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Effect of the Addition of Sodium Dodecyl Sulfate Surfactant on the Formation of Alginate/ Carrageenan Microbeads using the Ionic Gelation Technique

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Abstract: ***This study aims to determine the effect of adding Sodium Dodecyl Sulfate (SDS) as a surfactant in encapsulating citronella oil using alginate/carrageenan (Alg/Car). The functional groups of microparticles were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and morphologically by Scanning Electron Microscope (SEM) analysis. The FTIR results show that the SDS causes a new peak spectrum to be formed at 1110 cm^{-1}, due to stretching of the S=O sulfate groups from SDS. SEM analysis showed that the addition of SDS resulted in beads having a coarse structure with a multi-void surface. The encapsulation efficiency of Citronella in SDS/Alg-Carr beads was found significantly higher (95.825%) compared to that of beads without SDS. The addition of SDS increased the antioxidant activity of citronella-loaded alginate-carrageenan beads. The release study showed controlled release in an acidic solution (pH 1.2) and a higher release rate at pH 6.8 (neutral). Alg/Car/Citronella beads modified with SDS can improve their properties and acid resistance, which makes them suitable for numerous applications.***

Keywords: Encapsulation, Sodium Dodecyl Sulfate, Citronella oil, Alginate, Carrageenan

1. Introduction

Bioactive compounds are a widely used source of important chemical compounds such as citronellal, geraniol, and citronellol [1]. Citronella research shows many health benefits for their antioxidant activity, antifungal, antibacterial, insecticidal, and mosquito-repellent activity [2,3]. Regardless citronella suffers from high volatility, and sensitivity to oxygen, light, humidity, and temperature contributes to compound degradation during storage and affects the productivity of commercial production systems. Encapsulation is an alternative technology currently used to protect and limit the loss of components of bioactive compounds [4]. Encapsulation is a method to create an external layer on top of other materials to capture the bioactive compounds contained therein. In the encapsulation method, one of the things that affect is the wall material. Wall material will affect the properties of the core material, including drying yield, encapsulation efficiency, moisture content, and dispersibility properties [5]

Alginates are widely used as encapsulation materials because of their biocompatibility, low toxicity, relatively low cost, light gelation, and safe use in food [6]. Nevertheless, they contain carboxylate functional groups and can easily dissociate in the aqueous phase, giving emulsions a negative charge [7]. Adding carrageenan to the encapsulation provides a double advantage, namely improving the nutritional and functional properties of the material [8]. Carrageenan and alginate are used as drug-release materials because they are biocompatible and make the delivery system sensitive to changes in pH and [2,9][2]temperature so that it can provide an appropriate response to the physiological environment [10]

However, it was reported that encapsulation using polymers faces several difficulties, as mentioned by Sharipova et al. [11], that the polymeric encapsulation microcapsules prepared without surfactant have low encapsulation efficiency, which is the consequence of weak intermolecular bonding. The solution to overcome this limitation is polymer/surfactant complexes formed to alter the adsorption layer around the oil droplets, thereby affecting the stability of the emulsion and hence the possibility of microencapsulation. Interactions of surfactants with synthetic or natural polymers have been explored for decades owing to their widespread applications in the pharmaceutical, food, and cosmetic industries and biotechnology [12–14]. In the encapsulation process, the surfactants often used are Tween 80, Span 80, Poloxamer 407, and SDS (Sodium Dodecyl Sulfate) [14–16] The most studied anionic surfactant known to science and commonly used sulfate surfactant is Sodium Dodecyl Sulfate (SDS). SDS is an organic compound commercially found in pellet or powder form, less toxic, and soluble in water. The surfactant SDS has an amphiphilic molecule containing both hydrophobic and hydrophilic moieties. Previous research has shown that SDS is not carcinogenic when consumed or applied directly to the skin [17]. Besides that, SDS can also increase the stiffness of beads and encapsulation efficiency [14,18]

