Microencapsulation of lambda-cyhalothrin with polyurethane-urea and application on peppermint plant leaves containing a two-spotted red spider mite (tetranychus urticae)

Hatice Yılmaza, Hüseyin Enginar a and Cemal Çifci b

aDepartment of Chemistry, Art and Science Faculty, Afyon Kocatepe University, Afyonkarahisar, Turkey; bDepartment of Chemical Engineering, Afyon Kocatepe University, Afyonkarahisar, Turkey

ABSTRACT

In this study, lambda-cyhalothrin (LC) used as a pesticide was microencapsulated with polyurethaneurea (PUU) at 55°C temperature for 180 min. Wall thickness and dimensions of the microcapsules, the effect of mixing speed on the capsule size, active substance release times of LC-PUU microencapsules under UV rays and alcohol/water medium, microencapsulation yields and the effect of microencapsulated active substance on the red spider on peppermint plant leaves (mentha piperita) were investigated. The microcapsule yield was found 77.4–85.5%, also capsule shell thickness was 512.3–724.5 nm. The highest release percentage of the microcapsules was found to be 35.00% at 20°C for 4 h under UV light. When the LC-PUU microcapsules applied to the peppermint plant leaves (mentha piperita) which contained a two-spotted red spider mites (tetranychus urticae), it remained active for 8 weeks and during this period no insect formation was observed on the peppermint leaves.

1. Introduction

The world population is growing steadily and is predicted to rise to 9 billion by the end of 2050. More productive agricultural practices are required to meet the food demands of this increasingly growing population [1]. The use of pesticide products used to protect and develop the plant is growing in agricultural applications. It has been widely used in agriculture to minimize losses in agricultural production due to pests, diseases and weeds, and to increase productivity [2]. Pesticide has been estimated that pesticides have recovered more than 30% of the world’s total production of agricultural products [3]. However, only a small amount of the pesticide will remain on the leaves, depending on the application methods and climatic conditions [4] and just around 0.1% can eventually affect the pests [5].

Today, commonly used active pesticide formulations are usually water-insoluble compounds which have to be mixed with a solvent, an emulsifier, and a dispersant in order to produce emulsifiable concentrates and wettable powders for spray application in an appropriate water-based formulation [6].

Pesticide spraying is a difficult issue where, due to the methods of application and climate conditions, more than 90% of pesticides run off from crop leaves and are unable to ultimately harm pests [7]. And also, their effects are low in target areas due to photolysis, active ingredient degradation, loss of evaporation, leakage hydrolysis and flow without adherence to the surface. Therefore, it is necessary to apply the chemicals to the target area repeatedly in order to obtain the optimum effect.

The use of high doses of dispersing agents or organic solvents in these systems may cause environmental pollution [8]. Pesticides not only kill target organisms, but also affect other invertebrates and vertebrate organisms. As an example of side effects; mortality of non-target organisms such as fish, birds, micro-organisms, bees and invertebrates, loss in reproductive capacity of fish, birds and other animals and alteration in ecological structure and number of species have long-term impacts [9]. In addition to these effects, pesticides which injected into the soil in high concentrations can cause damaging in ecological systems, creating in loss of biodiversity, polluting in the environment and groundwater. In order to solve or reduce environmental pollution problems caused by pesticides and organic solvents, changes are made in pesticide formulations. And also, in order to solve the above problems, studies on suitable carrier systems loaded with pesticides are increasing day by day. Selected suitable carrier systems and controlled release system will ensure the continuity,
stability and adhesion of the pesticide on the leaf surface for a long time [10–12].

Lambda-cyhalothrin (LC) is commonly used in various crops such as cotton, apple, potato, wheat, barley, rice, sugar beet, tomato, pistachios, hazelnut, olive, cabbage, soybean, grape and corn due to a wide variety of highly efficient bionic insecticidal properties [13–16]. Owing to low water solubility, it restricts direct application [3]. Therefore, some materials such as alginate derivatives, SiO2, different copolymer and polylactic acid have been used as carriers for the development of LC loaded systems in recent years [17]. LC loaded systems must have good adhesion to the leaves, stable environmental conditions and long release time. Microencapsulation method is one of the systems that will protect the LC loaded system from environmental conditions. They have a long active substance release period and cause the least harm to the environment. Polyurethane, a synthetic polymer material, is widely used in drug release systems, adhesives, automotive industry, thermal insulation and industrial applications due to their good compatibility with core material and excellent physical properties.

