УДК 579.68

Хармони Али
Аспирант колледжа химической и нефтяной инженерии
Университет Аль-Баас
сирийско-Хомс
Зиад Сфур
Кандидат технических наук в колледже химического и нефтяного машиностроения
Университет Аль-Баас
сирийско-Хомс
We'aam Al Ali
Graduate student of the College of Chemical and Petroleum Engineering
ALBaath University
Syrian Hummus
Ziad Saffour
Ph.D in Chemical and Petroleum Engineering
ALBaath University
Syrian Hummus

MICROENCAPSULATION OF CAMPHOR IN CALCIUM ALGINATE FOR USING IN FABRIC FINISHING AS FRAGRANCE AND ANTIBACTERIAL FINISHING

Annotation: *In this research, microcapsules of calcium alginate as shell material which contains camphor as core material was formed using ionotropic gelation method of sodium alginate by cross-linking alginate with divalent positive charge-calcium ions Ca^{+2}, by the homogenizer. Microcapsules were applied onto cotton fabric by printing method. The resulting microcapsules were characterized by the optical microscope (OM) and scanning electronic microscope (SEM), their diameters were calculated by ImageJ software. Existing of microcapsules on samples*

was examined by Fourier Transform Infrared Spectrophotometer (FTIR). Properties of antibacterial for fabric finished with microencapsulated camphor and fabric finished traditionally with camphor were studied, also effect of washing on losing of fragrance was tested by GC-FID Gas chromatography analysis.

***Keywords*:** *Fabrics finishing, microcapsules, core, shell.*

МИКРОКАПСУЛИРОВАНИЕ КАМФОРЫ В АЛЬГИНАТЕ КАЛЬЦИЯ ДЛЯ ИСПОЛЬЗОВАНИЯ В ОТДЕЛКЕ ТКАНЕЙ В КАЧЕСТВЕ АРОМАТИЗАТОРА И АНТИБАКТЕРИАЛЬНОЙ ОТДЕЛКИ

***Аннотация*:** *В данном исследовании микрокапсулы альгината кальция как материала для покрытия, содержащего камфару в качестве основного материала, были сформированы методом ионотропного гелеобразования альгината натрия путем поперечного сшивания альгината с двухвалентным ионами кальция с положительным зарядом Ca^{+2} с использованием гомогенизатора. Микрокапсулы наносили на хлопчатобумажную ткань методом печати. Характеристика полученных микрокапсул была дана оптическим микроскопом (ОМ) и сканирующим электронным микроскопом (СЭМ). Диаметры микрокапсул были рассчитаны с помощью программного обеспечения ImageJ. Наличие микрокапсул на образцах исследовалось с помощью инфракрасного спектрофотометра с преобразованием Фурье (Фурье-ИКС). Изучены антибактериальные свойства ткани, отделанной микрокапсулированной камфарой, и ткани, отделанной традиционно камфарой, а также исследовано влияние отмывания на потерю аромата методом анализа газовой хроматографии.*

Ключевые слова: *Отделка тканей, микрокапсулы, ядро, оболочка*.

1. Introduction:

Developments in criteria of life requires production of fabrics with new functions to meet changing needs, many processes are used to add these functions to fabrics, these

processes are called fabric finishing, as flame retarding, water repellent, and other important fabrics finishing, in which a lot of chemicals and polymers are used, but the traditional application of these substances on fabrics (application of materials on fabrics directly) has several disadvantages, like poor performance... That prompted researchers to search for appropriate solutions for these disadvantages. Therefore, in this paper we have applied one of the new methods of fabric finishing, it is the technique of microencapsulation by which polymers are used to form a continuous polymeric film called *shell* which encapsulates a very small active substance called *core,* that can be liquid droplets, solid or gaseous particles, and preserves them from being lost. [1,C.49]

There are three main groups of microencapsulation techniques [2,3]: *chemical methods:* as interfacial polymerization[2,C.370], in-situ polymerization [3,C.13], *physio-chemical methods:* as complex coacervation, simple coacervation, ionotropic gelation, *physical or physio-mechanical methods:* as spray drying.