Many encapsulation methods are being used in the food industry. Methods can be used for encapsulation depending on the core material, size of required particles, physical state, or sensitivity to high temperature. Encapsulation by ionic gelation has emerged as an effective technology to contain liquid samples in a biopolymer matrix due to the low temperatures involved in the encapsulation process [19]. Thus, this method allows minimal modification of the quality properties in the aqueous solution encapsulated. In particular, the ionic gelation method corresponds to the interaction between polymers with oppositely charged polymers or polymers with polycations or polyanions [20] Wherein hydrogel beads obtained by ionic gelation have been widely used to immobilize different food solutions, protecting critical bioactive compounds, such as betacyanin, betaxanthin, ellagic acid, quercetin, kaempferol, caffeic acid, anthocyanins, and polyphenols[21].

To our knowledge, studies regarding the encapsulation of citronella oil using alginate/carrageenan modified with SDS are still limited. The objective of this study was to encapsulate citronella oil into biopolymer (Alg/Car) modified particles by SDS surfactant to increase its stability and bioavailability. These polysaccharides were ionically cross-linked with $CaCl_2$. Furthermore, the effect of SDS concentration on encapsulation efficiency and swelling was studied. The particles obtained were morphologically characterized by SEM, functional groups by FTIR spectroscopy, and the citronella oil release in various pH was studied.

2. Material and method

2.1 Materials

Bioactive compounds Citronella oil was obtained from Intan Chemical Ltd., Surabaya, Indonesia, with specification relative density at 20/20 °C: 0.87-0.89 and carbonyl compounds content (minimum 75%). The chemical materials such as sodium alginate (molar mass 216.12 g/mol with CAS Number 9005-38-3SIGMA-Aldrich, USA), carrageenan, calcium chloride ($CaCl_2$), Sodium dodecyl sulfate (SDS), hydrochloric acid (HCl), Sodium hydroxide (NaOH), and buffer solution (Merck Chemical Co., Darmstadt, Hesse, Germany). All chemicals used analytical grade.

2.2 Preparation of Blank Alginate-Carrageenan Bead

Blank alginate-carrageenan beads were prepared by dissolving 2% (w/v) sodium alginate using distilled water and homogenized with a magnetic stirrer for 30 minutes at 28°C. Carrageenan solution was prepared by dissolving 1% (w/v) carrageenan in distilled water and homogenized with a magnetic stirrer for 30 minutes at 28°C. After that, a solution of alginate and carrageenan with a 2:1 ratio is mixed for 15 minutes until homogeneous. After stirring, the alginate-carrageenan solution was dripped with a syringe into the CaCl2 solution with concentrations of 0.2 M. The mixture will form beads in the CaCl2 solution. Wait for 30 minutes. Filter the hydrogel and then dry at 30°C for 48 hours.

2.3 Encapsulation Citronella essential oil (Cymbopogon nardus)

The encapsulation method was adapted from Camacho et al. [22] with some modifications. Alginate carrageenan (2:1 w/v) solution was prepared as in the previous point. After that, the alginate-carrageenan solution was added with SDS (0,1%, 0,3%, 0,5%, 0,7%, and 0,9% (v/v) and Citronella essential oil (10%) to the mixture. Then the mixed solution was homogenized using a magnetic stirrer for approximately 10 minutes. After homogeneous, the mixture was dripped with a syringe into a $CaCl_2$ solution with various concentrations. The mixture will form a hydrogel in the $CaCl_2$ solution for 30 minutes. Filter the hydrogel and then dry at 30°C for 48 hours.

2.4 Encapsulation Efficiency

The encapsulation efficiency of beads (EE) was calculated by subtracting the total losses (Q_r) during the gelation steps from the initial amount of Citronella (Q_t) added to the alginate/carrageenan/SDS solution. After that, the bioactive content was determined using the Spectrophotometer Genesys 20 UV-Vis at a wavelength of 367 nm. Encapsulation efficiency is calculated using the following equation Cirri et al. [23]:

$$EE\ (\%) = \frac{Qt - Qr}{Qt} \times 100\% \quad (1)$$

Qt is the amount of citronella bioactive present in the Citronella essential oil and Qr is the bioactive of the citronella in Citronella essential oil present in $CaCl_2$ solution after encapsulation.