The aim of encapsulation is to protect the core material from external factors such as moisture, air, light and micro-organism but also to protect the coexisting substances from physical and chemical effects [18]. Due to its high encapsulation efficiency of polyurethaneurea (PUU) with interfacial polymerization, it is a widely used for many substances which are sweetener [19], ammonium phosphate [20], cellulose [21], octadecane [22, 23], fragrance and natural volatile oils [24], PCM [25], maltogenic α-amylase [26], butyl stearate [27], insecticide (pyrimiphos-methyl) [28], PolyHIPE [29], OCA (tissue adhesive) [30], lavender oil [31], lemon oil [32], and galangal essential oil [33].

The proper protection under environmental conditions of the encapsulated active material depends on the stability of the capsule shell. PUU capsule shell is a polymeric structure formed by isocyanate, glycol and amine groups. It will be tried to determine how the capsule is affected by the change in the amount of glycol and amine in the shell structure.

In previous studies; the isocyanate substance reacted with amine and glycol in constant molar ratios during the formation of microcapsules to obtain a wall material for PUU. In our study, PUU microcapsules were produced by changing the mole ratio of amine and glycols by keeping the mole ratio of the isocyanate substance constant during microencapsulation. The encapsulation yields and sizes of the produced microcapsules, the active material release rates, the effects of different glycol and amine ratios (Table 1) on the microcapsules and their effectiveness on the peppermint plant leaves (mentha piperita) (it was described by Prof Mustafa Kargioglu, Molecular Biology and Genetics Department, Afyon Kocatepe University, Turkey) with a two-spotted red spider mites (tetranychus urticae, C. L. Koch, 1836) (they were described by Prof Uğur Cengiz Erismis, Molecular Biology and Genetics Department, Afyon Kocatepe University, Turkey) in their leaves were investigated.

### 2. Material and method

Polyvinyl alcohol (PVA, 99.0% purity, Aldrich), Triglyceride (Lipostrol, > 97.0% purity), Toluene diisocionitate (TDI, > 97.0% purity, Sigma Aldrich), Hexamethylene diamine (HMDA, 99.8.0% purity, Aldrich), Hexamethylenediisocyanate (HMDI, > 99.0% purity, Sigma Aldrich), Butyl glycol (99.8% purity, Aldrich), Dibutyltin Dilaurate (DBTDL, 95.0% purity, Aldrich), Lambda-cyhalothrin (LC, 99.0% purity it was received as a gift sample of from Biokon Kimya Ltd. Sti, Konya, Turkey), Sep-Pak millipore filter (0.45 μm, Merck), Ethyl alcohol (99.90% purity, Merck). The chemicals used in the experiment are of analytical purity and were used without any purification.

#### 2.1. Microcapsule formation

0.35 grams of PVA were dissolved in 10.0 mL of water. 1.0 gram of lambda-cyhalothrin (LC) was dissolved in 3.0 mL triglycerides and mixed with 0.70 mL toluene diisocyanate (TDI). Water and triglyceride solutions were blended in the homogenizer and homogenized for 1.0 min at 3000–6000 rpm to obtain 1–40 μm droplets. These emulsified droplets were put into a reactor and then mixed at 600 rpm for 5 min at 35°C. Then, 3.8 mL propyl glycol of 10% and 30 μL dibutyltin dilaurate (DBTDL) mixture was added by drops. Meanwhile, the temperature was increased from 35°C to 55°C gradually, and continued to be mixed at this temperature for an hour. 4.6 mL hexamethylenediamine (HMDA) solution of 1% added to the solution in the reactor, and mixed at the same temperature for another 1.0 h. Finally, 2.5 mL hydrazine hydrate solution of 3% was added and mixed at the same temperature for another hour, then cooled at room temperature, and stored at room temperature for analysis. Microcapsulating scheme and mechanism for preparing microcapsules are shown in Figures 1 and 2, respectively.

