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Application of chitosan encapsulated clove essential oil microcapsules on cotton fabrics for antibacterial finish

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The current investigation delves into the viability of spray-dried environment-friendly clove essential oil (CEO) microcapsules in chitosan biopolymer to enhance the antibacterial activity of cotton fabrics. The process parameters, such as core-to-wall ratio, oil concentration, sheath, surfactants, cross-linkers, and spray drying machine parameters like inlet temperature, feed rate, and atomization pressure, are optimized using Box Behnken design and central composite design. The investigation ascertains the average particle size for the CEO microcapsules to be below 2 µm, with microencapsulation efficiency ranging from 40% to 72%. The microcapsules are characterized using Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy and thermogravimetric analysis. The CEO microcapsules are also prepared using sodium tripolyphosphate as cross-linker with the chitosan sheath. The study involves applying CEO microcapsules prepared with and without cross-linker on 100% cotton fabrics by a padding technique with three different cross-linkers, viz malic acid, maleic acid and Eudragit S 100. The evaluation of wash durability, antibacterial efficacy, and physical characteristics, such as tensile strength and air permeability, has been carried out using appropriate methods. A comparative assessment of using different cross-linkers to apply microcapsules on cotton fabrics is undertaken. The Eudragit S 100 is found to be the most appropriate cross-linker to achieve antibacterial properties and better physical attributes of the treated cotton fabrics.

Keywords: Chitosan, Clove essential oil, Cotton, Cross-linker, Microcapsules, Sustainable finishing

1 Introduction

Sustainable finishing of cotton and other cellulosic fabrics is required to satisfy environmentally conscious clients, comply with environmental laws, and mitigate hazardous chemicals[1–3]. Environmentally friendly materials, such as biopolymers and essential oils are the subject of intensive research to enhance the functionality of textiles by enclosing essential oils, in biopolymer sheaths. Essential oils are complex mixtures of compounds extracted from different parts of the plants, such as roots, stems, bark, leaves, flowers & fruits, and are characterized by a strong odor[4,5]. These oils are unstable and are affected by light, temperature, and oxygen/humidity, thus necessitating encapsulation[4,5].

Microencapsulation is an efficient technique to encapsulate essential oils as it offers controlled release, environmental protection, better processability, degradative prevention, and cost-effectiveness[6–11]. Amongst several microencapsulation techniques, spray drying is one of the oldest and most versatile methods for preparing essential oil microcapsules[6,12,13].

Spray drying is defined as the transformation of a feed from a fluid state (solution, dispersion, or paste) into a dried particulate form by spraying the feed into a hot drying medium[14,15]. The properties of the spray-dried microcapsules are affected by various process parameters, viz., properties of essential oil and wall material, emulsion properties, machine parameters (feed flow rate and type of atomizer used, as well as inlet and outlet air temperature), and morphology of the microcapsules[14,16]. Despite the high inlet temperature in spray drying, the loss of volatile content is prevented since the quick evaporation (within seconds) of the solvent takes place, and the core temperature rarely exceeds 100°C[14,15]. Advantages of spray drying include quick, flexible, economical production, spherical and small particles, a simple continuous process, and short contact time[14,15,17].

Clove essential oil (CEO) is obtained by distillation of the flowers, stems, and leaves of the clove (*Eugenia caryophyllata*) and belongs to Myrtaceace family[17]. Its constituents include eugenol, eugenyl acetate, β-caryophyllene, 2-heptanone, ethyl hexanoate, humulenol, α-humulene, calacorene and calamenene. The oil is extensively used in antimicrobial, anti-viral, anti-fungal, anti-tumor and insect repellent purposes[18].

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Chitosan biopolymer, chemically composed of D-glucosamine linked to N-acetyl d-glucosamine by β-1,4 glycosidic bonds, is obtained from deacetylation (40% to 98%) of polysaccharide chitin[19,20]. Chitosan is non-toxic, biodegradable, biocompatible and widely used in antimicrobial, UV protection, antistatic, antiodor, and crease-resistant finishes, along with other agents[21]. Chitosan has been used as an encapsulating agent to entrap various essential oils like cinnamon, jasmine, patchouli, lime, and lavender[19,22-31]. Chitosan microcapsules are prepared using cross-linking agents, such as sodium tripolyphosphate (STTP), glutaraldehyde, and transglutaminases to enhance physical properties, stability, and encapsulation process, while surfactants such as Tween, Span, and SDS control particle size and reduce molecular interactions[31-33].

The pad-dry-cure is the most effective method for applying microcapsules on textiles[34-39]. Microcapsules are applied onto textile substrates using binders or cross-linkers, such as polyurethane and acrylic-based binders, and common cross-linking agents like citric acid, BTCA, polyethylene glycol, and 2D resin. Most cross-linkers studied to date for microcapsules application on textiles are formaldehyde-based. The available literature on cross-linking microcapsules with textiles by formaldehyde-free cross-linkers is limited to polycarboxylic acids, namely citric acid and BTCA[21,40-,43]. However, non-formaldehyde-based alternatives have gained widespread acceptance in the finishing of textiles[44]. Formaldehyde-free cross-linkers include glyoxals, polycarboxylic acids, and acrylates methacrylates, with polycarboxylic acids being the most commonly used[45]. Carboxylic acids form ester bonds with cotton cellulose using sodium hypophosphite (SHP) as the most effective catalyst[21,46–48]. Malic acid, maleic acid, and tartaric acid along with sodium hypophosphite (NaH_2PO_2) as a catalyst, are extensively explored to provide cross-linking and other desirable properties[46,48–51]. Maleic acid, in particular, has been utilized for cross-linking and anti-crease finishes on textiles[50].

In this study, an attempt has been made to use two carboxylic acid-based cross-linkers, viz. maleic acid and malic acid, along with SHP catalyst to cross-link CEO microcapsules on cotton fabrics to explore the efficacy of antimicrobial finish. The study aims to prepare CEO microcapsules using eco-friendly sheath material chitosan. A response surface methodology is employed to optimize various parameters involved in the synthesis of microcapsules using the spray drying technique. The chitosan microcapsules are prepared with and without the use of STTP cross-linker. The microcapsules are characterized, and storage stability is assessed using a UV-visible spectrophotometer. The microcapsules are applied with three cross-linkers, viz. maleic acid, malic acid, and Eudragit S 100, by padding. The kinetics of CEO's release is studied by employing the Korsmeyer-pappas kinetics model. The interaction between cellulose, chitosan microcapsules, and cross-linker is proposed. The treated cotton fabrics are tested for antibacterial properties. The outline of the work is highlighted in Fig. 1.