2.5 Swelling Analysis

The swelling percentage was calculated by the swelling assay determined using a buffer solution at pH 7. Dry beads (0.2 grams) were diluted in 20 ml of buffer solution for 30 minutes. The percentage of swelling is calculated using the equation:

$$\text{Swelling}\ (\%) = \frac{Ws - Wd}{Wd} \quad (2)$$

Ws is the weight of the swollen beads and *Wd* is the weight of the dried beads [24].

2.6 SEM Analysis

The morphological results of the encapsulation of citronella with alginate-carrageenan were characterized using a Scanning Electron Microscope (SEM) JEOL JSM-6510LA.

2.7 FTIR Analysis

The results of the citronella encapsulation using modified alginate/carrageenan beads were analyzed with a Perkin Elmer Spectrum IR 10.6.1 spectrophotometer (Perkin Elmer Inc., US) to determine the functional groups in the 4000-450 cm^{-1} spectrum.

2.8 Encapsulation Release Study

The release study was conducted in pH 1.2 and 6.8 solutions. Encapsulated citronella oil (0.2 grams) was dissolved in 30

ml of each solution and soaked for 24 hours. For each time interval, 5 mL of sample was taken to be analyzed with Spectrophotometer Genesys 20 UV-Vis at a wavelength of 367 nm to determine the release of bioactive from citronella oil at a time.

3. Result and Discussion

3.1 Citronella oil composition analysis using GC-MS

Identification of citronella oil components using the GC-MS test can be seen in Figure 1. GC-MS chromatogram of citronella oil results shows that the sample contains Citronella and Geraniol compounds. Citronella compounds appeared at a retention time of 16.303 minutes and Geraniol at a retention time of 29.923 minutes.

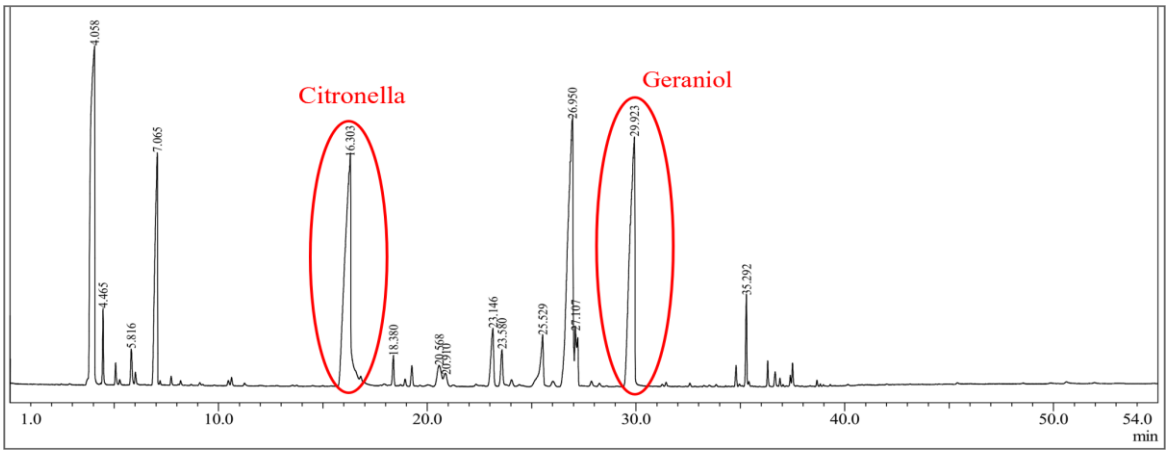

Figure 1: GC-MS chromatogram of Citronella oil

Table 1 shows the result of GC-MS chromatogram the identification of citronella oil, which contains the main compounds, such as Citronella and Geraniol. The GC-MS results show that there are 15 components contained in citronella essential oil (Table 1).