2. Materials and methods:

2.1. Materials: sodium alginate $C_6H_9NaO_7$ (Indian) was used as the shell material, calcium chloride $CaCl_2$ (Indian), camphor powder (Europe) was used as core material, sunflower oil as the organic phase (a carrier phase of camphor), polyoxyethylene sorbitan monooleate as an emulsifier, and distilled water.

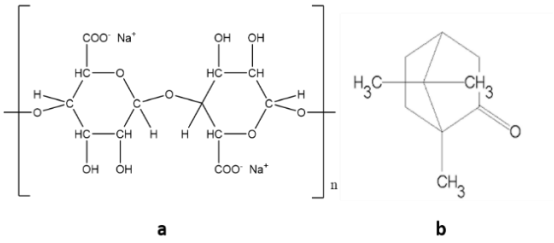

Figure 1: Chemical structure of sodium alginate a) and camphor b)

2.2. Method: [4,C.4070] 200 ml of sodium alginate solution 2% was prepared, then 5 g of tween 80 was added. After that, 10% camphor powder was dissolved in 50 ml of sunflower oil, then it was added to the alginate solution to form O/W emulsion, and the emulsion was mixed using homogenizer at 10000 rpm for 5 min. After that the speed was reduced to 800 rpm, and 30 ml of 7% calcium chloride solution was added dropwise, as it hydrolyzes and calcium ions replace sodium ions and crosslink alginate

polymer chains, causing hardening the wall around the core to form a microcapsule of calcium alginate contains the active material. Mixing was continued for 15 min at room temperature. Finally, microcapsules were obtained and separated from the emulsion by filtering with a 1 μm filter paper, then they were washed with distilled water and dried in the air for 24 hours.

2.3. Fabric used: A mercerized plain 100 % cotton woven fabric (weight 139.75 g/m^2) was chemically bleached with peroxide was used.

☒ **Application of microcapsules onto fabrics:** Microcapsules were applied onto the samples by printing method using a blade squeegee. Table 1 shows the quantities of materials used in the printing paste, where 100 ± g/m^2 of paste was applied on the sample, then the sample was dried at room temperature.

Table 1: Concentrations of materials used in printing method [5,C.100]

Material	Concentration (g/Kg)
Distilled water	400
Microcapsules	130
Sodium alginate (thickener)	34
Poly acrylate (binder)	260
Ammonium chloride (acid donor)	6

☒ **Conventional fabric finishing with camphor:** O/W emulsion was formed with the ratio: 20:80, the organic phase consists of camphor powder dissolving in sunflower oil, the amount of camphor powder is the same as the amount of microcapsules that were applied onto the fabric, and this phase was dispersed in an aqueous phase that consists of distilled water with tween 80 as an emulsifier, then the sample was immersed in the bath with liquor ratio (40: 1) for 1 h at 40ºC, then it was dried at room temperature. [3,C.7]

2.4. Devices and instruments used:

2.4.1. Rotor-stator homogenizer: This device can work at high speeds up to 25,000 rpm, it helps in mixing, homogenizing, emulsification and forming small droplets well.

2.4.2. Scanning electron microscope (SEM): Vega II Teskan SEM has been used to study the shape of microcapsules and finished fabrics.

2.4.3. Optical microscope (OM): OPTIKA NA1.25 with digital camera DCE-2 was used to study the shape of microcapsules in the emulsion.

2.4.4. Fourier Transform Infrared Spectrometry (FTIR): FTIR instrument (IRAffinity-1S, SHIMADZU, Japan) was used to examine the effectiveness of application of microcapsules on fabrics, where the finished and unfinished samples were examined by FTIR in the 400- 4000 cm^{-1}.