#### Table 1. PUU shell prepared in different molar ratios with isocyanate/glycol/amines.

| TDI (mol) | Glycol (mol) | HMDA (mol) | HYD (mol) | Totalamines (mol) |
|----------|-------------|------------|-----------|-------------------|
| 1        | 0.0054      | 0.0055     | –         | 0.0015            |
| 2        | 0.0054      | 0.0050     | 0.0004    | 0.0015            |
| 3        | 0.0054      | 0.0045     | 0.0009    | 0.0015            |
| 4        | 0.0054      | 0.0040     | 0.0014    | 0.0015            |
| 5        | 0.0054      | 0.0035     | 0.0019    | 0.0015            |
| 6        | 0.0054      | 0.0030     | 0.0024    | 0.0015            |

Note: TDI: Toluene diisocyanate, Glycol: butyl glycol; HMDA: Hexamethylene diamine; HYD: Hydazyme monohydrate.
2.2. Microencapsulation yield

The absorption-concentration graph of LC was prepared in the UV-visible spectrophotometer (Shimadzu, UV-1700, Kyoto, Japan). A calibration chart was prepared 5.0 ml of Lambda-Cyhalothrin in various concentrations (10–50 ppm in hexane) and their absorbance values were measured at 218 nm [34]. The PUU microcapsule solution was filtered through blue band filter paper and the capsules were dried in a drying-oven at 75°C for 1 d. 0.2 g dry capsules were taken into a closed test tube and 5.0 mL hexane was added. Then the hexane phase was removed after shaking in the vortex mixer (Nüve NM-110, Ankara, Turkey) for 2.0 min. 100.0 μL hexane phase containing LC was taken and put into a 2nd test tube, which had 5.0 mL of hexane inside. Three-five dilutions were performed by repeating this method and measured of LC absorbance at 218 nm in the UV–VIS spectrophotometer device by matching the absorbance value in the calibration chart. After 5 dilutions, the amount of LC in the solution was found. From this result, it was found that the LC amount in 0.2 grams of PUU microcapsule and then the total LC amount in the PUU microcapsule, which was filtered and dried, was between 0.774-0.885 g.

2.3. Pesticide release in microencapsules alcohol/water medium

0.1 g of aqueous PUU microencapsule was placed in test tubes containing 12.0 ml alcohol/water mixture (10:90, v/v) and taken 2.0 mL per hour from this solution and passed through Sep-Pak millipore filter which has 0.45 μm pores. Then the solution was diluted for measurements in UV–VIS spectrophotometer device. The results of the measurements were obtained using the concentration graph against the absorbance previously obtained.

2.4. Pesticide release from microencapsules under UV light

10.0 g of PUU microencapsule solution was taken and put under UV light of $2 \times 18$ W power. 2.0 mL samples were taken every hour and filtered through the Sep-Pak millipore filter which has 0.45 μm pores. 2.0 mL hexane was added on this solution then it was shaked for 2.0 min in the vortex device. The last solution was put into the centrifuge device for 5.0 min at 2500 rpm for removing the hexane phase. The required dilutions were performed with hexane, and the absorption value against the wavelength was measured in the UV–VIS spectrophotometer.

2.5. Dimensional analysis of microcapsules

After drying and coating with carbon, the encapsulate samples were analysed with SEM instrument. Microencapsule size distribution was analysed in aqueous medium using the Malvern Nano-Zs device (Malvern Mastersizer 2000, Malvern, UK).

2.6. Optical microscopy and SEM

The stability of emulsified drops, the structures during the formation of the PUU microencapsules, the time of
formation of stable capsules, the formation stage of the capsules’ shell, and the impurities in the environment were observed with the Olympus CH20 optical microscope. The images of microencapsules were taken with 4X and 10X magnification. Surface and shell wall thickness of microencapsules are visualized in SEM device (LEO 1430VP, Carl Zeiss, Oberkochen, Germany).