Table 1: List of identified chemical compounds in Citronella oil

Peak#	R.Time (min)	Percentage (%)	Name
1	4.06	19.57	α-pinene, (-)-
2	4.46	0.95	Camphene
3	5.82	0.74	Delta 3-carene
4	7.06	8.72	1-Methyl-4-(1-methyleneallyl) cyclohexene
5	16.30	19.77	Citronella
6	18.38	0.64	Linalool
7	20.57	1.34	β-elemene
8	20.91	0.62	Trans-Caryophyllene
9	23.15	2.32	Citronellyl acetate
10	23.58	1.05	Z-citral
11	25.53	1.81	Z-citral
12	26.95	20.60	Neryl acetate
13	27.11	2.13	α-amorphene
14	29.92	17.98	Geraniol
15	35.29	1.77	Elemol

There are two main compounds of citronella oil contained in the sample, namely citronella by 19.77% with a retention time of 16.30 minutes and geraniol by 17.98% with a retention time of 29.92 minutes. In addition, other compounds have a high % area including neryl acetate of 20.60% with a retention time of 26.95 minutes and α-pinene of 19.57% with a retention time of 4.06 minutes. The percentage is acceptable as it is similar to what was reported by Bayala et al. [25] : citronella oil's main component is citronella (33.06%) and geraniol (28.40%). Other minor components identified at percentages below 10% similar with previous research, such as neryl acetate, citronellil acetate, camphene, β-elemene, delta 3-carene, 1-methyl-4-(1 methylene allyl) cyclohexene, linalool, trans caryophyllene, z-citral, α-amorphene, and elemol. [26–28]. Previous studies announced the composition of citronella oil consists of 17 compounds [28], 33 compounds [29] and 37 compounds [30]. This difference could be explained by several factors, including genetic factors, age of the plant, season of harvest or plant environment [25,30].

3.2 Scanning Electron Microscopy Analysis

SEM images were taken to examine the morphology of the beads. Figure 2. shows the surface morphology of beads investigated by SEM at a magnification of 7500×. The Alg/Car beads formed an undulant and coarse structure with cylindrical and spherical solid-shaped aggregates as shown in Figure 2(a). The presence of these aggregates can be attributed to the interaction between the Alg/Car and Ca^{2+} ions. Figure 2(b) shows that the citronella-loaded Alg/Car beads exhibited a crimpy surface with noticeable lumps, which was additionally attributed to citronella's presence on the surface. The shape of the aggregates on the surface of the Alg/Car/citronella oil beads is different from Alg/Car beads; this can be explained based on the deposition of citronella droplets onto the outer or inner surface of the external layer of alginate microbeads, where the presence of oil components onto alginate surfaces can lead to plasticize their structure and forming these lumps [31,32]. This result is similar to Lacerda et al. [33] that the addition of rifampin causes the alginate surface to become

crimpy. The study of Maniecka et al. [34] also showed that the encapsulation of esculin with alginate microparticles resulted in a crimpy surface. Furthermore, the surface morphology of the Alg/Car matrix containing citronella oil is porous, and it can support the release of citronella through the pores [35].

