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Determining the Optimum Application Recipe for Microcapsules of Ozonated Vegetable Oils to Save Antibacterial Activity to Textiles

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Abstract

This paper proposed to determine optimum application recipe for the microcapsules of the ozonated vegetable oils, in order to save the antibacterial activity to the textiles. For this aim, the olive oil was ozonated during three hours and the ozonated oil was characterized via GC and FTIR analyses and antibacterial property of the oil wasalso researched. After characterizing of the ozonated oil, it was encapsulated into Arabicgum by basic coacervation method. The microcapsules were characterized through optical microscope and FTIR analyses. Finally, in order to determine optimum application recipe for saving the antibacterial activity to textile surfaces, different application solutions were prepared and the prepared solutions applied to the cotton fabrics by padding method. After applications,the SEM images of the fabrics were investigated and the antibacterial efficiencies of samples were also quantitatively evaluated by the ASTM 2149 01 against *Escherichia coli*. The results of the study showed that the ozone could easily react with the double bonds of the olive oils and the antibacterial properties of the olive oil improved. The ozonated olive oil was able to be microcapsulated with basic coacervation method, successfully. In addition, the optimum application recipe for the microcapsules of the ozonated vegetable oils could be determined.

Keywords: Ozonated vegetable oil, Microcapsule, Application, Antibacterial activity, Textile

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Tekstil Yüzeylerine Antibakteriyel Aktivite Kazandırmak için Ozonlanmış Bitkisel Yağ Mikrokapsüllerinin Aktarılacağı En Uygun Aplikasyon Reçetesinin Belirlenmesi

Öz

Bu makale, tekstil yüzeylerine antibakteriyel aktivite kazandırılmak için ozonlanmış bitkisel yağ mikrokapsüllerinin aktarılacağı en uygun aplikasyon reçetesini belirlemeyi amaçlamıştır. Bu amaçla zeytin yağı 3 saat ozonlanmış ve ozonlanmış yağ GC ve FTIR analizleri ile karakterize edilmiştir, aynı zamanda yağın antibakteriyel özelliği araştırılmıştır. Karakterizasyon sonrası ozonlanmış yağ, basit koaservasyon yöntemi ile Arap zamkı içine enkapsüle edilmiştir. Hazırlanan mikrokapsüller optik mikroskop ve FTIR analizleri ile karakterize edilmiştir. Son olarak, tekstil yüzeylerine antibakteriyel aktivite kazandıracak optimum aplikasyon reçetesinin belirlenebilmesi amacıyla, farklı aplikasyon çözeltileri hazırlanmış ve hazırlanan çözeltiler pamuklu kumaşlara emdirme yöntemi ile aplike edilmiştir. Aplikasyon sonrası kumaşların SEM görüntüleri incelenmiş ve E.coli bakterisine karşı antibakteriyel etkinliği ASTM E 2149 01 standardına göre kantitatif olarak değerlendirilmiştir. Sonuçlar, ozonun zeytinyağındaki çift bağlarla kolaylıkla reaksiyona girebildiğini ve yağın antibakteriyel aktivitesini geliştirdiğini göstermiştir. Ozonlanmış yağ basit koaservasyon yöntemi ile başarılı bir şekilde kapsüllenebilmiştir. Ayrıca, ozonlanmış bitkisel yağ mikrokapsülleri için optimum aplikasyon reçetesi belirlenebilmiştir.

Anahtar Kelimeler: Ozonlanmış bitkisel yağ, Mikrokapsül, Aplikasyon, Antibakteriyel aktivite, Tekstil

1. INTRODUCTION

The ozone (O_3) is known as one of the best bactericidal, antiviral, and antifungal agents, and it is used for chronic wounds. The beneficial effects of ozone on wound healing might be considered to be due to decreased bacterial infection or increased oxygen tension by ozone exposure in the wound area [1]. The ozone cannot be stored, but it can be carried by way of materials having double bonds [2]. When literature was analyzed, it was found out that ozone could be reacted with the unsaturated fatty acids of the oils, thus they could be stored and gained antibacterial and wound healing property [1,3-10]. It may be concluded that they are good candidates to produce medical textile surfaces by using them as core materials in microcapsules.

