Preparation and characterization of acetylated starch mediated silver nanoparticles: The effect of solution ratio and time-varying exposure

Zatil Izzah Tarmizi[1*], Muhammad Fahmi Burhan Burhanuddin[1], Mohd Shahrul Nizam Salleh[1,2], Mohamad Aizad Mohd Mokhtar[1], Justin Chan Zhe[1], Siti Husnaa Mohd Taib[1], Siti Nur Amalina Mohamad Sukri[1]

[1] Chemical Environmental and Engineering Department, Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia, 53200 Kuala Lumpur, Malaysia
[2] Faculty of Chemical Engineering, UiTM Cawangan Terengganu, Bukit Besi Campus, 23200 Dungun, Terengganu, Malaysia

E-mail: zatil.izzah@utm.my

Abstract. Plastic packaging is widely used in food industry to protect and maintain food freshness. However, plastic packaging also contributes to solid waste problem and can become the contamination area of microbial activities which in turn affecting the shelf-life of the food product and may causing food-borne illness towards consumer. Thus, the demands on biodegradable polymer as plastic packaging has grown widely especially among the food industry. The employment of silver nanoparticles (AgNPs) can improve physical properties of biopolymer as well as promoting antimicrobial properties on the plastic packaging. The aim of this study is to synthesize of AgNPs by utilising acetylated starch (AS) as reducing agent with different parameters via microwave irradiation method. The effect of different ratio of acetylated starch and microwave time-varying exposure is evaluated. The synthesized silver nanoparticles were characterized via UV-VIS spectroscopy (UV-VIS), X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) analysis. The absorbance peak emerges at 420nm on UV-VIS shows that silver nanoparticles is successfully produced. 15 minutes microwave time exposure and 1:1 ratio is identified as the optimum condition to produce silver nanoparticles. The peak emerges on FTIR spectra shows the involvement of starch in reduction process in synthesizing AgNPs. The XRD results shows the amorphous structure of starch and crystalline peak of silver appear in 2Θ regions 37.4°, 43.4°, 63.1° and 75.7°. In conclusion, the significant outcome from the study is the AgNPs were successfully synthesized via microwave irradiation method and be a function of time varying exposure and acetylated starch ratio.

1. Introduction
In the current era of globalization, many industries have been emerged and developed rapidly to supply the demands among the consumer that also growth in rapid pace. One of the industries that is growing excellently is food packaging industry with expected market at USD $378.58 billion by 2022 [1]. Regardless the demand in the market, the employment of single-use plastic has become a major contribution for solid waste problem [2]. A single plastic can take about 1000 years to degrade upon disposal [3]. However, plastic packaging is handy to be utilised for the purpose of protecting the food

product from microbial contamination. Microbial could lead to food-borne illness towards the consumer [4]. High population of microbial can be on the surface of the most of process and fresh food product [5]. The occurrence may shorten the shelf-life of the food products [6]. Despite the case, food-borne pathogen may accumulate on the packaging's surface that poses a food-borne illness threat to consumer [7]. A new trend has been widely implemented in preserving the food quality as well as an initiative to solve the environmental issue which utilizing a biodegradable plastic packaging that encompass with antimicrobial properties. Nowadays, AgNPs is widely employed as active agent into biodegradable polymer in making a bioplastic packaging with improved in physical properties as well as imposing antimicrobial properties [8][9].

On the other hand, the conventional process of synthesizing AgNPs involving a toxic reagent as reducing agent is found to be hazardous [10][11]. The occurrence has led to other initiatives in employing microwave method and carbohydrate compound such as starch to be part as reducing and capping agent. The employment of starch in synthesizing AgNPs using microwave method is inexpensive, renewable, natural-occurring and non-toxic as chemical method [12]. Microwave-irradiated AgNPs can be synthesized rapidly with uniform size that do not require high temperature and pressure [12]. Therefore, in these study, AS mediated AgNPs was produced using microwave irradiation method. The effect of acetylated starch ratio with different time varying exposure is determine and characterized using UV-VIS, FTIR and XRD.

