MICROENCAPSULATION OF C.I. REACTIVE ORANGE 122 VIA SOLVENT EVAPORATION

Dutra F. [1], Lis M.J. [2], García O. [2], García C. [2], Plath A. [3], Scacchetti F. [1], Maestá Bezerra F. [1]*

1 Núcleo de Inovação Industrial (NI2), Federal Technological University of Paraná—UTFPR, Apucarana, Brazil

2 Chemical Engineering Dept. ESEIAAT, UPC. Campus de Terrassa, Terrassa, Spain

3 Federal Technological University of Parana—UTFPR, Londrina, Brazil

* Corresponding author: fabriciom@utfpr.edu.br

ABSTRACT

Microencapsulations protects the dye molecule from secondary reactions and release until contact with the fiber, triggered by stimuli. The procedure was performed using poly(lactic-acid-co-glycolic-acid), PLGA, and polyvinyl alcohol, PVA, and was confirmed via optical microscopy. UV-VIS spectroscopy assessed the efficiency of the encapsulation; and, the mathematical models of Korsmeyer-Peppas and Higuchi quantified controlled-release of dye. The microcapsules formed a core-shell structure, with a perfect sphere shape and homogeneous size. The release adjustments yielded the apparent diffusion coefficient.

Key Words: Reactive Dye; microcapsule; solvent evaporation

1. INTRODUCTION

As an alternative to the conventional dyeing for cellulosic fibers, the industry created reactive colorants that have become the most used for cotton fibers. Their principle consists in the addition and substitution reactions with the hydroxyl groups of the fiber [1, 2], allowing intense colors and excellent water fastness [3]. According to Habibah *et al* [4], the high solubility and undesired reaction of the colorant groups with water reduce the efficiency of the dyeing process. Furthermore, depending on colorant and textile substrate natures, 40 to 50% of the colorant remains in the effluent [5-7]: low exhaustion caused by secondary reactions.

The system is homogeneous, alkaline, and catalyzed; however, the heterogeneous nature of the fibers modifies the mechanisms. As a consequence, secondary reactions occur with the approximate magnitude of the primary reactions. The fiber and the water molecules in the solution react with the alkaline environment. The hydrolysis – reaction with water – provokes a great reduction in the dyeing yield and lower wash fastness [7]. The modification of superficial interactions between fiber polar groups and polymer chemical groups minimize these effects [8]. Fang *et al* [7] pointed out the following setbacks in this process: excessive costs, complex techniques, and industrial development problems.

For this reason, protecting dye molecules and impeding undesired reactions increases the process yield. Another advantage is the economy in the treatment of the effluent, considering that reactive colorant removal requires advanced systems of purification of water [9].

One alternative to increase the yield and protection of the colorant is the microencapsulation: the application of a fine layer of polymer (shell) to a material (core) (core) [10]. The textile field has demonstrated great interest and an increase in the use of

microcapsules [11]. The applications are repellents, colorants, vitamins, drugs, oils, and others [12,13].

The suitable method of encapsulation depends on: physical and chemical characteristics of the core, polymer interaction, core solubility [14]. From the many existing procedures, the main categories are: physical (spray drying, spray coating, fluidized bed, lyophilization, and others), chemical (molecular inclusion, *in situ* polymerization, interfacial polymerization, and others) and physical-chemical (simple or complex coacervation, solvent evaporation, and others) [15,16].

The Solvent Evaporation Process (SEP) is indicated for the substances with high solubility in aqueous systems. Many methods are applicable in the evaporation of solvents, depending on their hydrophilicity or hydrophobicity, and the core used [14].

For hydrophilic substances, the method w/o/w is the most recommended. According to Freiberg and Zhu [17], this method consists of emulsifying an organic phase of the aqueous solution forming the base (w/o/w). The compatibility with the shell and desired triggering mechanism affect the polymer choice. The PLA (poly (lactic acid)) and the PLGA (poly (lactic-co-glycolic acid)) are the most used polymers used in this method for presenting both characteristics [18]. In this study, the PLGA will be used for the encapsulation of the Reactive Orange 122 dye via solvent evaporation due to: biocompatibility, biodegradability [19], and high encapsulating power to hydrophilic substances.

2. METHODOLOGY

The wall material, PLGA (Sigma Chemical, Germany) and host molecule, C.I. Reactive Orange 122 (RO122, Golden Technology, Brazil) were the precursors of the microcapsules. PVA (Sigma Chemical, Germany) and the reagent of purity, dichloromethane, (Panreac, Spain) were also used.