2.7. Thermo gravimetric analysis (TGA)

TGA device (Shimadzu TGA-60, Kyoto, Japon) was used to measure mass change in decomposition and evaporation of microencapsules with and without (empty capsule) LC. From the microencapsules containing and not containing LC, 2.0–5.0 mg of samples were taken separately, and the temperature was raised to 450°C as to increase by 10°C per minute in the nitrogen environment. Then, the mass change was measured and recorded as a function of temperature.

2.8. Fourier-transform infrared spectroscopy (FT-IR)

FT-IR (Shimadzu, Kyoto, Japon) was performed in 3000–400 cm\(^{-1}\) operating range, by forming KBr pellets. Empty microcapsules without LC were completely dried, then mixed with 2.0–6.0 mg KBr which powdered in mortar to form discs under pressure in order to make measurements in the IR device. The liquid materials used in the shell material of the capsule were dripped over the KBr pellets which formed under pressure to measure their spectra.

3. Results

Figure 3 shows the FTIR spectrum of the formed microencapsules of PUU. Multiple infrared vibrations, typical of PUU systems could be classified. The N–H stretching mode is assigned at 3250–3500 cm\(^{-1}\), the urea carbonyl at 1740–1750 cm\(^{-1}\), and the amide II and amide III vibration modes at 1556 and 1244 cm\(^{-1}\), respectively. The vibration assigned at 1106 cm\(^{-1}\) corresponds to the stretching mode of the aether group C–O–C. The low intensity due to this vibration also confirms the urethane character of the microcapsules produced and suggests that there was a reaction of glycol and isocyanate. The fact that the isocyanate (TDI) stretching vibration at 2270 cm\(^{-1}\) seen in the toluendisocyanate spectrum was absent in the empty microcapsule shell at the same location confirms that all TDI was completely depleted by reaction with butyl glycol, HMDA and HYD.

In our study, it was found that the UV rays producing from the UV lamp with 2 × 18 W power broke the shell of the PUU microencapsules and 35% substance release occurred after four hours. One of the factors affecting the stability of microcapsules in external conditions is the UV rays from the sun. Ultraviolet A rays pass through the earth’s atmosphere and reach the earth’s crust and their energies range between 3.1–3.94 (315–400 nm) eV [35]. The energies required to break the chemical bond between C–C and C–N are 3.52 and 3.00 eV, respectively. UV rays from the sun break the bonds between the molecules and cause the compounds to degrade over time.

As shown in Table 2, the release percentages of microencapsules containing butyl glycol in their shell material were examined under UV ray and in the alcohol–water medium. LC release from the PUU microencapsule in alcohol–water environment was 15.10%, 19.49%, 20.07% and 25.00% at the end of the first, second, third and fourth hours, while UV radiation was realized as a percentage at the same time interval at 22.48, 26.40, 33.54, 35.00.

Figure 4 shows the size distribution chart, obtained using the Malvern Nano-Zs device, of the microencapsules made with butyl glycol at a mixing speed of 5000 rpm. According to the graph, distribution of

### Table 2. Release percentages of PUU microencapsules containing LC.

| Time (hour) | 0 | 1  | 2  | 3  | 4  |
|------------|---|----|----|----|----|
| Alcohol–water medium | – | 15.10 | 19.49 | 23.07 | 25.00 |
| UV ray | – | 22.48 | 26.40 | 33.54 | 35.00 |

Figure 3. FT-IR spectra of toluendisocyanate (1) and empty micencapsule (2).

Figure 4. Particle size distribution of PUU microencapsules containing LC.
microcapsules varied from nm to 45 μm. The size of the microcapsules larger than 4% was found to be between 8.47 and 33.87 μm. Before microencapsulation were formed, O/W microemulsions were homogenized at 3000–6000 rpm for 1 min. It was observed that the size of the microemulsion droplets decreased as the mixing speed increased.