2. Method

2.1 Materials

Silver nitrate salt ($AgNO_3$) and acetylated starch (AS) powder was purchased from Sigma Aldrich, USA. These materials are analytical grade and were used directly and dissolved in deionized water without further purification.

2.2 Preparation of Acetylated Starch Mediated Silver Nanoparticle

The nanoparticle was synthesized via reduction of $AgNO_3$ solution that was mixed with AS that taking place as reducing agent. The aqueous solution of $AgNO_3$ (0.1 M) was prepared by dissolving 1.7 g of $AgNO_3$ salt into 100 ml of deionized water. Meanwhile, 2.0 g of AS powder was prepared by mixed into 200 mL of deionised water and stirred at 500 rpm in magnetic stirrer (IKA C-MAG) for 1-hour duration at 90 °C which will turned into cloudy solution. The solution was cooled down around 30 minutes before mixed into $AgNO_3$ solution with different AS ratio and microwave time exposure.

2.2.1 The Effect of Acetylated Starch Ratio. The study on the effect of starch ratio to silver nanoparticles, six sets of experiments were prepared by mixing the prepared starch solution and $AgNO_3$ solution according to the respected ratio listed in the Table 1. The solution was stirred for 60 minutes with 500 rpm at 65 °C by using magnetic stirrer. Once the solution was mixed well, the prepared solution was put into microwave (NN-GF574MMPQ, Panasonic, Japan) for reduction process with the power of 270 W and the duration for 15 minutes as a constant parameter. The procedure was repeated with each set of starch to silver nitrate solution.

Table 1. The ratio of acetylated starch to silver nitrate in 50 mL solution

Silver nitrate solution (mL)	Acetylated starch solution (mL)	Ratio (Ag:AS)
10	40	10:40 or (1:4)
20	30	20:30 or (2:3)
25	25	25:25 or (1:1)
30	20	30:20 or (3:2)
40	10	40:10 or (4:1)
50	00	50:00 or (5:0)

2.2.2 Effect of Microwave Time Exposure on AgNP Production. Seven set of samples that contains starch and $AgNO_3$ solution at ratio 1:1 (50 ml) was prepared by continuous stirring for 1 hour at 65 °C with 500 rpm. This process results in formation of cloudy solution. Then, the prepared solutions were placed in microwave (Panasonic NN-GF574MMPQ) at 3,5,7,9,12,15, and 17 minutes for different exposure time in microwave irradiation at constant power of 270 W (1bar).

2.3 Characterization of Silver Nanoparticles

2.3.1 UV-Vis Spectrophotometer. The synthesized AgNPs/AS was characterized by using UV-Vis (UV– 2600, Shimadzu, Japan) with a wavelength ranging from 300 nm to 700 nm. The study is a crucial part to observe the formation of silver nanoparticle that has been reduced by using AS from aqueous $AgNO_3$ solution. The synthesized AgNPs can be observe at the wavelength of 420 nm.

2.3.2 X-ray Diffraction (XRD) Analysis. XRD analysis (D8 Quest, Burker, Germany) is important to observed on the crystalline structure of the silver nanoparticle at 2 angles ranging from 30° to 80°. The speed scan used for the study is at 2°/min. The crystallite size can be determined by using Scherrer formula.

2.3.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis. The functional group present in the synthesized acetylated starch mediated silver nanoparticles (AS/AgNPs) can be observed through FTIR analysis (IRTracer-100, Shimadzu, Japan). All the samples were scanned in ATR mode with a 16 scan, the wavenumber ranging from 500 cm^{-1} to 4000 cm^{-1}.