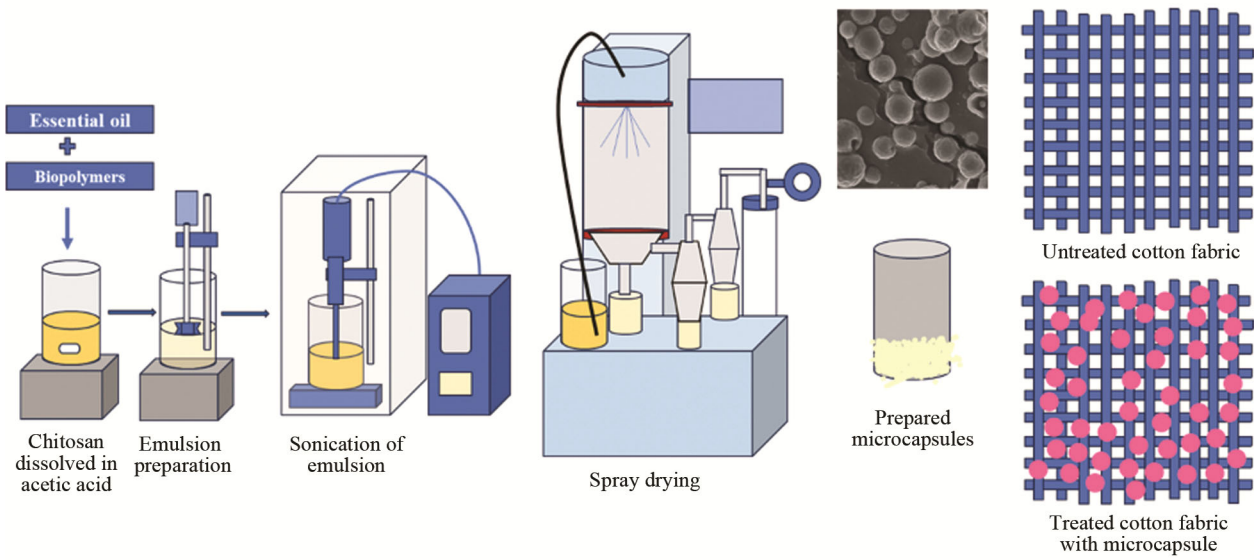

Fig. 1 — Schematic diagram for preparation of microcapsules by spray drying and their subsequent application on cotton fabrics

2 Materials and Methods

2.1 Materials

Pre-treated cotton fabric with EPI: 90, PPI:72, warp: 30^s, weft:20^s, and areal density: 130 g/m^2 was used in this study. Chitosan, Tween 80, acetic acid, malic acid, maleic acid, sodium tripolyphosphate (STTP), and sodium hypophosphite (SHP) were procured from SRL Chemicals, Mumbai. CEO was brought from SD Fine Chemical Limited, Mumbai, and silicon softener was procured from Clariant, Mumbai. The Eudragit S 100 was supplied by Evonik India Private Limited, Mumbai.

2.2 Methods

2.2.1 Preparation and Optimization of Microcapsules

Preliminary experimentation was performed to select the impactful concentration of chitosan (sheath) and Tween 80 (surfactant) to conduct the study. The central composite design was employed to optimize the process, with the variables and responses detailed in Table 1.

The microcapsules were prepared in two steps, viz (a) emulsion preparation and (b) extrusion of the uniform emulsion in the spray drying machine. In the first step, chitosan was dissolved in 1% acetic acid by heating the solution for 60 min at 50^{o}C on a magnetic stirrer at 1500 rpm. CEO and surfactant (Tween 80) were added and agitated on a magnetic stirrer for 15 min at 2000 rpm, which was succeeded by sonicating the solution on a sonicator for 10 min to form a uniform emulsion. The second step, to obtain powder in the spray drying machine, was carried out with the following machine parameters: (i) inlet temperature 160^{o}C, (ii) aspirator flow rate 60%, (iii) feed pump flow rate 3 mL/min, and (iv) atomisation pressure 1.5 bar.

2.2.2 Characterisation of Microcapsules

The morphology of the microcapsules was studied using high-resolution field emission scanning electron microscopy (ZEISS Sigma 500VP, Germany) equipped with an EDS detector for elemental analysis. Each sample was spread onto a clean glass surface and coated with a thin film of gold by the sputtering method before the Field Emission Scanning Electron Microscopy (FESEM) observation.

The functional groups associated with the sheath biopolymers, microcapsules, and the finished fabric were analyzed with ALPHA-II FTIR spectrometer (Bruker, USA) in transmittance mode in the wave number range 4000 - 600 cm^{-1}.

Thermal gravimetric analysis (TGA) was employed to investigate the thermal decomposition behavior of cotton, chitosan, and microcapsules. The equipment used for the study was TGA 8000 (PerkinElmer, USA) with a heating rate of 10^{o}C/min, within the temperature range of 30–500^{o}C, in a nitrogen atmosphere.

The size (z-average) and size distribution of the microcapsules were analyzed using a dynamic light scattering (DLS) instrument (Mastersizer 2000, Malvern Panalytical Ltd., UK). Microcapsules were dispersed in distilled water and then sonicated before the particle size measurement.

Transmission electron microscopy (TEM) was used to assess the structure of the microcapsules. TEM images were obtained on a Philips EM208, operating at an accelerating voltage of 100 kV. The microcapsule powder was dispersed using an ultrasonic bath before TEM observation. A drop of the sample suspension was dried on a carbon-coated copper grid and then observed under TEM.

2.2.3 Final Preparation and Optimization of Microcapsules for Application on Cotton Fabrics

Based on the preliminary preparation, the concentration of chitosan (wall/sheath) was kept at 1% and that of surfactant at 0.2% for the final preparation of the microcapsules. The Box-Behnken design was used to optimize the process and machine parameters with microcapsule size and microencapsulation efficiency as responses to visualize interactions between them. The parameters related to process and machine, such as concentration of core (%) and the machine parameters, viz. inlet temperature, feed pump flow rate, drying temperature, and atomization pressure, were optimized based on their significance (Table 2). The experimental data was analyzed statistically using design expert software. A comparative analysis of the two types of microcapsules, viz, CEO microcapsules without any cross-linker and CEO microcapsules using STTP cross-linker was carried out, and both types were successfully applied to cotton fabrics.

Table 1 — Factors and levels in central composite design for the preliminary preparation of microcapsules

Independent variables	Levels			Responses
	-1	0	1	
Concentration of Sheath, %	1	1.5	2	Microcapsule size, nm
Concentration of surfactant, %	0.2	0.3	0.4	Encapsulation efficiency (EE), %

Table 2 — Factors and levels in Box–Behnken design for optimization of the microcapsules for application on cotton fabrics

Independent variables	Levels			Responses
	-1	0	1	
Core	0.75	1.0	1.25	Microcapsule size, nm
Feed rate, mL/min	2	2.5	3	Encapsulation efficiency (EE), %
Atomisation pressure, bar	1.25	1.5	1.75	
Drying temp., ^{o}C	150	165	180	

Table 3 — Factors and levels in Box–Behnken design for application of microcapsules on cotton fabrics

Independent variables	Levels			Responses
	-1	0	1	
Microcapsules, %	5	10	15	Wash durability
Cross-linker, %	2.5	5	7.5	
Catalyst, %	0.5	1	1.5	
Softener, %	0.5	1	1.5	
*Curing temperature, ^{o}C	120	135	150	

*Curing temperature for Eudragit S 100 is kept at 60, 80, and 100^{o}C and no catalyst was used for this cross-linker.

2.2.4 Application of Microcapsules on Cotton Fabrics

The finishing dispersion was prepared by adding chitosan microcapsules and STTP-chitosan microcapsules, cross-linkers (maleic acid, malic acid and Eudragit S 100), catalyst, and softener (Table 3). The prepared dispersion was then used to finish the cotton fabrics by the pad-dry method. The wet pick-up was kept at 80%, drying was done at 70-80^{o}C for 3 min, and curing at 120^{o}C, 135^{o}C, 150^{o}C for 1 min.