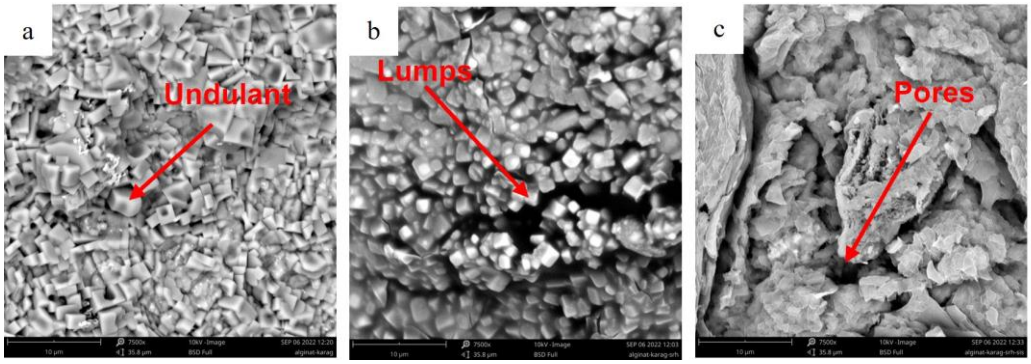

Figure 2: Scanning electron microscope images of the beads: (a) Alg/Car, and (b) Alg/Car/citronella oil, (c) Alg/Car/citronella oil/SDS

The picture shows that SDS incorporation significantly changed the morphology of the beads, as seen in Figure 2(c). The results of SEM showed that the interaction between SDS and alginate and carrageenan biopolymers resulted in significant morphological changes. The addition of SDS resulted in the formation of cavities or pores which were observed in the wall cracks. According to the research of Devi & Kakati [37], adding surfactants will form porous alginate microparticles. Beads with this surface morphology can generate capillary forces that facilitate liquid penetration into the beads and help release bioactive compounds through the pores [31]. In addition, Kaygusuz et al.[18] reported that adding SDS increased Young's modulus of alginate beads. Thus a more rigid and stable bead is obtained by adding SDS to the alginate.

3.3 Fourier Transform

The functional properties of the citronella oil beads were investigated using FTIR. Figure 3. In the spectrum of citronella oil from Figures 3(a), 1730 cm^{-1} and 2922 cm^{-1} were associated with symmetrical and asymmetric C=C vibrations and C-H strain of methyl groups of aromatic compounds in citronella oil. The absorption band at 2366 cm^{-1} indicates the presence of an aldehyde group. In the spectrum of Alg/Car from Figure 3(b), the absorption at 894 cm^{-1} was assigned to galactose sulfate of carrageenan. There is also an intense band at 1066 cm^{-1} caused by the valence vibration of the C–O bond. An absorption band is also seen at 1528 cm^{-1}, due to the asymmetric and symmetrical vibrations of the carboxylate anion of the alginate.

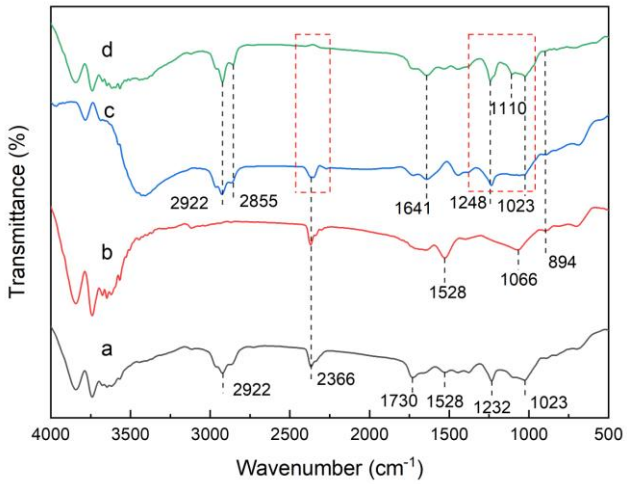

Figure 3: FTIR spectra for (a) citronella oil, (b) Alg/Car, (c) Alg/Car/citronella oil, (d) Alg/Car/citronella oil/SDS

The spectrum of microcapsule citronella oil is presented in Figure 3(c) shows the bead with the addition of citronella oil to Alg/Car. The absorption bands at 1641 cm^{-1}, 2922 cm^{-1}, and 2855 cm^{-1} are indicated as C=C vibrations and C-H strains of the methyl groups of aromatic compounds in citronella oil. Figure 3(d) shows the granules with the addition of SDS into Alg/Car/citronella oil. The absorption peak of 2366 cm^{-1} experienced a shift, this occurred due to the addition of SDS. In addition, a new peak spectrum was formed at 1110 cm^{-1}, due to stretching of the S=O sulfate groups from SDS.