Figure 5 shows the percent yields of LC microencapsulation efficiency at different glycol/amines mol ratio (1: 0.0055 / 0.0015; 2: 0.005 / 0.0019; 3: 0.0045 / 0.0025; 4: 0.004 / 0.0029; 5: 0.0035 / 0.0034; 6: 0.003 / 0.0039).

As seen in Figure 5, the highest LC microencapsulation efficiency was 85.5% in the fourth study, the lowest efficiency was 77.4% in the sixth study and the efficiency in other studies was between these two values.

When Figure 6 is examined, it is seen in TGA graphs that the mass losses of triglyceride and LC and PUU microcapsules containing LC and triglyceride in the core. Degradation of LC starts at about 183°C, and its weight sharply decreased from 100% to 0% between 183°C and 329°C (Figure 6(1)). Triglyceride started to decompose around 208°C, its mass loss starts 100–2.5% between 208.7°C and 340°C (Figure 6(2)). The TGA of curves Figure 6(3) showed that PUU microencaples started to decompose around 208.7°C, and its sharply weight loss 100–80% between 208°C and 345°C. Within this range, the shell wall degrades and the core material evaporates immediately. And second decomposition of PUU microencapsules started 345–430°C and the total mass loss for that temperature interval is that 80–5.5%. There was a gradual decomposition between this temperature and the degradation was due to the microcapsule shell breakdown.

According to the SEM and light microscope images in Figure 7 of the PUU microencapsules homogenized at 5000 rpm mixing speed, it was observed that the microcapsules were spherical, slightly flattened and their environments were clean.

According to the SEM images given in Figure 8, it was observed that the faces of the microencapsules were smooth, the width of the capsule was between 7.28–22.2 μm, and the thickness of the capsule wall varied between 512–724 nm.

Seven leaf samples were taken from the mint plant with two-spotted red spider mites on the leaves. The two-spotted red spider mites on each leaf were counted by light microscopy. An average of 12 two-spotted red spider mites were found on the leaves. One spray was applied to peppermint plant leaves from PUU microencapsules (200 μL / 200 mL, capsule solution / water) emulsified at 5000 rpm and the highest encapsulation efficiency. Leaves taken from mint plant were examined with light microscopy every three days for the presence of two-spotted red spider mites on them. It was seen
that all of the two-spotted red spider mites died in 6 days. It was determined that insects did not occur on mint leaves for 8 weeks following the application of PUU microencapsules. When Figure 9 was examined, it was found that the LC-PUU microencapsules were found on the peppermint plant leaves that were applied of LC-PUU microencapsule were greener than those that were not applied.

4. Discussion and conclusions

In this study, microcapsules with pesticide (LC) core material and PUU shell material were produced by the method of interfacial polymerization. Microcapsules’ shell materials were formed by the chemical reaction of isocyanate, glycol and amine of different molar ratios. Emulsified droplets need to be formed at room temperature (around 20°C) in order to make them more stable. After establishing the stability, the capsules were found to be pure when the temperature was gradually increased from 20°C to 55°C, however, the medium was found to have impurities when the temperature was suddenly increased from 20°C to 55°C. The reason for this is that the PVA solution, which aims to sustain the stability of emulsified droplets, cannot maintain the stability at high temperatures. LC’s emulsions were prepared with different mixing speeds and PUU microencapsulation of LC in various glycol / amine molar ratios was performed. The highest efficiency was obtained in the emulsion made at 5000 rpm and the mixture with a glycol / amine molar ratio of 0.004 / 0.0029 (mol / mol).

Podshivalov et al., encapsulated essential oil with PUU, the capsule size decreased as mixing velocity increased [33]. In a study where the softener scent is encapsulated with polyurethane; they found an inverse correlation between the speed of mixing and the size of the capsule. As the mixing speed increased, capsule sizes decreased [28]. Similar results were obtained in our study.
Rodrigues and her friends produced PUU microcapsules containing lemon oil as the core material, and produced stable structure by using HMDI as an isocyanate [36]. In our studies with HMDI, the capsules were not sufficiently stable. The main reason for this is that HMDI dissolves both in the oil (organic) phase and in the water phase. During the formation of polymer by the reaction of water-soluble HMDI with glycol and amine, some of the polymers are wrapped over the capsule, while the others remain in the water medium, causing impurities. In the microencapsulation study we carried out with TDI, it was determined that the microcapsules are stable and no impurities occur in the aqueous environment. This is because TDI dissolves only in the oil phase, reacts with water-soluble glycols and diamines and forms the formation of polymer on the microcapsule surface.