2.4.5. GC-FID Gas chromatography analysis: SHIMADZU- Japan (GC-FID 2010) was used to study the effect of washing on the finished fabric, and to determine the efficiency of microencapsulation, using a fused silica polar column with dimensions: 30m × 0.32mm × 0.5µm. The oven temperature was at first isothermal at 50°C for 2 min, then it was increased at 250°C with heating ratio 10°C/ min, with setting the temperature of the injector and detector on 250°C, the carrier gas was nitrogen with a constant flow rate of 1 mL/1 min.

3. Results and discussion:

3.1. Form and diameter of microcapsules: Resulting microcapsules were examined by OM and SEM, their diameters were measured by ImageJ software, and the histogram chart was obtained using Excel Microsoft. The shape of microcapsules was spherical, their mean diameter was 9.74 µm.

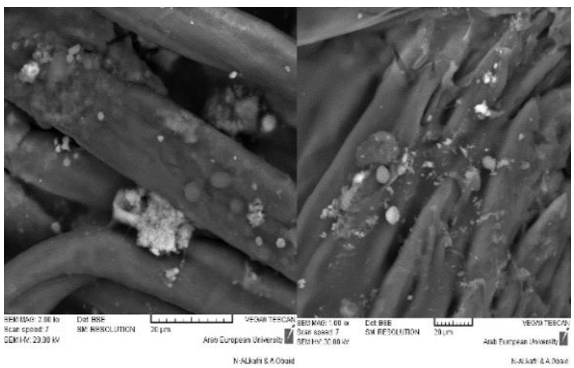

Figure 2: Scanning electron microscope pictures of fabric finished

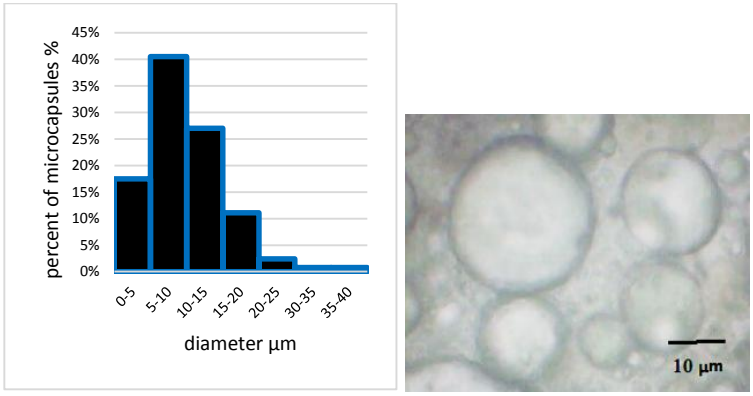

Figure 3: OM picture and histogram chart for microcapsules.

3.2. Encapsulation efficiency and yield: It was calculated by GC-FID chromatography as following: [7,C.5526] 2 ml of microcapsules suspension and 1 ml of ethanol were mixed and centrifuged at 3000 rpm for 5 min, the resulted supernatant was filtered through a 0.2 µm pore size polypropylene filter. Thereafter, 1 ml was injected. All measurements were done in triplicate, and quantification was based on a previously prepared calibration curve. The encapsulation efficiency (*EE*) was calculated according to the following equation:

$$EE = \frac{MASS\ total - MASS\ nonencapsulated}{MASS\ total} \times 100\% \text{..... Eq (1)}$$

where MASS total is the mass of the loaded core material in the experiment (g), MASS nonencapsulated is the mass of the nonencapsulated core material, as determined by GC-FID (g). The encapsulation efficiency was 97.2%.

Microencapsulation yield can be calculated as following: [8,C.20]

$$Yield = \frac{Weight\ of\ microcapsules}{Total\ weight\ of\ core\ and\ shell\ material} \times 100\% \text{ … Eq (2)}$$

The yield was 82% in our experiment.