2.1. Microcapsules Preparation

The microcapsules were formed from a double emulsion ($W_1/O/W_2$). The dissolution of 360mg of the PLGA in 15 mL of dichloromethane (2.5% of polymer), in a temperature of 4 ºC for 10 minutes, 300 rpm produced the emulsion W_1/O. Then, 10mL of the yellow reactive colorant in a concentration of 5 gL^{-1} was dripped, with stirring of 24,000 rpm, at 4 ºC during 15 minutes. According to Li *et al.* [14], stirring facilitates the emulsion between the used polymer and the active compound. The resulting emulsion was added, at an appropriate rate, while stirring at 24,000 rpm for 10 minutes, in a solution containing 3.06 grams of PVA dissolved in 150 mL of distilled water (2% polymer) at 80 ºC. The double emulsion was stirred for 8 hours at 100 rpm to evaporate the solvent and form the microcapsules.

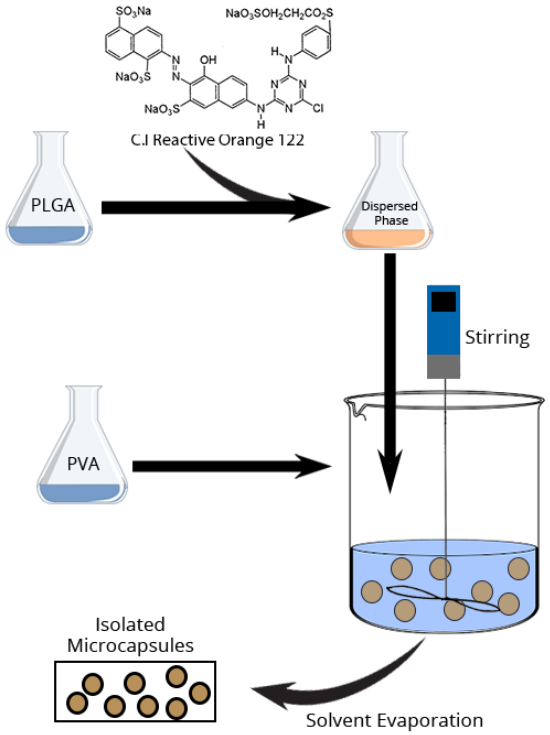

Figure 1. Schematics to obtain the microcapsules (PLGA/RO122) via solvent evaporation.

2.2. Microcapsules Analysis

Optical microscopy made with the equipment Olympus BX43 and the software ImageJ revealed structural characteristics of the microcapsules. Bezerra et al. method [13] based the calculations of the microencapsulation efficiency in the liquid phase using ultraviolet-visible (UV–Vis) spectroscopy (UV-240 LPC, Shimadzu) with UV Probe photometric software (version 2.43).

2.3. Drug-Delivery

Lis et al [20] technique with modifications allowed the determination of the colorant release profile. The microcapsules were allocated into a thermostatic bath at 37 ℃ ± 0,5 ℃, agitated with equipment WNB14 Memmert. Aliquots of 2mL were taken in pre-determined times and filtered (1,5 µm); UV spectroscopy determined the absorbance of the aliquots using UV-240LPC – Shimadzu, in 488 nm (Abs_{cor}). The procedure was performed in triplicates. The equations of Higuchi [21] and Korsmeyer-Peppas[22] provided the mathematical adjustment.

The approach of Korsemeyer-Peppas is based on the calculation of an exponent n that classifies the observed experimental with the geometric shape of the substrate analyzed. The possible diffusion mechanisms are: Fickian ($n \leq 0.43$), Anomalous ($0.43 < n < 0.85$) and Non-Fickian ($n \geq 1.00$) [20].

3. RESULTS

3.1. Microcapsules Analysis

The morphology of the microcapsules formed with PLGA/dye via solvent evaporation can be observed with optical microscopy (Figure 2).

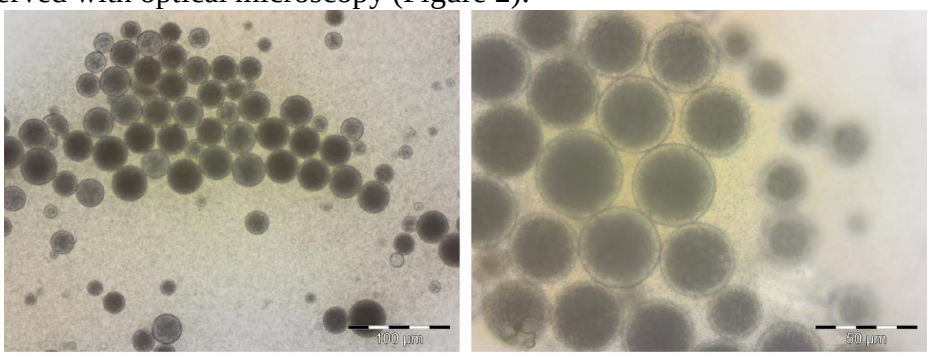

Figure 2. Optical microscopy image of microcapsules formed by solvent evaporation.