By looking Figure 3 at the IR spectra was a strong sharp peak at 2270 cm$^{-1}$ originating from the isocyanate group of TDI, it was observed that this peak was disappeared after the formation of capsule shell, and that the isocyanate group in TDI was completely consumed in the reaction.

Microcapsule walls must be of a certain thickness in order to have a long shelf life, resistant to environmental conditions and to carry the core material easily. The wall thicknesses of the obtained PUU microcapsules were found between 512–724 nm. According to these results, it is revealed that the percentage ratio of the nucleus materials to the total mass is $(80/100) \times 100$%.

According to these results, the subsequent degradation of microcapsules from the substances that make up the nucleus indicates that the capsules retain the substance contained and the formation of stable capsules.

One of the most important properties of the shell covering the pesticide active substance is to adhere to the applied plant surface and ensure that the microencapsulated active substance is to adhere to the applied plant surface and ensure that the microencapsulated active substance is to adhere to the applied plant surface and ensure that the microencapsulated active substance is to adhere to the applied plant surface. Some of the PUU microencapsules were found to stick on the mint leaves and still hold on the leaf surface after 8 weeks. There are a large number of urethane-urea groups capable of forming hydrogen bonding with the water molecules, amine, hydroxyl, carboxyl and aldehyde groups on the surface of the leaves [37,38]. This interaction of hydrogen bonding improved the adhesion strength between PUU microencapsulated active substance and the leaf surface and promotion of longer accumulation of pesticides.

In this study, lambda-cyhalothrin (LC) used as a pesticide was microencapsulated with polyurethaneurea (PUU). Wall thickness and dimensions of the microcapsules, the effect of mixing speed on the capsule size, active substance release times of LC-PUU microcapsules under UV rays and alcohol/water medium, microencapsulation yields and the effect of microencapsulated active substance on the red spider on peppermint plant leaves (mentha piperita) were investigated. PUU resin and the main component of the capsule shell were synthesized using toluene diisocyanate/butyl glycol/amines (hexamethylene diamine and hydrazine monohydrate) in a different molar ratio at 55°C temperature for 180 min. The microcapsule yield was found to be 77.4–85.5%, also capsule shell thickness was 512.3–724.5 nm. The highest release percentage of the microcapsules was found to be 35.00% at 20°C for 4 h under UV light. When the PUU microcapsules formed were applied to the peppermint plant leaves (mentha piperita) which contained a two-spotted red spider mites (tetranychus urticae) on its leaves, it remained active for 8 weeks and during this period no insect formation was observed on the peppermint leaves.

In conclusion, this study aims to perform microencapsulation of LC, a widely used pesticide in agriculture industry, with polyurethane-urea. For this purpose, lambda-cyhalothrin was successfully encapsulated with PUU resin by the method of interfacial polymerization. The stages of microcapsule formation were examined by optical microscopy, and the surface morphology of the microcapsules was examined by SEM. The sizes of the microcapsules were found to be in the range from nm to 45 μm, the thicknesses of the capsule shells were between 512.3–724.5 nm and the maximum microencapsulation yield was found as 85.5%. The pesticide containing PUU microcapsules were found to remain on peppermint leaves for 8 weeks and was effective against insects in peppermint leaves during this time.

Acknowledgements
The authors would like to thank Biokon Chemistry company for supplying Lambda-cyhalothrin.

Disclosure statement
No potential conflict of interest was reported by the author(s).

Funding
This work was supported by the Afyon Kocatepe University, Scientific Research Projects (BAP) [grant number 18.FEN.BIL.60].