2.2.5 Functional Testing for Textile Applications

The air permeability of the finished fabrics was assessed using the ASTM D 737 standard test method. This was done by subjecting the samples to a pressure of 100 Pa using an SDL Atlas air permeability tester. The bending length of the finished fabric was assessed using a paramount stiffness tester, following the ASTM D 1388-18 standard test procedure. The tensile strength of the finished cloth was evaluated using the ASTM D 5035-11 standard test method. The AATCC 100-2012 standard was used to evaluate the antibacterial activity of the cotton fabrics, and the assessment of wash fastness was conducted following the ISO-3 standards.

3 Results and Discussion

3.1 Preliminary Preparation of Chitosan Microcapsules

The CEO microcapsules are preliminarily prepared to optimize the sheath and the surfactant concentrations, while ensuring the minimum size and maximum encapsulation efficiency. Table 4 presents the encapsulation efficiency and particle size from trials conducted according to the central composite design. Increasing chitosan concentration results in high emulsion viscosity, hindering the proper emulsion preparation at increased concentrations beyond 1.5%. Increasing surfactant concentration reduces encapsulation efficiency due to decreased interfacial tension. It is evident from Table 4 that the maximum encapsulation efficiency and minimum particle size of the prepared microcapsules occur at 1% sheath concentration and 0.2% surfactant concentration. These chitosan and sheath concentrations are used for further investigations.

Table 4 — Runs performed for optimization process for chitosan

Std	Run	Sheath, %	Surfactant, %	Encapsulation efficiency, %	Particle size, nm
5	1	0.79	0.3	40.89	1440.6
3	2	1	0.4	43.69	1447.75
4	3	2	0.4	NA*	NA*
1	4	1	0.2	48.51	1400.65
9	5	1.5	0.3	42.22	1546.0
6	6	2.20	0.3	NA*	NA*
7	7	1.5	0.16	40.28	1532.1
8	8	1.5	0.44	41.91	1574.4
11	9	1.5	0.3	45.34	1539.7
10	10	1.5	0.3	46.31	1522.8
2	11	2	0.2	NA*	NA*

NA* -Microcapsules could not be prepared due to the high viscosity of the emulsion.

3.2 Final Preparation of the Microcapsules

Following preliminary preparation, other process and machine parameters are optimized to prepare the final set of microcapsules. Parameters such as core concentration, feed rate, atomization pressure, drying temperature, and the two responses, viz. maximum encapsulation efficiency and minimum size, are selected based on the available literature. Table 5 shows the trial responses, analyzed statistically using design expert software.

3.3 Size of Microcapsules

The statistical analysis suggests a quadratic equation for the size distribution of chitosan microcapsules containing CEO (Table 6).

ANOVA indicates the model is significant with the Model F-value of 16.91 (Table 7). There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.05 indicate model terms are significant. In this case, model terms A, B, C, D, CD, A^2, B^2, C^2 are significant.

Table 5 — Runs performed to optimize microcapsule size and microencapsulation efficiency

Std	Run	Core, %	Feed rate mL/min	Atomisation pressure bar	Drying temp. °C	Size, nm	Encapsulation efficiency, %
9	1	0.75	2.5	1.5	150	1723	59.4
8	2	1	2.5	1.75	180	1665	50.4
26	3	1	2.5	1.5	165	1622	50
21	4	1	2	1.5	150	1410	53.3
11	5	0.75	2.5	1.5	180	1990	50.8
16	6	1	3	1.75	165	1954	60.3
23	7	1	2	1.5	180	1474	47.4
27	8	1	2.5	1.5	165	1531	50.6
3	9	0.75	3	1.5	165	2465	62.4
7	10	1	2.5	1.25	180	1674	48.7
4	11	1.25	3	1.5	165	1966	56.1
19	12	0.75	2.5	1.75	165	2022	57.2
14	13	1	3	1.25	165	1544	48.9
25	14	1	2.5	1.5	165	1601	50
1	15	0.75	2	1.5	165	1632	49.6
13	16	1	2	1.25	165	1306	45.7
22	17	1	3	1.5	150	1934	55.6
24	18	1	3	1.5	180	2114	53.1
17	19	0.75	2.5	1.25	165	1573	54.6
12	20	1.25	2.5	1.5	180	1826	56.1
15	21	1	2	1.75	165	1391	51.1
20	22	1.25	2.5	1.75	165	1484	59.8
18	23	1.25	2.5	1.25	165	1285	53.7
10	24	1.25	2.5	1.5	150	1272	52.8
2	25	1.25	2	1.5	165	1529	60.7
6	26	1	2.5	1.75	150	1436	55.2
5	27	1	2.5	1.25	150	986	46.9

Table 6 — Size distribution of chitosan microcapsules

Source	Sequential p-value	Lack of fit p-value	Adjusted R^2	Predicted R^2	
Linear	<0.0001	0.0553	0.6301	0.5094	
2FI	0.6860	0.0484	0.5917	0.1717	
Quadratic	0.0003	0.1710	0.8954	0.7283	Suggested
Cubic	0.0919	0.3441	0.9664	0.5084	Aliased

The 'Lack of Fit' F-value of 5.23 implies the 'Lack of Fit' is not significant relative to the pure error. There is a 17.10% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good; hence, the model is fit. The statistics thus obtained is shown in Table 8.

The predicted R^2 of 0.7283 is in reasonable agreement with the adjusted R^2 of 0.8954, i.e. the difference is less than 0.2. Adeq precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. A value of 18.637 indicates an adequate signal. This model can be used to navigate the design space. The final equation in terms of coded factors is :

$$\text{Size}=+1584.67-170.25\times A+269.58\times B+132.00\times C+165.17\times D-99.00\times AB+62.5\times AC+71.75\times AD+81.25\times BC+29\times BD-114.75\times CD+151.25\times A^2+145.25\times B^2-154.625\times C^2-6.62\times D^2$$

Size =-5871.95-5198× wall-to-core ratio -3186.83 ×feed rate +12374 × atomization pressure +37.82778 × drying temperature -792 × wall-to-core ratio × feed rate -1000 wall-to-core ratio × atomization pressure +19.13 wall-to-core ratio × drying temperature + 649.99 feed rate × atomization pressure + 3.86 feed rate × drying temperature -30.60 × atomization pressure × drying temperature +2420 wall-to-core ratio² +580.99 feed rate² -2474 × atomisation pressure² -0.029 × drying temperature².

Figure 2 depicts response surface plots influencing the size of prepared microcapsules against various parameters.

3.4 Encapsulation Efficiency

The statistics suggest a quadratic equation for the encapsulation efficiency of chitosan microcapsules containing CEO, as mentioned in Table 9.

Table 7 — ANOVA analysis on microcapsule size

Source	Sum of squares	df	Mean square	F-value	p-value	
Model	2.433E+06	14	1.738E+05	16.91	<0.0001	Significant
A: wall-to-core ratio	3.478E+05	1	3.478E+05	33.83	<0.0001	
B: feed rate	8.721E+05	1	8.721E+05	84.83	<0.0001	
C: atomization pressure	2.091E+05	1	2.091E+05	20.34	0.0007	
D: drying temp	3.274E+05	1	3.274E+05	31.84	0.0001	
AB	39204.00	1	39204.00	3.81	0.0746	
AC	15625.00	1	15625.00	1.52	0.2413	
AD	20592.25	1	20592.25	2.00	0.1824	
BC	26406.25	1	26406.25	2.57	0.1350	
BD	3364.00	1	3364.00	0.3272	0.5779	
CD	52670.25	1	52670.25	5.12	0.0429	
A^2	1.220E+05	1	1.220E+05	11.87	0.0049	
B^2	1.125E+05	1	1.125E+05	10.94	0.0062	
C^2	1.275E+05	1	1.275E+05	12.40	0.0042	
D^2	234.08	1	234.08	0.0228	0.8826	
Residual	1.234E+05	12	10280.88			
Lack of fit	1.188E+05	10	11882.99	5.23	0.1710	Not significant
Pure error	4540.67	2	2270.33			
Core total	2.557E+06	26				

Table 8 — Fit statistics details for microcapsule size

Parameter	Values
Std. dev.	101.39
Mean	1644.78
CV%	6.16
R^2	0.9517
Adjusted R^2	0.8954
Predicted R^2	0.7283
Adeq Precision	18.6371

The ANOVA suggests that the model is significant with the Model F-value of 46.29. P-values less than 0.05 indicate significant model terms. In this case, B, C, D, AB, AD, BC, CD, A^2, B^2 are significant model terms (Table 10).