3. Results and Discussion

3.1 UV-Vis Analysis

3.1.1 UV-Vis Analysis for the Effect of Acetylated Starch and Silver Nitrate Ratio. The formation of silver nanoparticle can be detected using UV-Vis spectroscopy by observing the peak at the wavelength range around 410 to 460nm [13][14]. Figure 1 shows the effect of different ratio of $AgNO_3$ and AS at constant microwave irradiation time (15 minutes). Based on that figure, by increasing the volume of starch, the peak observed at 427nm were increase sharply. However, the $AgNO_3$/AS solution with ratio 20:30 and 10:40 is not suitable to be used due to high viscosity and difficult to be read under UV-Vis. Highest peak intensity of AgNPs is observed at ratio 25:25. For the ratio of 30:20, the peak of AgNPs is slightly shifted to lower wavelength at 426nm showing an interaction was occur between $AgNO_3$ and AS. The same trend was observed in other study where that researcher has synthesizing AgNPs with potatoes starch by using heating technique and the highest absorbance peak was appear at 410nm [15].

Besides that, the formation of AgNPs can be observed through the colour changes on colloidal suspension [16][17][18]. The colloidal colour solution getting darker as the ratio of starch loading is getting higher (Figure 2). The solution with ratio $AgNO_3$ to AS at 10:40 has the darkest colloidal colour solution among other samples. However, the solution became too dried and high viscosity that is hard to handle and not suitable to be used for further study. The viscosity occurred due the employment of starch or complex polymer chain that functional group of polysaccharides which take part in encouraging the formation of AgNPs [15]. The same condition goes to solution with the ratio $AgNO_3$ to AS at 20:30 that happen to be too viscous to handle. $AgNO_3$/AS at 25:25 produced the highest intensity peak of AgNPs indicates that 25:25 or 1:1 is optimum formulation ratio suitable for these techniques. The colourless silver nitrate ($AgNO_3$) without the presence of starch remains the same after 15 minutes of microwave time exposure indicated that no reduction to AgNP occurred without the presence of starch. Thus, the employment starch is the key component as reducing agent in synthesizing AgNP with assisted by microwave irradiation [18][19].

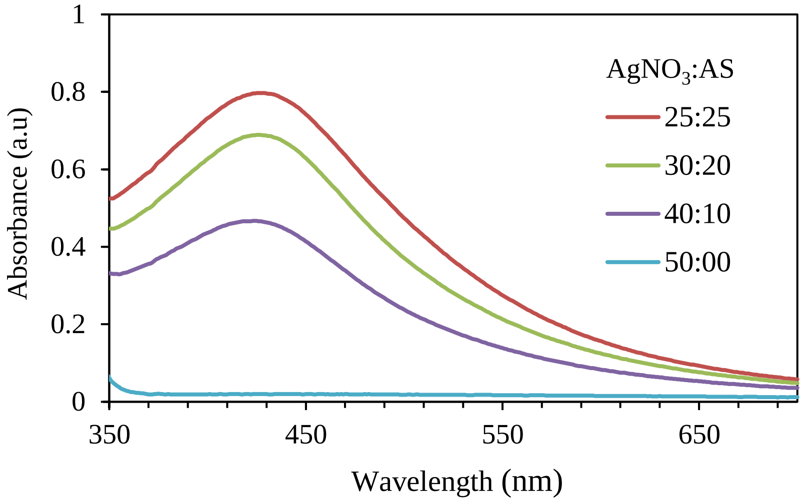

Figure 1. UV-Vis spectra of AgNPs produced at different acetylated starch and silver nitrate ratio