3.4 Encapsulation Efficiency and Swelling Study

Encapsulation efficiency of Alg/Car/citronella oil/SDS were calculated by subtracting the lost amount of Citronella oil during the filtration steps from the initial amount of citronella oil. Alg/Car bead encapsulation efficiency for Citronella oil was significantly improved by the addition of SDS. The lowest encapsulation efficiency occurred at 0.1% SDS concentration of 92.87%, and the highest at 0.9% concentration of 95.82%. The presence of SDS can reduce the surface tension between Alg/Car and citronella oil to

form a more stable emulsion and cause faster microcapsule dispersion. The same thing also happened in the research of Chuacoren et al. [38] . When the concentration of SDS increases, the contact between the bioactive substance and Alg/Car also increases which causes encapsulation efficiency to increase [39]. In ionotropic bonding, SDS molecules will lose their hydrophilicity due to bonding with crosslinking cations, such as Ca^{2+}[40]. This causes the encapsulation matrix to be hydrophobic and resistant to drug release from the Alg/Car matrix so that the encapsulation efficiency increases [41,42]. In addition, the increase in encapsulation efficiency of citronella oil in SDS-containing beads is also caused by the interaction of SDS with citronella oil, and it can be predicted that the diffusion of citronella oil from the depth of the cavity will slow down [15].

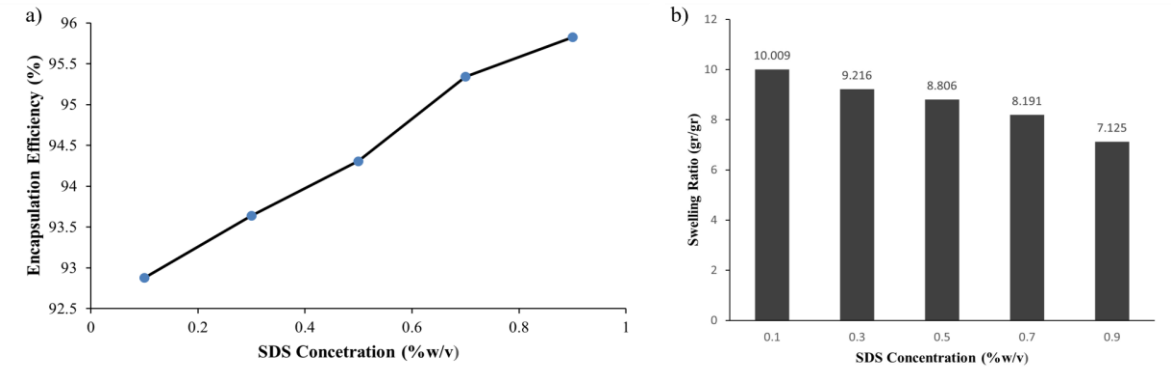

Figure 4: Effect of SDS concentration on: (a) efficiency encapsulation and (b) swelling ratio

The obtained beads have a hydrogel character, so it was considered beneficial to determine their capacity to retain water, usually quantified by the swelling ratio. Figure 4 shows the swelling ratio at different ratios of concentrations of SDS.

The swelling degree will decrease with the addition of SDS. As shown in Figure 4, SDS concentration from 0.1 to 0.9% resulted in a swelling ratio of 10.009 to 7.125. The swelling concentration of 0.1% is more substantial than 0.9%. SDS has a critical micelle concentration (CMC) value of 8mmol/L (0.2% w/v). In this study, the concentration of SDS used was above the critical micelle concentration (CMC). When SDS was added to the medium above the CMC value, the alginate gained electrophoretic mobility. It can be assumed that half micelles are formed along the alginate chain, which increases the density of molecules containing the negative charge of the Alg/Car/SDS association. This additional charge offers more adsorption areas for the divalent cations and, therefore, a higher amount of crosslinkers than the beads without the addition of SDS [14,18]. The increase in SDS concentration causes a decrease in the swelling ratio due to the presence of a stronger crosslink, and many beads will be challenging to swell [43]. When swelling is low, the spheres' disintegration rate decreases, and the beads show more stable behavior. It is similar to the previously published study showing that SDS has improved the stiffness of alginate [18].