The Lack of Fit F-value of 9.78 implies a 9.63% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good, indicating the model is fit. This relatively low probability (<10%) is troubling (Table 11).

Predicted R^2 of 0.8966 is in reasonable agreement with the Adjusted R^2 of 0.9606, as the difference is less than 0.2. Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. A value of 25.632 indicates an adequate signal. This model can be used to navigate the design space.

Once the statistical analysis is completed, the software suggests 100 solutions. Among these, one theoretical solution with a desirability of 1, higher encapsulation efficiency, and minimum particle size are selected. The selected parameters for further analysis are core 1.25%, feed rate 2 mL/min, atomization pressure 1.5 bar, and drying temperature 165^{o}C. The microcapsules are prepared using the theoretical values of the parameters and validated practically. The optimized microcapsules are then stored in sealed boxes to avoid degradation before their application on cotton fabrics.

Chitosan microcapsules are also prepared by using STTP as a cross-linker with the optimized data

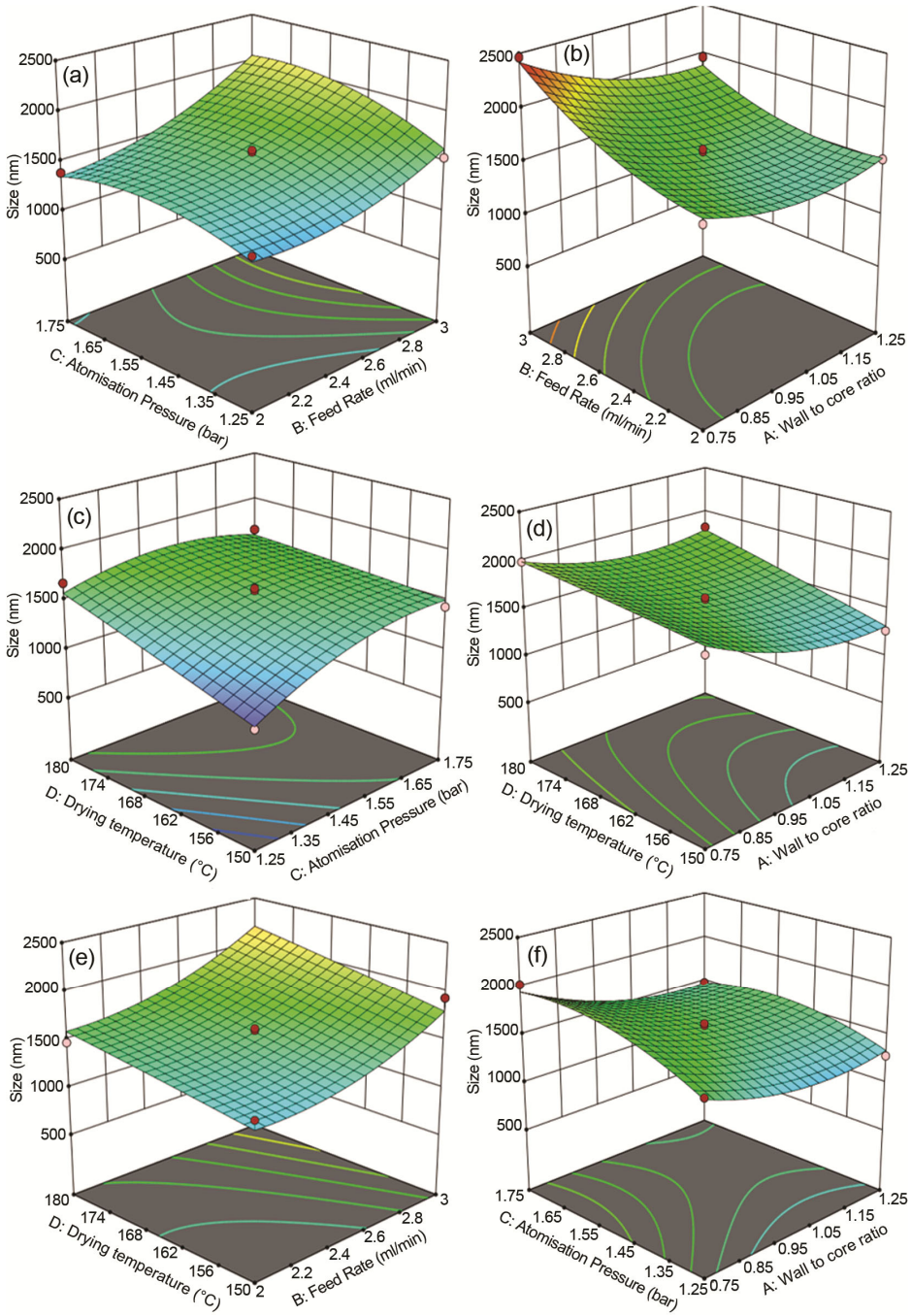

Fig. 2 — Response surface plots indicating the influence of various parameters on microcapsule size (a) atomisation pressure & feed rate, (b) feed rate & wall-to-core ratio, (c) drying temperature & atomisation pressure (C), (d) drying temperature & wall-to-core ratio, (e) drying temperature & feed rate, and (f) atomisation pressure & wall-to-core ratio

Table 9 — Distribution of microencapsulation efficiency

Source	Sequential p-value	Lack of Fit P-value	Adjusted R^2	Predicted R^2	
Linear	0.2691	0.0046	0.0570	-0.2245	
2FI	0.0332	0.0069	0.3993	-0.0842	
Quadratic	<0.0001	0.0963	0.9606	0.8966	Suggested
Cubic	0.0304	0.3424	0.9931	0.8984	Aliased

Table 10 — ANOVA analysis of microencapsulation efficiency

Source	Sum of squares	df	Mean square	F-value	p-value	
Model	646.63	14	46.19	46.29	<0.0001	Significant
A: Wall-to-core ratio	0.4033	1	0.40	0.4043	0.5368	Significant
B: Feed rate	46.41	1	46.41	46.52	<0.0001	
C: Atomisation pressure	63.02	1	63.02	63.17	<0.0001	
D: Drying temp.	23.24	1	23.24	23.29	0.0004	
AB	148.84	1	148.84	149.18	<0.0001	
AC	3.06	1	3.06	3.07	0.1053	
AD	35.40	1	35.40	35.48	<0.0001	
BC	81.00	1	81.00	81.19	<0.0001	
BD	2.89	1	2.89	2.90	0.1145	
CD	10.89	1	10.89	10.92	0.0063	
A^2	155.04	1	155.04	155.40	<0.0001	
B^2	56.91	1	56.91	57.04	<0.0001	
C^2	4.60	1	4.60	4.62	0.0528	
D^2	4.52	1	4.52	4.53	0.0547	
Residual	11.97	12	0.99			
Lack of fit	11.73	10	1.17	9.78	0.0963	Not significant
Pure error	0.2400	2	0.12			
Core total	658.61	26				

Table 11 — Fit statistics details for microencapsulation efficiency

Parameter	Values
Std. dev.	0.9989
Mean	44.05
CV%	2.27
R^2	0.9818
Adjusted R^2	0.9606
Predicted R^2	0.8966
Adeq Precision	25.6324

mentioned above. The concentration of the STTP is kept at 0.2 %. The results of chitosan microcapsules with and without the use of cross-linker are compared in this study (Fig. 3).