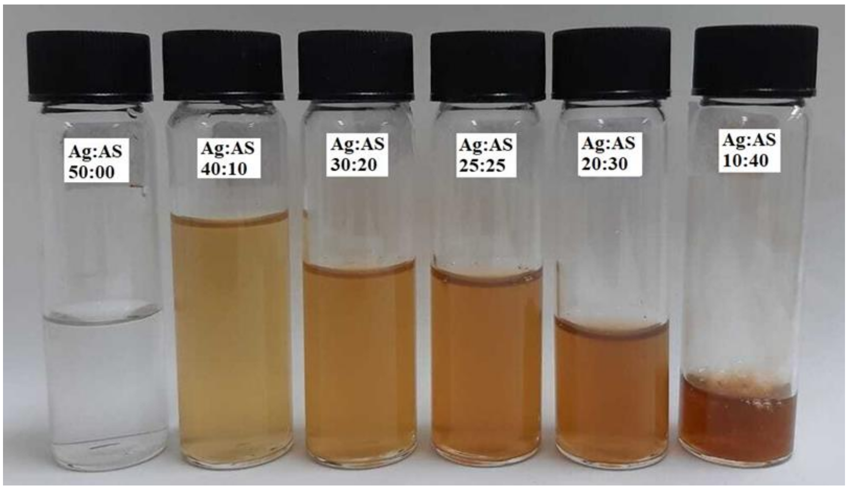

Figure 2. The colour changes on the solutions at different silver nitrate: acetylated starch ratio.

3.1.2 UV-Vis Analysis for The Effect of Different Microwave Time Exposure. Figure 3 shows the absorbance spectra of acetylated starch mediated AgNP at different time of exposure in the microwave. At 3 minutes until 9 minutes of microwave irradiation time, the absorbance peak of AgNPs slightly appear however difficult to be differentiate. This shows that more energy is needed to produce sharp peak of AgNPs. By increasing the microwave time exposure until 17 minutes, the absorbance peak become increases [12]. Based on Figure 4, by increasing exposure time towards microwave irradiation from 3 to 17 minutes, the darker the colour of colloidal solution. The AgNPs production at 17 minutes time of exposure shows the highest peak compared to the other solution. However, AgNP/AS solution at 17 minutes microwave exposure is not suitable for further study as the solution quite viscous that is difficult to be handle as well as not suitable to be implement on further study. Therefore, 15 minutes time of microwave exposure is an optimum time for synthesizing the AgNPs by using acetylated starch as reducing agent. This results also produced similar trend with another researcher. Faxian and co-authors produced silver nanoparticles with microwave irradiation in extreme basic condition at different time interval (8, 15 and 20 minutes). As the results, the size of AgNPs getting bigger gradually over the exposure time and 15 minutes is the optimum condition compare to other times and it also improve surface enhancement Raman scattering (SERC) activities with rhodamine probe molecules [12].

Meanwhile, Kahrilas and teams have conducted research on AgNPs using microwave irradiation method and lemon peel extract as reducing agents and found out that AgNPs was obtained an optimum peak of 425 nm at 15 minutes time of exposure [19]. Thus, the $AgNO_3$/AS solution with microwave exposure at 15 minutes has been selected as optimum condition for these techniques.