The microencapsulation is a process of covering the core material with wall material such as polymers. The term of microcapsules is used to describe particles with diameter between 1 and 1000 μm, whereas particles smaller than 1 μm are called nanocapsules. The microcapsules can be formed by various techniques such as in situ polymerization, interfacial polymerization, coacervation and spray drying [11,12]. Among these methods, coacervation is generally used for encapsulation of the oils. The coacervation, based on the phase separation of one or many hydrocolloids, is divided into as simple and complex coacervation. While the simple coacervation involves the use of a single polymer in organic or aqueous media, the complex coacervation involves the use of two oppositely charged polymeric materials [13].

The ozonide of the ozonated oils has limited stability to the temperature. It is stable for up to 1 year in the temperature between -10ºC and +8ºC, while up to 6 months at room temperature (25-30ºC). Higher than this temperature, the stability of the ozonide along with antibacterial activity of the ozonated oils diminishes [6]. This property restricts the application conditions of the

ozonated oils to the textiles, and impose obligation for applying at room temperature. Therefore, in this experimental study, the optimum application recipe tried to be determined for the microcapsules of the ozonated oils. The study was divided to three parts. In the first part, the olive oil was ozonated during three hours at the laboratory condition. In the second part of the study, the microcapsules of the ozonated olive oil were prepared and the prepared microcapsules were characterized via optical microscope and FTIR. In the third part of the study, the optimum application recipe for padding method was tried to be determined in order to save antibacterial activity to textile surfaces.

2. MATERIAL VE METHOD

2.1. Material

In this study, in order to produce ozonated oil; the olive oil purchased from Zade Vital (Istanbul, Turkey), an ozone generator with the capacity of 25 g/h (Teknozone TKZ, İzmir, Turkey) and a glass bubbling colon (20 mm diameter, 900 mm height) with a glass diffuser placed at the bottom were used.

In the preparation of the microcapsules of the ozonated olive oil; Arabic gum as awall material, ethanol as a coacervation material supplied from Sigma Aldrich and low formaldehyde resin as a cross linker agent (Evopret RSF)supplied from Dystar were used. The microcapsules of ozonated oil were carried out by using a high shear mixer (L5M) purchased from Silverson.

In order to determine the optimum application recipe for the microcapsules, binder agent (Rucoat EC 4811) purchased from Rudolf Duraner and hydrophilic silicone emulsion (CML-N) supplied from CHT were used in the application solutions. The prepared application solutions were padded to the textile surfaces through laboratory scale fulard. The textile surface used in the study were 100% cotton woven fabrics (46 thread/cm warp, 22 thread/cm weft, 270 g/m^2). The fabric was desized, scoured and bleached by the supplier (Matesa, Kahramanmaraş, Turkey). The distilled water was used in the study.

2.2. Method

The produced ozone gas by the ozone generator was directed to the olive oil through the diffuser placed at the bottom of bubbling colon (Figure 2). The ozonation process was carried out with the 100 ml oil volume during 3 hours at the room temperature with the flow rate of 4 l/min. The experimental setup of ozonation process was given in Figure 2. After the ozonation, the ozonated oil was stored at the refrigerator for the further analysis and studies.