3.5 Particle Size

The average particle size of CEO is found in the range of 1-2 μm (Fig. 4).

3.6 FESEM Analysis

The FESEM images of the chitosan microcapsules are shown in Fig. 5. It is evident that the spray-dried microcapsules are spherical, with a few slightly wrinkled. The wrinkled appearance results from the dehydration of the chitosan sheath, likely due to the slightly higher temperature in the spray drying machine.

3.7 FTIR Analysis

Figure 6 displays the FTIR spectra of the microcapsule, cotton fabrics, chitosan, and STTP-chitosan cross-linked microcapsule. In the case of chitosan, a peak appeared at 1340 cm^{-1} for the amine group in the deacetylated chitosan ring and another at 1647 cm^{-1} for the amide I in the acetylated chitosan ring. The peaks at 2800, 3335, and 1041 cm^{-1} could be attributed to hydroxyl moieties, C-H network, and C-O bonds, respectively, in the polymer structure. For chitosan-encapsulated CEO microcapsules, a peak appears at 1238 cm^{-1} for C-O-C stretching, 1514 cm^{-1} for amide II, and 2915 cm^{-1} again for the CH backbone structure of the polymer. Both peaks indicate a complex formation due to electrostatic interaction between the amino group of chitosan and the phosphoric group of the STPP. Furthermore, there is an increase in the intensity of the CH stretching peak of the ester group at 2915 cm^{-1}. A closer peak at 2991 cm^{-1} is reported on the incorporation of essential oil into the chitosan microcapsules. The peaks between 1200 cm^{-1} and 1050 cm^{-1} are attributed to the stretching vibrations of C-O. The peaks at 913 cm^{-1} and 816 cm^{-1} are ascribed to the aromatic ring, while the peaks between 750 cm^{-1} and 600 cm^{-1} are because of the benzene ring = CH vibrations.

3.8 TGA Analysis

The weight loss of chitosan, cotton, and microcapsule materials is obtained from the TGA curve profile depicted in Fig. 7. The residual weight % is analyzed through three stages on the thermographs as the temperature increases from 50°C to 500°C. For

microcapsules, the first stage is due to the evaporation of the oil from 100°C to 220°C. The second stage, from 240°C to 320°C, is mainly due to the weight loss of oil and partial loss of the shell material. The third stage, starting from 320°C onwards, indicates the complete degradation of the shell material.

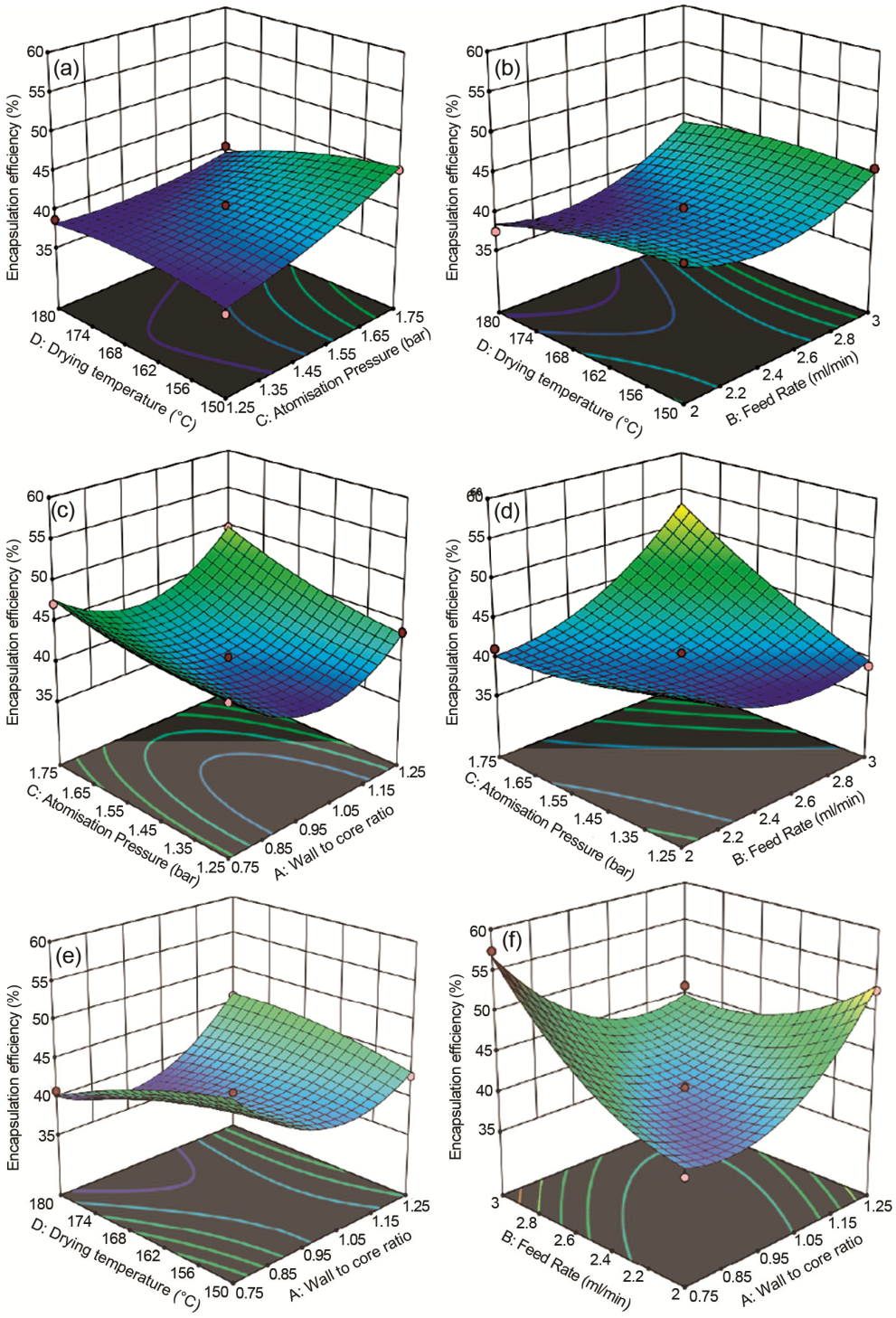

Fig. 3 — Response surface plots indicating the influence of various parameters on microencapsulation efficiency (a) drying temperature & atomization pressure, (b) drying temperature & feed rate, (c) atomization pressure & wall-to-core ratio, (d) atomization pressure & feed rate, (e) drying temperature & wall-to-core ratio, and (f) feed rate & wall-to-core ratio

3.9 TEM Analysis

The TEM image (Fig. 8) shows a distinct core and sheath within the microcapsules. This distinct structure may be attributed to the insoluble nature of the chitosan.