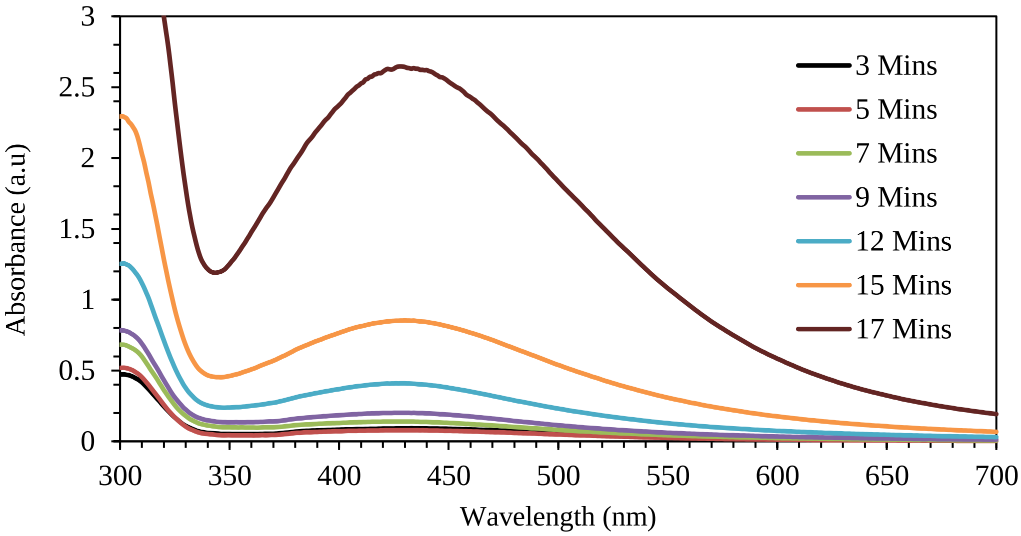

Figure 3. UV-Vis spectra of $AgNO_3$ with AS at different microwave irradiated time

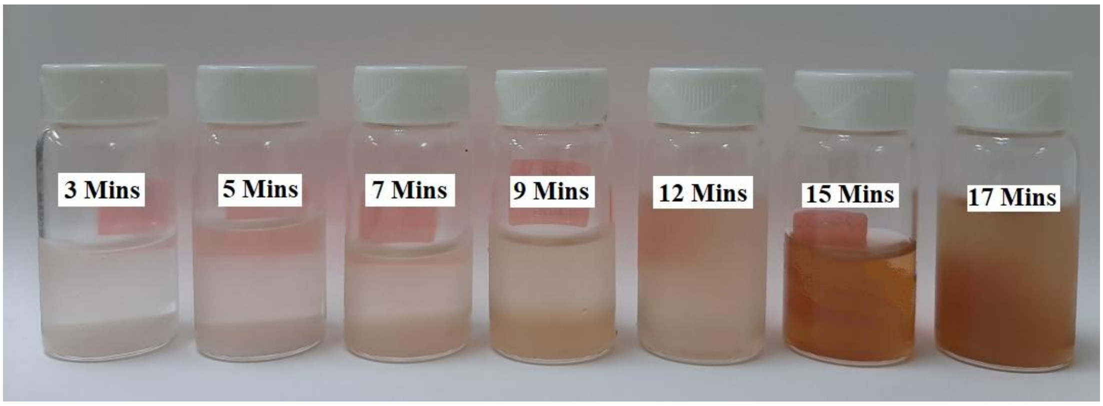

Figure 4. The colour changes occurred when increasing microwave irradiation time (3 to 17 minutes).

3.2 XRD Analysis

The four diffraction peaks emerge from 2Θ region are 37.4°, 43.4°, 63.1°, and 75.7°. These four peaks correlating to set of lattice planes of (111), (200), (220) and (311) crystalline structure respectively (Figure 5). The topographic nature of the peaks can be viewed as face-centered cubic (FCC) crystallographic planes which do not shows any formation of Ag_2O or AgO [20]. The appearance of the four peaks can be reflected with the standard theoretical figures of NIST bulk silver reference in International Centre of Diffraction Data (ICDD:98-042-6921) http://www.icdd.com/ [20][21]. Additionally, the average crystallite size of synthesized AgNPs is 44.79 nm.