References
[1] Yearla SR, Padmasree K. Exploitation of subabul stem lignin as a matrix in controlled release agrochemical nanoformulations: a case study with herbicide diuron. Int J Environ Res. 2016;23:18085–18098.
[2] Xu Y, Wang L, Tong Y, et al. Study on the prepa-
ratation, characterization, and releasebehavior of carbo-
sulfan/polyurethane microcapsules. J Appl Polym Sci. 2016;133:43844.
[3] Zhao X, Cui H, Wang Y, et al. Development strategies and prospects of nano-based smart pesticide formulation. J Agric Food Chem. 2018;66(26):6504–6512.
[4] Xu X, Bai B, Wang H, et al. A near-infrared and temperature-responsive pesticide release platform through core-shell polydopamine/pnippam nanocomposites. ACS Appl Mater Interfaces. 2017;9:6424–6432.
[5] Massinon M, De Cock N, Forster WA, et al. Spray droplet impaction outcomes for different plant species and spray formulations. Crop Prot. 2017;99:65–75.

[6] Liu B, Wang Y, Yang F, et al. Development of a chlorantraniliprole microcapsule formulation with a high loading content and controlled-release property. J Agric Food Chem. 2018;66:6561–6568.

[7] Nuruzzaman M, Rahman MM, Liu Y, et al. Nanoencapsulation, nano-guard for pesticides: a new window for safe application. J Agric Food Chem. 2016;64:1447–1483.

[8] Yussof SNM, Kamari A, Aljafree NFA. A review of materials used as carrier agents in pesticide formulations. Int J Environ Sci Technol. 2016;13:2977–2994.

[9] Tiryaki O, Canhilal R, Horuz S. Tarım ilaçları kullanımı ve riskleri. Erciyes Üniversitesi Fen Bilimleri Enstitüsü Der-gisi. 2010;26(2):154–169.

[10] Sun C, Shu K, Wang W, et al. Encapsulation and controlled release of hydrophilic pesticide in shell cross-linked nanocapsules containing aqueous core. Int J Pharm. 2014;463:108–114.

[11] Dowler CC, Dailey OD, Mullinix BG, et al. Polymeric microcapsules of alachlor and metolachlor: preparation and evaluation of controlled-release properties. J Agric Food Chem. 1999;47:2908–2913.

[12] Patil DK, Agrawal DS, Mahire RR, et al. Synthesis, characterization, and controlled release study of polyurea microcapsules containing mitribuzin herbicide. Rus J of Appl Ch. 2015;88:692–1700.

[13] Djojaka M, Soglo F, Kusimo MO, et al. The rapid degradation of lambda-cyhalothrin makes treated vegetables relatively safe for consumption. Int J Environ Public Health. 2018;15:2–17.

[14] Sahu DK, Rai J, Bhatt C, et al. UV-visible spectrophotometric determination of lambda-cyhalothrin insecticide in vegetables, soil and water samples. J Ravishankar Univ Part B Sci. 2018;31(1):1–9.

[15] Bownik A, Kowalczyk M, Barczerowski J. Lambda-cyhalothrin affects swimming activity and physiological responses of Daphnia magna. Chemosphere. 2019;216:805–811.

[16] Hamid A, Yaqub G, Ayub M, et al. Determination of malathion, chlorpyrifos, λ-cyhalothrin and arsenic in rice. Food Sci Technol Int. 2020;1:6. DOI:10.1590/fs.01020.

[17] Liu Y, Wang Y, Yang F, et al. Construction of a controlled-release delivery system for pesticides using biodegradable PLA-based microcapsules. Colloids Surf B. 2016;144:38–45.

[18] Erkan G. Bazı antifungal ajanların mikrokapsülasyonu ve tekstil materyallerine aplikasyonu [Doktora Tezi]. İzmir: Dokuz Eylül Üniversitesi, Fen Bilimleri Enstitüsü; 2008.

[19] Salaün F, Bedek G, Devaux E, et al. Microencapsulation of a cooling agent by interfacial polymerization: Influence of the parameters of encapsulation on poly (urethane–urea) microparticles characteristics. J Membr Sci. 2011;370:23–33.