The formed microcapsules have a highly monodisperse distribution, without the formation of aggregates and with spheric morphology, as also shown by Abulateefeh et al [23]. The results indicate an effective encapsulation protecting the dye molecule, core, with a polymer surrounding wall of PLGA of 36.679 ± 2.316 µm. The colorants' max peak of absorbance yielded microencapsulation efficiency, by scanning wavelengths from 250 to 700 nm. The Calibration Curve (Equation 5) at the maximum wavelength (488 nm) produced results to calculate the concentration of dye:

$$\boldsymbol{Abs = 4.868.10^{-5}C_{cor} - 5.5574.10^{-4}} \quad (1)$$

where C_{cor} is the concentration of dye (in $mLmL^{-1}$) and abs are the absorbance at 448 nm. The procedure, using the polymer PLGA, described previously, has shown efficiency in the encapsulation of the reactive dye, with a yield of 49.09 ± 0.11%.

In this work, *in vitro* experiments and mathematical adjustments using the software Pro 8.5.1 evaluated the release profile. These tools investigated the controlled release mechanism of the microcapsules formed using PLGA, combined with the equations of Higuchi [21] and Korsmeyer-Peppas [22].

Fig. 5 shows the kinetic release profiles in function of time. After 2000 seconds, the maximum amount of colorant is released.

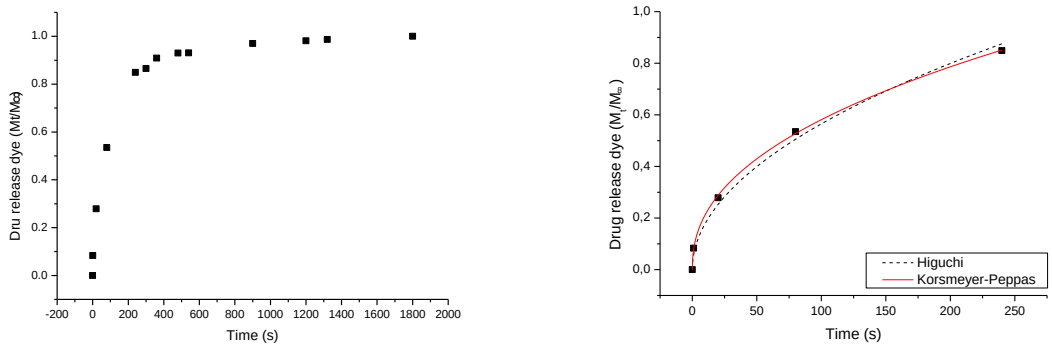

Figure 3. (a) release of microcapsules in the bath in function of time, **(b)** profile of concentration of the bath in function of the square root of time, for the two mathematical approaches suggested.

The parameters and the adjustment values using the models proposed by Higuchi and Korsmeyer-Peppas are shown in Table 1.

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Table 1. Parameters of controlled release modeling

Model	Parameter	First step	R^2
Higuchi	K_H	0.0601±0.0000	0.9938
	$D_f(10^{-2})$	0.1257	
Korsmeyer-Peppas	K_{KP}	0.0803±0.000	0.9996
	n	0.4743±0.0100	

Regarding the release profile, (Table 1 and Figure 3) the Korsmeyer model with R^2 = 0.9996 represents accurately the behavior when n= 0,4743±0,0100. The behavior is similar to a diffusional mechanism. What is curious is the close approach to the sphere geometry n value, describing the same mechanism (0,43), Fickian diffusion [20]. According to Surathi and Karbhari [24], this kind of mechanism is given due to the rate of the diffusion of the active principle (colorant) being inferior to the mobility of the segment of the polymer chain (PLGA). The average behavior between surface and sphere geometrical approach, are in accordance with the expected.

Table 1 presents the value of the diffusion coefficient 0.1257E-10 (mm ^{2}/s). This value represents a low mass transference of the colorant to the medium – what indicates high protection between the active principle and the shell. This liberation might have increased potential with alterations in the bath conditions such as pH and temperature. Therefore, the colorant is protected allowing its release according to the phase of the dyeing process, which may reduce the number of undesired interactions in the process and increase the exhaustion.

4. CONCLUSION

With the obtained results, the solvent evaporation method was efficient to encapsulate the reactive colorant. The control of the parameters, such as temperature, time and stirring in the emulsion showed extreme importance, once they exert direct influence in the capacity to form microcapsules. This method may be a tool to increase the yield of industrial colorant, since it modifies the properties of mass exchange, causing the liberation in specific conditions.

5. REFERENCES

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