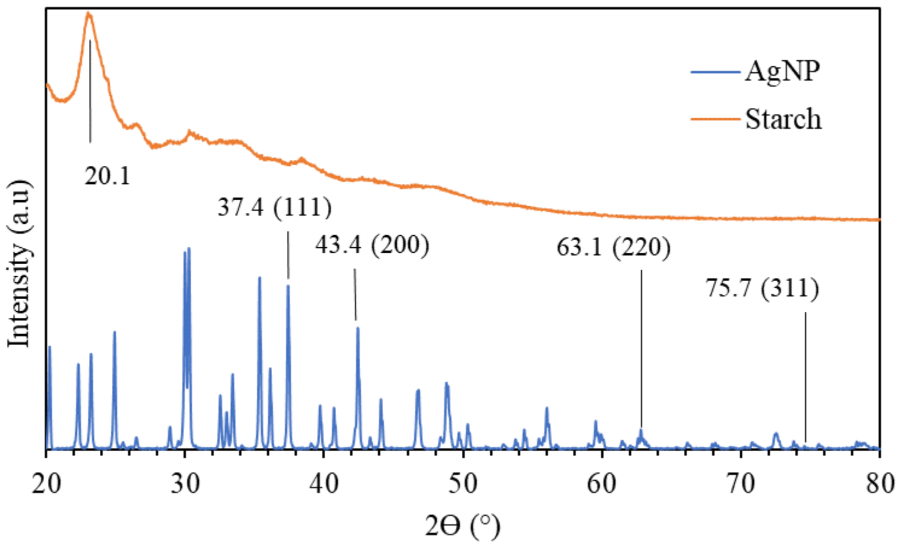

Figure 5. The XRD spectra for AS mediated AgNPs produced using microwave irradiation method

Besides, starch spectra show a peak emerges at 20.1° at 2Θ region. The characteristic pattern can be observed from various starch-acid complexes [22]. The starch-acid complex may come from the acetylation process by acetic acid for producing the acetylated starch. Ijaz and his teams also obtained a similar XRD spectra pattern for starch in his research that study the characterization of homogenized corn starch throughout palmitic acid, stearic acid, and lauric acid [22].

3.3 FTIR Analysis

Figure 6 shows the FTIR spectra for optimum acetylated starch and synthesized AgNPs at 15 minutes irradiation times with AS: $AgNO_3$ ratio 1:1. The starch exhibits a broad absorption band at 3284 cm^{-1} corresponding to OH stretching. The OH contributes to the inter and intra-molecular interaction that proves the characteristic for a starch structure of polysaccharides. Meanwhile, the absorption band at 2931 cm^{-1} corresponding to C-H stretching [23]. Another absorption band such as at 1637 cm^{-1} relating to C=O stretching vibration representing a carbonyl group that maybe carboxylic acid, ketone, or aldehyde. At 1076 cm^{-1} correlates to C-O-C symmetrical stretching and COH bending exhibits on absorption band at 995 cm^{-1} [24]. This result also produced similar trend with Ponsanti and his teams who conducted the study on the effect of different starch to synthesis AgNP via corn starch, cassava starch and sago starch. All the starches exhibit the same spectra pattern for FTIR analysis [25]. Almost similar FTIR spectra for both acetylated starch and acetylated starch mediated silver nanoparticles indicated that AgNPs was effectively coated by acetylated starch as capping agents [26].