3.3. FTIR results: Fig 4 shows FTIR spectra of unfinished and finished fabric, we can see O-H, C-H, C-C, C-O bands at 3284.77, 2899.01, 1647.21, 1112.93 cm^{-1} in cellulose structure. The spectra of fabric finished with alginate microcapsules showed a new peak at 1734.01 cm^{-1} that represents C=O stretching in the structure of fabric printed by poly acrylate binder and does not appear in the structure of unfinished fabric. The broad vibration at 3398.57 cm^{-1} represents the hydrogen bands that established between the cellulose chains in the fabric and the binder. That suggests the successful printing of microcapsules to the fabric by poly acrylate binder.

Fig 4: FTIR Spectra of untreated fabric (a, fabric grafted with poly acrylate binder (b, and fabric finished with microcapsules (c.

3.4. Washing effect on losing fragrance: [9,C.525]

Washing test was applied using ISO C01 standard, where the sample was immersed in washing solution contains soap 5 g/l with liquid ratio 50:1 for 30 minutes at a temperature of 40 ± 2°C, then the sample was dried at room temperature. Effect of washing on sample finished with microcapsules and sample traditionally finished was studied by extraction the fragrance from the fabric after mixing it with ethanol, and shaking it for releasing the fragrance outside the microcapsules, then 1 ml of the resultant supernatant was injected in GC column. Losing ratio (*L*) could be calculated by the following equal: [9]

$$L = \frac{M1-M2}{M1} \times 100\% \text{..... Eq (3)}$$

Where: *M1, M2* are the peak before and after laundering, respectively.

Microencapsulation method was better, where losing ratio was 15.29%, while it was 48.02% for fabric finished traditionally.

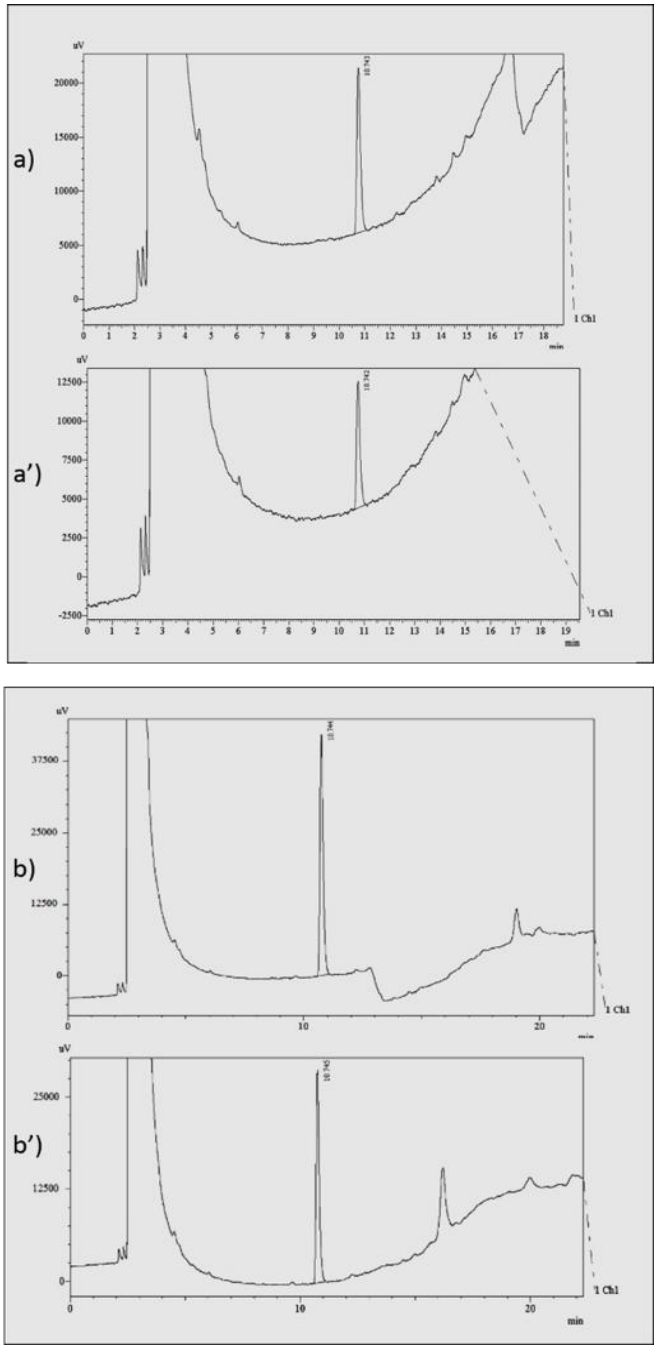

Fig 5: GC-FID spectra of fabric finished traditionally, a) before washing and a') after washing, fabric finished with microcapsules b) before washing, and b') after washing