[20] Salkh D, Wronan I, Giraud S, et al. Microencapsulation of anhydrous di-isodecyl phosphate with a polyurethane shell. Part II. Interfacial polymerization technique. React Funct Polym. 2006;66:1118–1125.

[21] Yoo Y, Martinez C, Youngblood P, et al. Synthesis and characterization of microencapsulated phase change materials with poly (urea–urethane) shells containing cellulose nanocrystals. ACS Appl Mater Interfaces. 2017;9:31763–31776.

[22] Zhang H, Wang X. Synthesis and properties of microencapsulated n-octadecane with polyurea shells containing different soft segments for heat energy storage and thermal regulation. Sol Energy Mater Sol Cells. 2009;93:1366–1376.

[23] Kim EY, Kim HD. Preparation and properties of microencapsulated octadecane with waterborne polyurethane. J Appl Polym Sci. 2005;96:1596–1604.

[24] Tekin R, Bac N, Erdogmus H. Microencapsulation of fragrance and natural volatile oils for application in cosmetics, and household cleaning products. Macromol Symp. 2013;333:35–40.

[25] Aydin AA. In situ preparation and characterization of encapsulated high-chain fatty acid ester-based phase change material (PCM) in poly (urethane-urea) by using amino alcohol. Chem Eng Sci. 2013;231:477–483.

[26] Maçiulytė S, Gutauskienė G, Niedrits J, et al. PVA and various diisocyanates based poly (urethaneurea) microcapsules for encapsulation of enzyme in water/butyl acetate emulsion: synthesis and study. Chemija. 2017;28:74–84.

[27] Liang C, Lingling X, Hongbo S, et al. Microencapsulation of butyl stearate as a phase change material by interfacial polycondensation in a polyurea system. Energy Convers Manag. 2009;50:723–729.

[28] He R, Wang J, Wang X, et al. Fabrication and characterization of core–shell novel PU microcapsule using TDI trimer for release system. Colloids Surf A: Physicochem Eng Asp. 2018;550:38–144.

[29] David D, Silverstein MS. Porous polyurethanes synthesized within high internal phase emulsions. J Polym Sci Part A Polym Chem. 2009;47:5806–5814.

[30] Gandham VD, Brochu A, Reichert W. Microencapsulation of liquid cyanoaacrylate via in situ polymerization for self-healing. MRS Proc. 2011;14:1711–1417.

[31] Cui G, Wang J, Wang X, et al. Preparation and properties of narrowly dispersed polyurethane nanocapsules containing essential oil via phase inversion emulsification. J Agric Food Chem. 2018;66:10799–10807.

[32] Silva M, Martins IM, Barreiro MF, et al. Functionalized textiles with PUU/limonene microcapsules: effect of finishing methods on fragrance release. Text Res J. 2017;108:361–367.

[33] Podshivalov AV, Bronnikov S, Zuev VW, et al. Synthesis and characterization of polyurethane–urea microcapsules containing galangal essential oil: statistical analysis of encapsulation. J Microencapsul. 2013;30:198–203.

[34] Sherrif SS, Madadi V, Mbugua JK, et al. Adsorption of lambda cyhalothrin on to Athi river sediments: apparent thermodynamic. Mod Chem Appl. 2017;5:2–4. DOI:10.4172/2329-6798.1000213.

[35] Available from: https://web.archive.org/web/20131029233428/http://www.spacewx.com/pdf/SET_21348_2004.pdf.

[36] Rodrigues S, Fernandes I, Martins I, et al. Microencapsulation of abamectin poly(lactic acid) nanoparticles with regulatable adhesion to enhance foliar retention. RSC Adv. 2017;7:11271–11280.

[37] Yu M, Yao J, Liang J, et al. Development of functionalized abamectin poly(lactic acid) nanoparticles with regulatable adhesion to enhance foliar retention. RSC Adv. 2017;7:11271–11280.

[38] Wagner P, Furstner R, Barthlott W, et al. Quantitative assessment to the structural basis of water repellency in natural and technical surfaces. J Exp Bot. 2003;54:1295–1303.