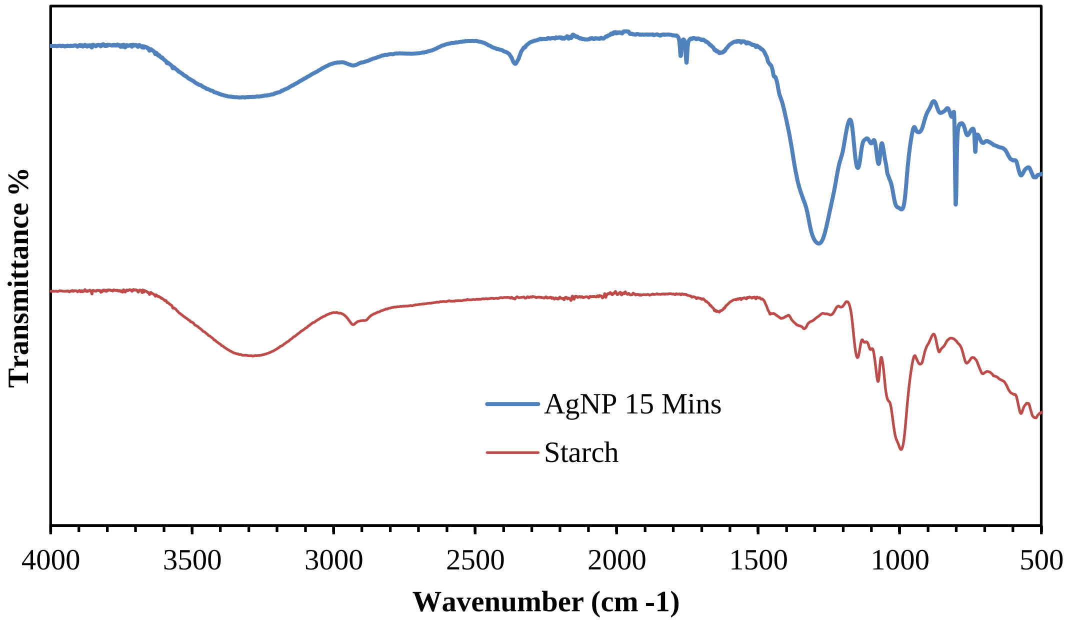

Figure 6. The FTIR spectra of pure acetylated starch and synthesized silver nanoparticles.

5. Conclusion

This research focused on two parameters to synthesis of AgNPs by acetylated starch as reducing agent with the assistance of microwave irradiation. The first parameter is the effect of different AS ratio to $AgNO_3$ results in the AgNPs/AS solution with ratio 25:25 is the optimum ratio for the reduction process. Second parameter is the effect of exposure time towards microwave irradiation exhibits that the time at 15 minutes of microwave exposure is the optimum time for synthesizing AgNP. Based on appearance and colour, UV-Vis analysis of synthesized AgNP proves that the starch loading to silver ratio 25:25 is the optimum ratio with 15 minutes of microwave exposure time. FTIR analysis confirmed the presence and interaction of AgNPs with starch. Lastly, the XRD analysis on the synthesized AgNPs shows the diffraction peak emerged is a face-centered cubic (FCC) crystallographic plane. Thus, proves the presence of crystalline structure of the synthesized AgNPs

Acknowledgement

The author would like to grateful acknowledge Nippon Sheet Glass Foundation for Material Science and Engineering grant (R.K.130000.7343.4B635) and Malaysia-Japan International Institute of Technology (MJIIT) for Industry-International Incentive grant (Q.K130000.3643.03M38). Special appreciation to Chemical and Environment Engineering (ChEE) department for the supports on the laboratory and facilities.

References

[1] Zhao X, Cornish K, Vodovotz Y 2020 Narrowing the gap for bioplastic use in food packaging: An update *Environmental Science and Technology* **54** 4712-4732.
[2] Walker T R, McGuinty E, Charlebois S, Music J 2021 Single-use plastic packaging in the Canadian food industry: consumer behaviour and perceptions. *Humanities and Social Sciences Communications* **8** 80.
[3] Kale S K, Deshmukh A G, Dudhare M S, Patil V B 2015 Microbial degradation of plastic: A review. *Journal of Biochemical Technology* **6** 925-961.
[4] Han J H 2005 Antimicrobial packaging systems. Ed J H Han. (London: Academic Press) Chapter 6. pp 80-107.