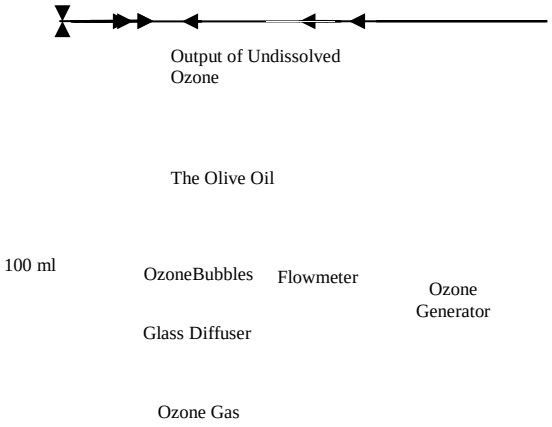


Figure 1. The experimental setup of the ozonation process [12]

The microcapsules of the ozonated oil were prepared according to diagram in Figure 2. The ratio of the ozonated olive oil: Arabic gum was determined as 1:5. The ozonated olive oil was drop wise added to 20% solution of the Arabic gumand they were stirred at 10.000 rpm during 1 hour for the formation of the emulsion. At the end of the stirring time, for actualization of the coacervation, the speed was reduced to the 3000 rpm, the ethanol (40% of the Arabic gum amount) was drop wise added to the emulsion and stirred for 10 minutes. Then, in order to stabilize the walls of the microcapsules, the cross linker agent (20% of the Arabic gum amount) was added to the solution and the mixture was stirred at 6000 rpm for 1 hour at

room temperature. At the end of the time, the solution was stored at the refrigerator for the further analysis and studies. The microcapsules in the solution were not filtered because of the necessity of the preparing solution of the microcapsulesfor the application [12].

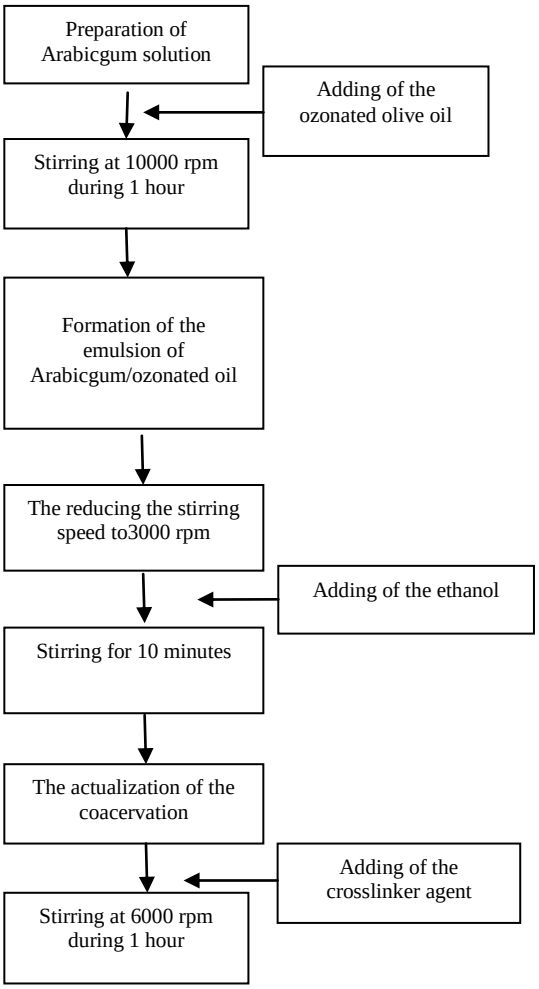


Figure 2. The work flow diagram for the reparation of the microcapsule [12]

In order to determine the optimum application recipe for the microcapsules of the ozonated oil, different six application solutions of the microcapsules were prepared (Table 1). The prepared solutions were padded to the fabrics by squeezing up to 95% pick up and the fabrics were dried at the room temperature.