3.10 Storage Stability of the CEO from Microcapsules

The long-term storage stability of spray-dried microcapsules is studied, specifically emphasizing the preservation of clove oil. The specimens are collected, dissolved in ethanol, and tested with a UV-visible spectrophotometer. The rate of release of essential oil at a stipulated time is calculated using the following equation:

$$\text{Rate of release of CEO at stipulated time} = \frac{\text{Conc.at 0 h} - \text{Conc.at stipulated period}}{\text{Conc.at 0 h}} \times 100$$

The study reveals that the shelf-life stability of the CEO is greatly enhanced by encapsulating it in chitosan. The shelf life of microcapsules is considerably affected by temperature and relative humidity. The most probable cause for this phenomenon is the elevated humidity, which causes the chitosan wall material to absorb water and swell. This leads to the formation of surface fractures on the microcapsule, enabling the evaporation of oil. Utilizing the STTP cross-linker further reduces oil loss (Table 12).

3.11 Application of Microcapsules on Cotton Fabrics

The microcapsules are applied on cotton fabrics separately with three different cross-linkers. The Box-Behnken design is employed to optimize the concentrations of microcapsule, cross-linker, catalyst, softener, and curing time. The number of trials, along with other attributes, are mentioned in Table 13. Optimization with Eudragit S 100 involves concentrations of microcapsule, Eudragit S 100, softener and curing time only.

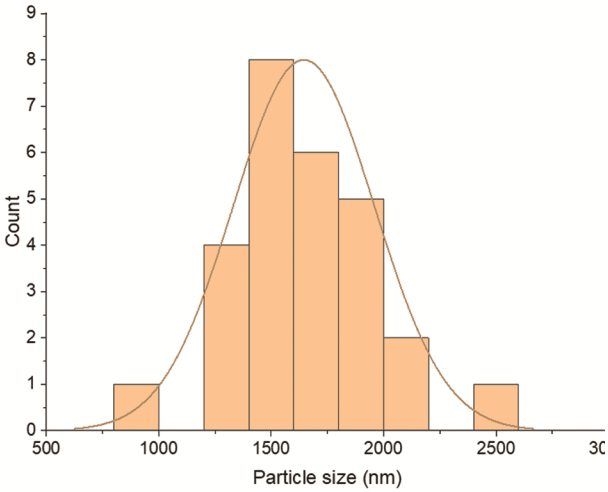

Fig. 4 — Size distribution curve of microcapsules

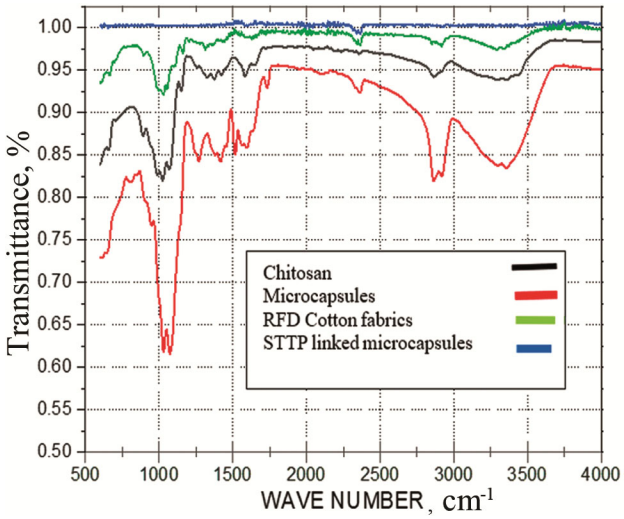

Fig. 6 — FTIR analysis

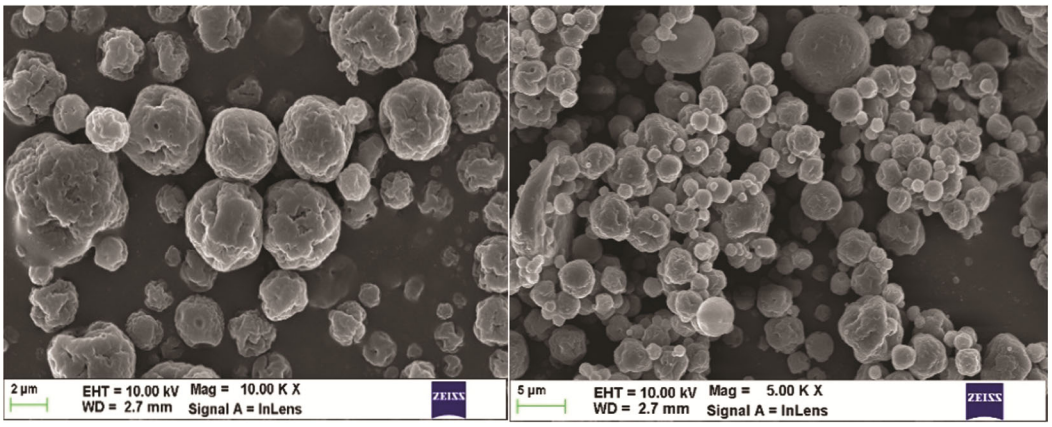

Fig. 5 — FESEM images of chitosan microcapsules

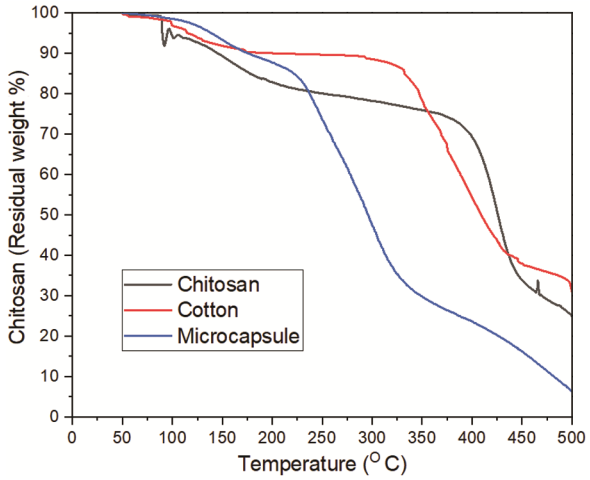

Fig. 7 — TGA of cotton, chitosan and microcapsules

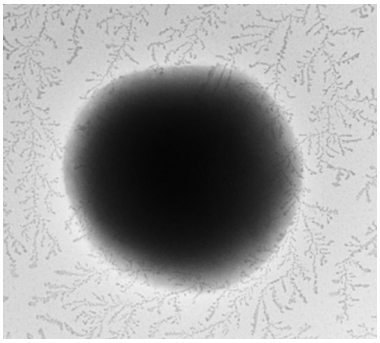

Fig. 8 — TEM image of chitosan microcapsule

Table 12 — Release of CEO from microcapsules

Microcapsule	CEO released, %											
	0 day	1 day	2 day	4 day	5 day	6 day	7 day	8 day	9 day	10 day	12 day	15 day
Chitosan microcapsules	0	3	4	7	8	9	11	12	15	18	21	25
STTP-Chitosan microcapsules	0	3	4	6	7	9	10	12	14	16	18	20

3.12 Wash Durability of Treated Cotton Fabrics

The cotton fabrics treated with chitosan microcapsules and STTP cross-linked chitosan microcapsules, using three different cross-linkers, are first assessed for their wash durability. In the case of maleic acid, the best wash durability with both types of microcapsules after the first wash is obtained with the following parameters: microcapsule (10%), cross-linker (5%), catalyst (1.5%), softener (1%), and curing temperature (150°C). Similar results are obtained with the malic acid cross-linker, except for a curing temperature of 135°C. Furthermore, the most favorable wash durability results with Eudragit S 100 as a cross-linker are obtained with microcapsule (10%), cross-linker (5%), softener (1%), and curing temperature (80°C).