3.5 Release Study of Encapsulation

Figure 5 shows the study releases determined at pH 1.2 and 6.8. Only 55.94% of the bioactive was released to a pH 6.8 solution within the first 2 hours, followed by a rapid release of up to 87% within 24 hours.. This increase in the drug release may be attributed to the fact that the drug that is bioactive of citronella adsorbed may be concentrated on the core encapsulation [44].

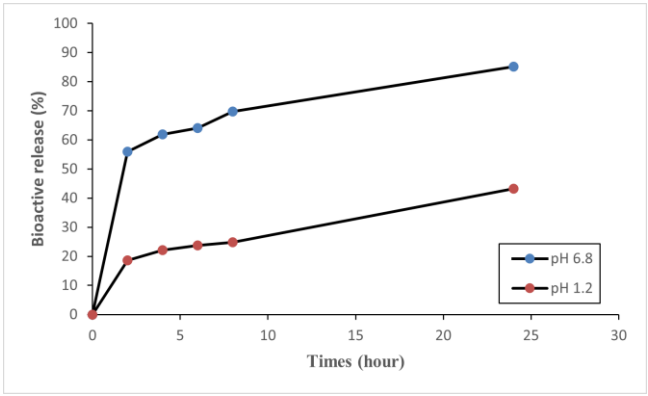

Figure 5: Release profiles bioactive of citronella oil in pH 1.2 & 6.8 from Alg/Car/citronella oil/SDS beads

Figure 5 shows that the initial 2 hours release of bioactive Citronella/Alg/Car/SDS at pH 6.8 has a concentration of 55.94%. while the pH of 1.2 showed a lower release of Citronella/Alg/Car/SDS bioactive which was 18.60%. The release of the bioactive more rapidly at pH 6.8 than pH 1.2. Effect of pH associated with the state of ionization group and carboxylic group in the whole structure of alginate. Alginate is a pH-sensitive copolymer. At the pH values above the pKa values of the mannuronate group (3.4) and guluronate group (3.6), alginate has a negative charge due to the dissociation of the carboxylic acid in the structure [14]. Since the carboxylic groups are fully protonated in the acidic environment, the polymer chain collapses. It causes a low relaxation rate so that the rate of release of the bioactive becomes slow [45].

Under neutral conditions (pH 6.8), the alginate carboxylic groups completely dissociate, the negative charges in the polymer chain repel each other, and the chain expands. As a result, the release of bioactive from alginate granules becomes faster [14,44]. The study is similar to Yousefi et al [42] that that encapsulation violaodorata in alginate beads indicated low release at pH of 1.5 and higher release at 7.

Another study by Nalini et al [44] also showed the release of quercetin from nanoparticles of alginate more quickly occurs at pH 7.4 than pH 5.5. This study showed that the bioactives of citronella were protected in acidic media and released at pH 6.8.

4. Conclusions

In this study it was shown that the addition of SDS concentration could increase the encapsulation efficiency of citronella oil in Alg/Car. The highest encapsulation efficiency of citronella oil was at 0.9% SDS concentration of 96.82%. The FTIR spectra showed that SDS affected citronella oil encapsulation in this process. The addition of SDS caused a shift in the absorption peak of 2366 cm^{-1} and a new peak spectrum appeared at 1110 cm^{-1}, due to the stretching of the S=O sulfate group from SDS. The results of the SEM analysis showed that the addition of SDS changed the morphology of the Alg/Car beads to a porous surface which was observed in the wall cracks. The study of bioactive release of citronella oil showed that at pH 6.8 the release of bioactive was more controlled than at pH 1.2. This study shows the potential for the addition of SDS to increase the stability of the encapsulant and to control the bioactive release behavior of the encapsulant properly.

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