Table 1. The prepared application solutions of the microcapsules [12]

Experimental number	Concentration of the microcapsule (g/l)	Hydrophilic silicone (g/l)	Binder (g/l)
1	50	0	0
2	100	0	0
3	250	0	0
4	500	0	0
5	500	100	0
6	500	0	20

2.3. The Characterization Analyses

GC-MS (Gas Chromatography-Mass Spectroscopy) analysis was carried out with an Agilent 5975 GC-MS system for both ozonated and raw oils. The oil samples had methylation process before the analysis. FTIR (Fourier Transform Infrared Spectroscopy) with ATR studies of the ozonated oil, raw oil, and the microcapsules were carried out by the transmission method using Perkin–Elmer spectrophotometer (Spectrum 400) between 400-4000 cm^{-1} of wave numbers. Resolution for the infrared spectra was 4 cm^{-1}, and there were four scans for each spectrum. The presence and the surface morphology of the microcapsules in the solution was researched via optical microscope (Nikon Eclipse 80i). The presence of the microcapsules on the fiber surface was evaluated through SEM (Zeiss Evo LS10). The antibacterial activities against *Escherichia coli* (ATCC 35218) of raw and ozonated olive oil samples were tested by AATCC 147 method and the antibacterial activities of the fabric samples against *Escherichia coli* (ATCC 35218) were tested by ASTM E2149-1 method.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Ozonated Olive Oil

The contents of the important fatty acids determined by the GC-MS analysis of the ozonated and raw olive oils were given in Table 2.

Table 2. The important fatty acids of the ozonated and raw olive oils [12]

Name of Fatty Acid	Raw olive oil (%)	Ozonated olive oil (%)
Nonanoicasid (C9:0)	-	32.88
Nonanal dimethyl acetal	-	1.07
Nonanedioicasid (C9:2)	-	25.49
Palmitic asid (C16:0)	12.07	30.06
Stearic asid (C18:0)	2.90	7.24
Oleic asid (C18:1)	73.79	-
Linoleic asid (C18:2)	9.38	-
Linolenic asid(C18:3)	0.60	-

It is known that the reaction of the ozone occurs at the carbon-carbon double bonds in the unsaturated fatty acid. Therefore, the amount of unsaturated fatty acids of the oil decreases by the ozonation process. When Table 2 was investigated, it could be seen that the oleic and the linoleic acids which were the most important unsaturated fatty acids of the olive oil for ozonation process were completely run out after the ozonation time lasting 3 hours. In addition, the ozone gas broke up the long chains of the fatty acids to the smaller chains and the nonanoicasid (C9:0), the nonanal dimethyl acetal, the nonanedioicasid (C9:2) were determined after the ozonation process.

The FTIR analysis was also used to observe the change at chemical structure of the olive oil by the ozonation process. The FTIR spectra of the ozonated and the raw olive oil were given in Figure 3.

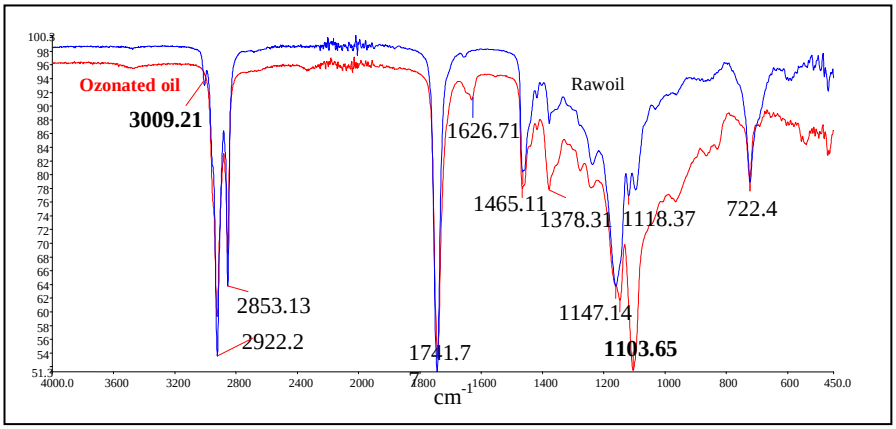


Figure 3. The FTIR spectra of the ozonated and raw olive oil [12]

For the FTIR assessment of the olive oil, =C–H stretching (ca. 3009 cm-1) and the C-O stretching (ozonide) (ca. 1105 cm-1) were crucial for ozonation process [12,14,15]. Figure 2 showed that C-O stretching (ca. 1105 cm-1) increased and C–H stretching (ca. 3009 cm-1) decreased, significantly after the ozonation process. Thus, it could be said that ozone bonded to the olive oil and the ozonide structure formed.