The concentration of the microcapsules varies from 5% to 15% for the three cross-linkers. A

Table 13 — Runs performed to optimize the application of microcapsules on cotton fabrics using maleic acid and malic acid with SHP catalyst

Std	Run	Microcapsules %	Cross-linker %	Catalyst %	Softener %	Curing time, °C
37	1	10	2.5	1	0.5	135
6	2	10	5	1.5	0.5	135
34	3	15	5	1	1	120
12	4	10	7.5	1	1	150
32	5	10	5	1.5	1	150
13	6	5	5	0.5	1	135
40	7	10	7.5	1	1.5	135
3	8	5	7.5	1	1	135
42	9	10	5	1	1	135
14	10	15	5	0.5	1	135
2	11	15	2.5	1	1	135
8	12	10	5	1.5	1.5	135
5	13	10	5	0.5	0.5	135
4	14	15	7.5	1	1	135
22	15	10	7.5	0.5	1	135
18	16	10	5	1	1.5	120
21	17	10	2.5	0.5	1	135
7	18	10	5	0.5	1.5	135
25	19	5	5	1	0.5	135
27	20	5	5	1	1.5	135
15	21	5	5	1.5	1	135
45	22	10	5	1	1	135
9	23	10	2.5	1	1	120
36	24	15	5	1	1	150
23	25	10	2.5	1.5	1	135
29	26	10	5	0.5	1	120
43	27	10	5	1	1	135
24	28	10	7.5	1.5	1	135
33	29	5	5	1	1	120
16	30	15	5	1.5	1	135
31	31	10	5	0.5	1	150
39	32	10	2.5	1	1.5	135
17	33	10	5	1	0.5	120
28	34	15	5	1	1.5	135
30	35	10	5	1.5	1	120
35	36	5	5	1	1	150
20	37	10	5	1	1.5	150
11	38	10	2.5	1	1	150
1	39	5	2.5	1	1	135
41	40	10	5	1	1	135
19	41	10	5	1	0.5	150
26	42	15	5	1	0.5	135
44	43	10	5	1	1	135
38	44	10	7.5	1	0.5	135
10	45	10	7.5	1	1	120

concentration of 10 % is found appropriate for all three cross-linkers, resulting in better wash durability. The cross-linker concentration varying from 2.5% to 7.5% is optimal at 5% for the best wash durability. SHP is employed as a catalyst for cross-linking the microcapsules onto the cotton fabrics with maleic acid and malic acid. The concentration of 1.5% yields better durability for maleic acid and malic acid.

The application of finishes often results in a harsher feel of the finished textiles. To counter this problem, softeners are used. A softener concentration of 1% results in better wash durability for all three cross-linkers. Curing temperature is crucial as higher temperatures may cause rapid evaporation of the oil from the fabric surface. This eventually necessitates the optimization of the process to obtain favourable outcomes. The curing temperature of 150°C for maleic acid, 135°C for malic acid, and 80°C for Eudragit S 100 ensures better wash durability.

3.13 Antibacterial Activity

The antibacterial activity of the treated and control fabrics is assessed as per test method AATCC 100. Considerable antimicrobial activity is observed against both Gram-positive *Bacillus* and Gram-negative *E. coli* (Fig. 9). Gram-positive bacteria are more susceptible to microcapsules as compared to Gram-negative bacteria due to the presence of an outer cell wall membrane in the latter. Essential oils perform antibacterial activity by damaging microorganisms' cell membranes[52,53]. CEO contains eugenol, eugenyl acetate, β-caryophyllene, 2-heptanone, ethyl hexanoate, humulenol, α-humulene, calacorene and calamenen[53,54]. Eugenol, the CEO's major component has been considered as the best antimicrobial compound, which shows antibacterial properties against most microorganisms[52,53]. Eugenol can enter microorganisms through the cell wall and cause cellular damage[53]. Chitosan is known for its excellent antibacterial activity through mechanisms, such as interacting with the cell wall of microorganisms, binding to DNA, adsorbing electronegative substances, and forming a protective barrier around the bacterial cells[55,56].

Chitosan and CEO in the microcapsules work synergistically, offering prominent antibacterial properties against both gram-positive and gram-negative bacteria. Additionally, using polycarboxylic acids along with SHP increases the self-life of essential oil by suppressing its volatility. Table 14 depicts the effect of different cross-linkers on the antibacterial properties of cotton fabrics, indicating higher antibacterial activity when treated with Eudragit S 100 in both chitosan and STTP-crosslinked chitosan microcapsules. This is likely due to better CEO retention since the lower temperature prevents quick oil evaporation from the fabric surface.

3.14 Physical Properties

The tensile strength of finished cotton fabrics is evaluated for specimens exhibiting the best wash durability with the three cross-linkers separately. The status of tensile strength, stiffness and air permeability of the microcapsule finished samples are reported in Table 15. The tensile strength is reduced by finishing treatments, with a substantial decrease in samples prepared without STTP cross-linker. The minimum tensile strength is observed in chitosan malic acid treated samples, while STTP-chitosan-Eudragit S 100 have the least affected tensile strength. The stiffness and air permeability of the finished cotton fabrics are also assessed and reported.

3.15 Retention of Clove Oil in Fabrics and Kinetics of Controlled Release

The investigation includes washing and drying cotton textiles, followed by examining their capacity to retain oil. The wall material, chitosan, which is insoluble in water, protects the core oil during washing and storage. The findings confirm that micro encapsulated clove oil is gradually released during storage, while free oil evaporates within a few hours. The kinetics of the controlled release of CEO from the fabrics are also studied. Several mathematical models describe the controlled release mechanism of oil from fabric, including those proposed by Higuchi, Korsmeyer, and Avrami[57–59]. This study utilize a Korsmeyer kinetics model to assess the controlled release of oil from the chitosan microcapsules on cotton fabrics. The model indicates that the value of 'n' falls between 0.5 and 1, suggesting a non-Fickian model. The release mechanism of oil is primarily influenced by diffusion and swelling, with the oil permeating through the polymeric layers due to variations in vapor pressure.

3.16 Probable Mechanism of Interaction between Microcapsules, Cross-Linkers, and Cotton Fabrics

Three distinct interactions may occur among microcapsules, cross-linkers, and cotton textiles, viz (i) chitosan and cellulose, (ii) cross-linker and cellulose, and (iii) chitosan and cross-linker. Interactions between chitosan and cellulose mostly occur via H-bonding and electrostatic interactions.