3.5. Antibacterial activity:

Antimicrobial activity of the unfinished sample and finished samples (traditionally and with microcapsules) were assessed by agar diffusion test (Halo method) according to the standard JIS L 1902-2002. The test was carried out using two bacterial species, Escherichia coli as the gram-negative bacteria and Staphylococcus aureus as the gram-positive bacteria. A colony of bacteria was inoculated on a petri plate containing a

nutrient agar which is MacConkey agar for E. coli and Baird-Parker-agar for S. aureus, then studied samples were cut into 2 ± 0.1 cm diameter pieces, and autoclaved at 121˚C for 15 min, then the plates were cultivated in an incubator at 37˚C for 48 h, then the extent of bacterial growth in the contact zone between the agar and the sample, and the width of the inhibition zone around the specimen was examined. Microencapsulation method was more efficient than the traditional method against E. coli, but it did not show a good efficiency against S. aureus, however it was pretty better than the traditional method. Table 2 shows the width of the inhibition zone around the sample in the antibacterial test.

Table 2: Width of the inhibition zone around the sample

Sample	E. coli	S. aureus
Unfinished sample	0 mm	0 mm
Traditionally finished sample	7 mm	5.6 mm
Microcapsules finished sample	24.9 mm	9.5 mm

4. Conclusion:

Microcapsules of calcium alginate as shell material enveloping camphor as core material have been formed by ionotropic gelation method. The shape of microcapsules was spherical with a mean diameter 9.74 μm. Microencapsulation method showed more efficiency than the traditional method of finishing for antibacterial properties, fragrance losing ratio of the microcapsules-finished sample after laundering was 15.29%, smaller than the fragrance losing ratio of the traditionally finished sample that was 48.02%.

References:

1. CHENG, S. Y., et al. Development of cosmetic textiles using microencapsulation technology. *Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hong Kong*, 12(4), 41-51, (2008).

2. Monllor, P., et al. Thermal behavior of microencapsulated fragrances on cotton fabrics. *Textile Research Journal*, 79 (4), 365-380. (2009).
3. Iqbal, K., et al. Phase change materials, their synthesis and application in textiles—a review. *The Journal of The Textile Institute*, 1-14, (2019).
4. Ghayempour, S., &. Mortazavi, S.M. Microwave curing for applying polymeric nanocapsules containing essential oils on cotton fabric to produce antimicrobial and fragrant textiles. *Cellulose*, *22*(6), 4065-4075. (2015).
5. Ocepek, B., et al. Printing of antimicrobial microcapsules on textiles. Coloration Technology, 128(2), 95-102. (2012).
6. Kumar, D. V., et al. Aesthetic finishes for home textile materials. International Journal of Textile Sciences, 1(3), 5-9. (2012).
7. Sharkawy, A., et al. Aroma-loaded microcapsules with antibacterial activity for eco-friendly textile application: synthesis, characterization, release, and green grafting. Industrial & Engineering Chemistry Research, 56(19), 5516-5526, (2017) .
8. Ghosh, S., & Bhatkhande, P. Encapsulation of PCM for thermo-regulating fabric application. International Journal of Organic Chemistry, 2(04), 366. (2012).
9. Zuobing, X. I. A. O., et al. Shuangshuang, M. A., Mingxi, W. A. N. G., & Zhen, L. I. Properties of aroma sustained-release cotton fabric with rose fragrance nanocapsule. Chinese Journal of Chemical Engineering, 19(3), 523-528, (2011).