The result of the antibacterial activity of the ozonated and the raw olive oil investigated via planting of the bacteria to the agar medium was given in Figure 4.

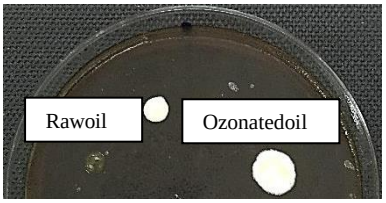


Figure 4. The antibacterial activity of the ozonated and raw olive oil [12]

In order to accept a sample as antibacterial, bacterial growth should not occur at the around, above or below of the sample. In addition, the size of the protection zone of the sample was the signal for the antibacterial activity. When the Figure 4 was investigated, it was seen that while the raw olive oil had low antibacterial activity, the ozonated olive oil showed high activity. As a conclusion, it can be said that ozone application to the olive oil improved the antibacterial activity of the oil.

3.2. Characterization of the Microcapsules of the Ozonated Olive Oil

The image of the optical microscope of the produced microcapsules of the ozonated oil was given in Figure 5.

When Figure 5 was investigated, it was clearly seen that the oil could successfully encapsulated and the capsules formed size of between 1 and 20 µm.

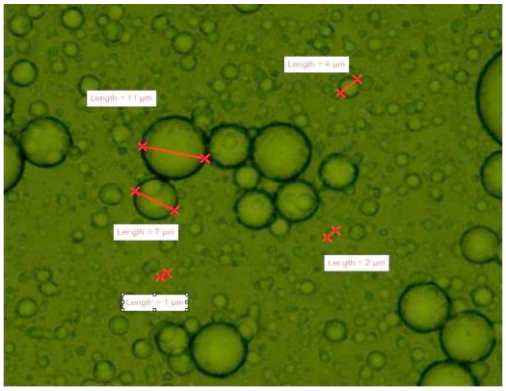


Figure 5. The image of the optical microscope of the microcapsules [12]

In order to be sure that the oil was encapsulated, the FTIR analyses were carried out to the core material, wall material and the prepared microcapsule. The IR spectra of the solution of the Arabic gum, the ozonated oil and prepared microcapsule as comparative were given in Figure 6.

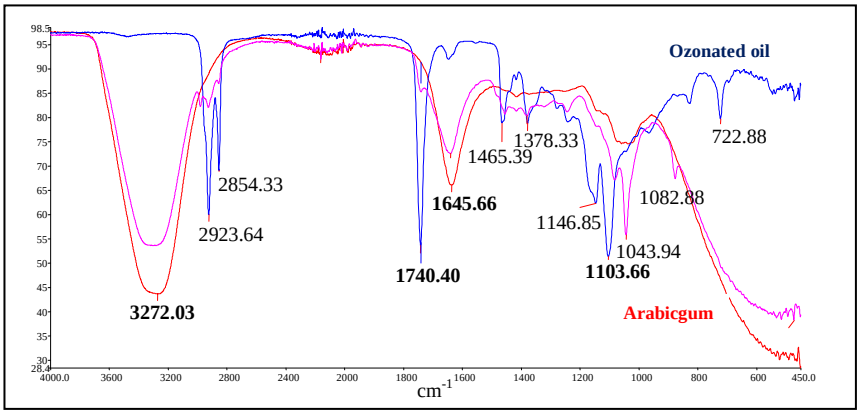
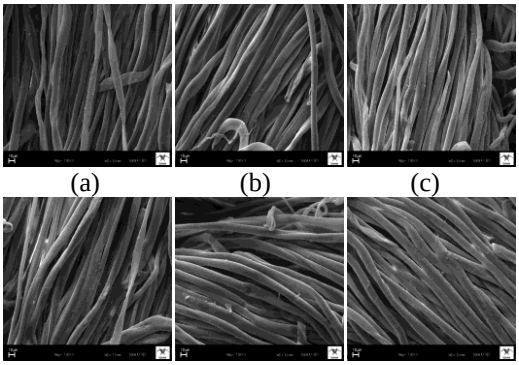