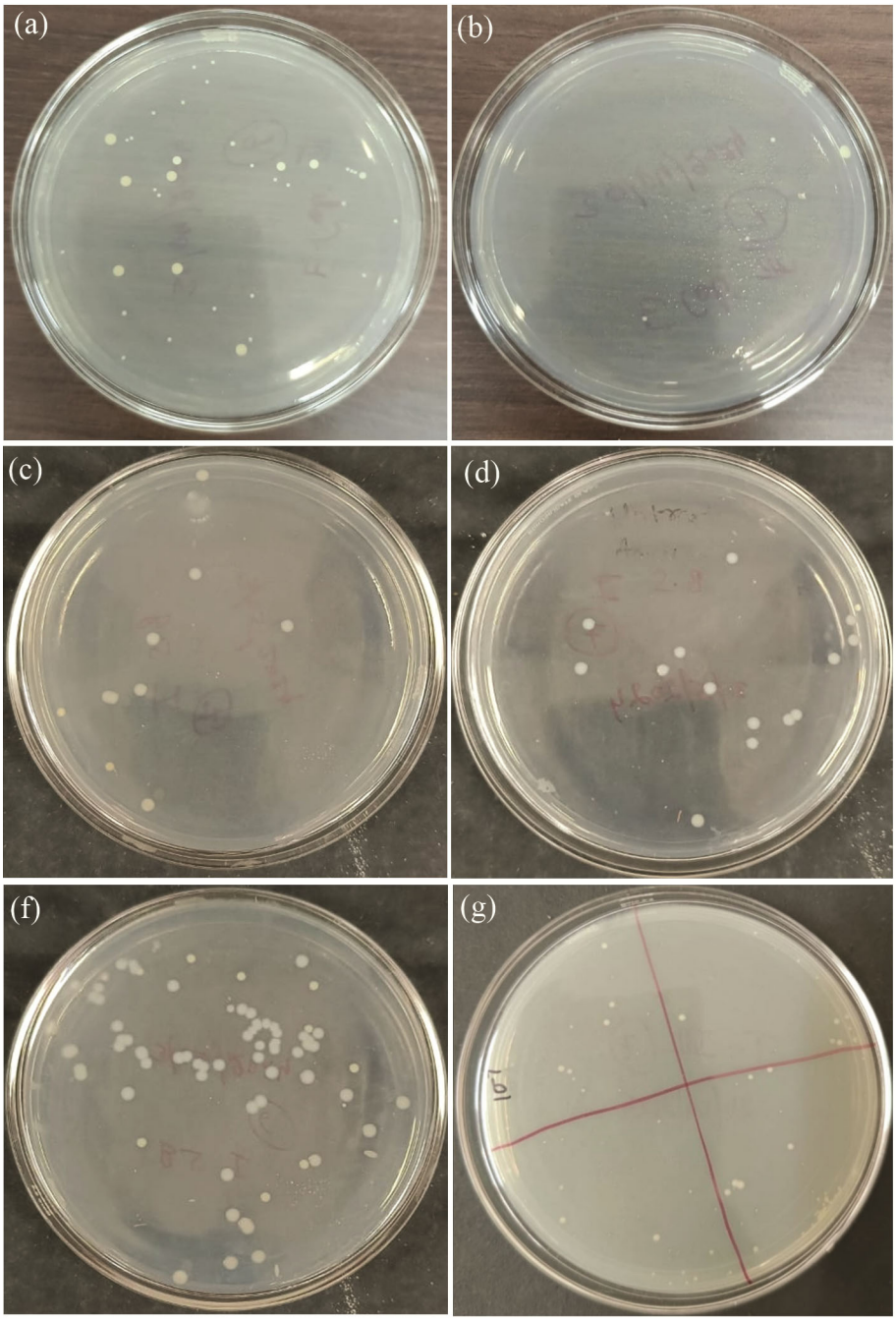

Fig. 9 — Antibacterial activity of cotton fabrics treated with CEO encapsulated in chitosan biopolymer after 5 washes: (a) Chitosan - Malic acid, (b) STTP- Chitosan – Eudragit S 100, (c) STTP- Chitosan- Maleic acid, (d) STTP- Chitosan- Malic acid, (e) Chitosan – Maleic acid, and (f) Chitosan – Eudragit S 100

When maleic acid is used as a cross-linker, it first forms a cyclic anhydride intermediate[48,50,60]. This intermediate then combines with cellulose to create an ester bond. Chitosan and maleic acid react to form chitosan-maleic acid conjugates, which interact with cotton cellulose. The OH- groups of cellulose connect to maleic acid residues by ester bonds, creating a cross-linked network. Due to similar chemical properties, malic acid undergoes reactions identical to maleic acid[46]. Malic acid exhibits superior whitening in comparison to maleic acid[51]. When Eudragit S 100 is used as a cross-linker, it may chemically react with chitosan via electrostatic interactions and H-bonding. Furthermore, it may undergo H-bonding and esterification reaction with cellulose.

Table 14 — Effect of different cross-linkers on the antibacterial property of cotton fabrics

Specimen	Bacteria	% Reduction in CFU of bacteria					
		0	1	2	3	4	5
Control	*E. coli*	NR*	NR*	NR*	NR*	NR*	NR*
	Bacillus	NR*	NR*	NR*	NR*	NR*	NR*
Chitosan-maleic acid	*E. coli*	95.12	95.01	94.3	94.16	93.2	91.8
	Bacillus	96.34	95.89	95.22	94.93	94.17	92.6
STTP-Chitosan-maleic acid	*E. coli*	99.0	98.6	98.1	97.1	96.1	95.0
	Bacillus	99.4	98.7	98.2	97.6	97.0	96.1
Chitosan-malic acid	*E. coli*	94.89	94.80	94.23	93.82	93.73	90.6
	Bacillus	95.76	94.93	94.68	94.19	93.11	91.8
STTP-Chitosan-malic acid	*E. coli*	99.0	98.8	98.4	97.4	96.5	95.3
	Bacillus	99.2	98.9	98.1	97.7	97.1	96.7
Chitosan-Eudragit S 100	*E. coli*	100	99.5	99.1	98.7	98.1	97.5
	Bacillus	100	99.8	99.3	98.9	98.3	97.9
STTP-Chitosan-Eudragit S 100	*E. coli*	100	100	99.6	99.2	98.9	98.5
	Bacillus	100	100	99.8	99.15	99	98.7

*NR-Not Required. Laundry cycle.

Table 15 — Effect of different cross-linkers on physical properties of cotton fabrics

Specimen	Tensile strength, N	Flexural rigidity, mg/cm	Air permeability $cm^3/cm^2/s$
Control	350	94	18.9
Chitosan-maleic acid	323	107	14.9
STTP-chitosan-maleic acid	336	117	12.6
Chitosan-malic acid	316	109	15.2
STTP-chitosan-malic acid	339	121	10.8
Chitosan-Eudragit S 100	319	112	14.8
STTP-chitosan-Eudragit S 100	330	126	13.6

4 Conclusion

Cotton fabrics are finished with CEO encapsulated in chitosan biopolymer to impart antibacterial properties. The microcapsules are prepared by spray drying technique in the range of 1-2 μm, with microencapsulation efficiency of 40-72%. The prepared microcapsules are optimized using response surface methodology with central composite design and Box-Behnken design. The best encapsulation efficiency and particle size results are obtained with core 1.25 %, feed rate 2 mL/min, atomization pressure 1.5 bar, and drying temperature 165°C. The chitosan microcapsules were prepared with and without the use of an STTP cross-linker. The release behavior of essential oils from the microcapsules is studied to ascertain the stability of the prepared microcapsules, which remain stable for more than a month when stored in appropriate conditions. Upon applying different cross-linkers, malic acid, maleic acid, and Eudragit S 100 by padding, the best results are obtained with Eudragit S 100 cross-linker. The kinetics of the release of CEO from the cotton fabrics are studied by employing the Korsmeyer kinetics model and the interaction between cellulose, chitosan microcapsules, and cross-linker is also proposed.

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