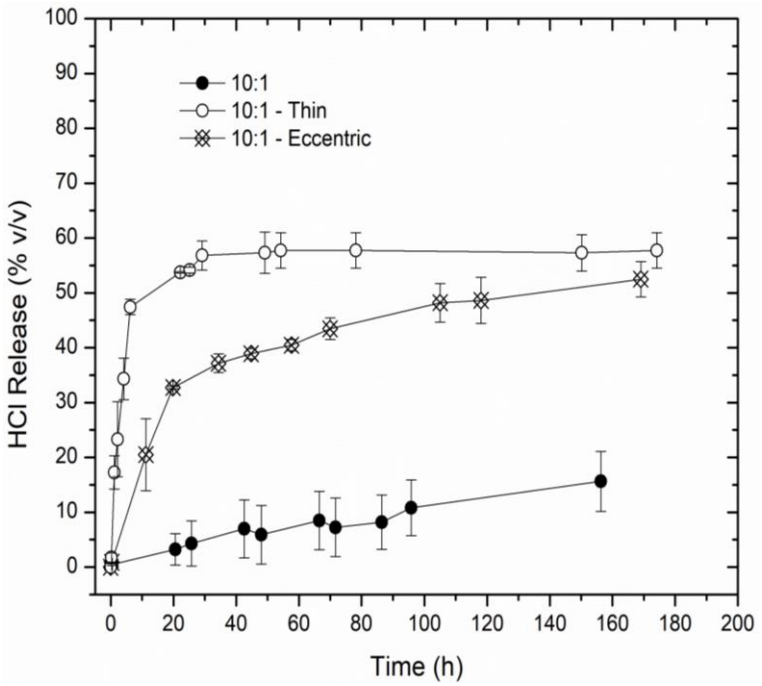

Figure 8: Eccentricity effect for 10:1 ratio.

Figure 8 above shows how this factor, in eccentric capsules 10:1, influences the dynamics of the release profile. In addition to delivering more HCl, the release is faster if compared with the thick 10:1 system, but its release is lower if compared with the thin 10:1 system.

At the end, we can see that more than 50% of the HCl were delivered. The acceleration might have been influenced by the weak spots that this type of capsule has.

4. CONCLUSIONS

It is possible to control HCl delivery by altering the geometry and shell composition of the PDMS microcapsules. Thus, the use for different types (geometries and constitutions) of microcapsules must be in accordance with the application purpose.

Each characteristic influences the release profile. When we have several rigidities, but with the same “thick” level, the more reticulate agent there is in the shell, slower the release profile is. But when the eccentricity parameter is applied, for the most rigid capsules studied, the release is faster. Furthermore, when a “thin” capsule is investigated, it has shown an even faster release dynamic. In other words, for a faster release, thinner microcapsules are more indicated, while for a slower release, thicker capsules must be used.

5. ACKNOWLEDGEMENTS

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