Figure 6. The IR spectra of the core material, wall material and the microcapsule [12]

When Figure 6 was investigated, it could be seen that the microcapsule had the important signal of the oil and the Arabic gum. In addition, while the peak intensityof theozonated olive oil showed at the wave number of ~1105 cm^{-1}, ~1741 cm^{-1} decreased, the peak intensities of the Arabic gum showed at the wave numberat ~1636 cm^{-1}, ~3272 cm^{-1} increased at the microcapsule solutions. Thus, we could understand that the Arabic gum covered the ozonated oil and the oil was successfully encapsulated.

3.3. The Characterization of the Fabrics Applied Microcapsule Solutions

The SEM images of the fabrics applied microcapsule solutions prepared according to the Table 1 were given in Figure 7.



(a) (b) (c)

(d) (e) (f)

Figure 7. The SEM images of the fabrics (a.1, b.2, c.3, d.4, e.5, f.6) [12]

Figure 6 showed that the microcapsules on the fiber surfaces increased depending on the increment of the concentration of the microcapsule, usage of the hydrophilic silicone and binder in the application solution.

The antibacterial activitiesa gainst *E.coli* of the fabrics treated with microcapsule solutions in Table 1 were given in Table 3.

Table 3. The antibacterial activity of the fabrics [12]

Experimental number (Table 1)	***% Reduction of the bacteria***
Raw fabric	*+257.14*
1	*+118.18*
2	*+45.45*
3	*+81.82*
4	*-33.33*
5	*-98.18*
6	*-38.33*

When Table 3 was researched, it could be seen that the antibacterial activity increased depending on the increment of the concentration of the microcapsule, usage of the hydrophilic silicone and binder in the application solution, similar with the results of the SEM images. The hydrophilic silicone increased holding the microcapsules onto the fiber surface due to the silicone oil. However, the binder also increased holding the microcapsules onto the fiber surface; the increment was insufficient because of the amount of the binder used in the application solution.As a result, 500 g/l microcapsule solution including 100 g/l hydrophilic silicone and higher than 20 g/l binder was determined as the optimum application recipe, in order to provide antibacterial activity to textile surfaces.

4. CONCLUSION

In the present study, it was aimed to determine the optimum padding recipe for the ozonated vegetable oils encapsulated by Arabic gum. The study was completed as three parts. Firstly, the olive oil was ozonated during 3 hours and characterized via GC and FTIR analyses along with antibacterial activity. Secondly, the ozonated olive oil was encapsulated into the Arabic gum and the prepared microcapsules were characterized via optical microscope and FTIR. Finally, the characterized microcapsules applied to the cotton fabrics with different padding recipes. The results showed that the ozone could easily react with the double bonds of the olive oils in the conditions of the experimental setup used in this paper and the antibacterial properties of the oil improved. The ozonated olive oil was able to be encapsulated into the Arabic gum with basic coacervation, successfully. In addition, the application solution including both the binder and silicone emulsion was determined as optimum application recipe, in order to save high antibacterial activity to textiles. As a conclusion, 500 g/l microcapsule solution including 100 g/l hydrophilic silicone and higher than 20 g/l binder was determined as the optimum application recipe, in order to provide high antibacterial activity to textile surfaces.

5. ACKNOWLEDGEMENTS

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