[5] Rocha M, Ferreira F A, Souza M M, Prentice C 2013 Antimicrobial films: a review *Microbial pathogens and strategies for combating them: Science, Technology and Education* **1** 23-31.
[6] Kanmani P, Rhum J W 2014. Physicochemical properties of gelatin/silver nanoparticles antimicrobial composite films *Food Chemistry* **148** 162-169.
[7] Al-Tayyar N A, Youssef A M, Al-hindi R 2020 Antimicrobial food packahing based on sustainable bio-based materials for reducing foodborne pathogens: A review *Food chemistry* **310** 125915.
[8] Srikhao N, Kasemsiri P, Ounkaew A, Lorwanishpaisarn N, Okhawilai M, Pongsa U, Hiziroglu S, Chindaprasirt P 2021 Bioactive Nanocomposite Film Based on Cassava Starch/Polyvinyl Alcohol containing green synthesized silver nanoparticles *Journal of polymers and the environment* **29** 672-684.
[9] Salleh M S N, Cheladorai S, Ali R R, Shameli K, Tarmizi Z I, Zhe J C 2021 Microwave irridiation assisted synthesis of silver nanoparticles using pullulan as reducing agents and its antibacterial activity *Journal of Research in Nanoscience and Nanotechnology* **2** 42-50.
[10] Raghavendra G M, Jung J, Kim D, Seo J 2016 Step-reduced synthesis of starch-silver nanoparticles *International Journal of Biological Macromolecules* **86** 126-128.
[11] Kanmani P, Lim S T 2013 Synthesis and Characterization of pullulan-mediated silver nanoparticles and its antimicrobial activities *Carbohydrate polymers* **97** 421-428.
[12] Faxian L, Jie L, Xueling C 2017 Microwave-assisted synthesis silver nanoparticles and their surface enhancement raman scattering *Rare Metal Materials and Engineering* **46** 2395-2398.
[13] Khan M J, Kumari S, Shameli K, Selamat J, Sazili A Q 2019 Green synthesis and charaterization of pullulan mediated silver nanoparticles through ultraviolet irridiation *Materials* **12** 2382.
[14] Ji T, Chen L, Mu L, Yuan R, Knoblauch M, Bao F S and Zhu J 2016 In-situ reduction of Ag nanoparticles on oxygenated mesoporous carbon fabric: exceptional cataylst for nitroaromatics reduction *Applied Catalysis B: Environmental* **182** 306-315.
[15] Martinez-Rodriguez M, Garza-Navarro M, Moreno-Cortez I, Lucio-Porto R, Gonzalez-Gonzalez V 2016 Silver/polysaccharide-based nanofibrous materials synthesized from green chemistry approach *Carbohydrate polymer* **136** 46-53.
[16] Jung J, Raghavendra G M, Kim D, Seo J 2018 One-step synthesis of starch-silver nanoparticle solution and its application to antibacterial paper coating *Int. J.Biol Macromol* **107** 2285-2290.
[17] Zafar S, Zafar A. 2019 Biosynthesis and characterization of silver nanoparticles using phoenix dactylifera fruits extract and their in vitro antimicrobial and cytotoxic effects *The open biotechnology journal* **13** 37-46.
[18] Cholula-Diaz J L, Lomeli-Marroquin D, Pramanick B, Nieto-Arguello A, Cantu-Casrillo L A, Hwang H 2018 Synthesis of colloidal silver nanoparticles clusters and their application in ascorbic acid detection by SERS *Colloids and Surface B: Biointerfaces* **163** 329-335.
[19] Kahrilas G A, Wally L M, Fredrick S J, Hiskey M, Prieto A L, Owens J E 2014 Microwave-assisted green synthesis of silver nanopartilces using orange peel extract *ACS Sustainable Chemistry and Engineering* **2** 367-376.
[20] Cepoi L, Zinicovscaia I, Rudi L, Chiriac T, Rotori I, Turchenko V, and Djur S 2020 Effects of PEG-coated silver and gold nanoparticles on *Spirulina Platensis* biomass during its growth in a closed system *Coatings* **10** 717.
[21] Ijaz M, Uddin N M, Khan F, Ali Z U, Khan N, Muhammad J, Iqbal N, Rehman N, Jan A K, Ahmad S 2020 Green production and structural evaluation of maize starch-fatty acid complexes through high speed homogenization *Journal of polymers and the Environment* **28** 3110-3115.
[22] Ponsanti K, Tangnorawich B, Ngernyuang N, Pechyen C 2020 A flower shape-green synthesis and characterization of silver nanoparticles (AgNPs) with different starch as a reducing agent *Journal of materials research and Technology* **9** 11003-11012.
[23] Liu C, Shen J, Yeung K W K, Tjong S C 2017 Development and antibacterial performance of novel polylactic acid-graphene oxide-silver nanoparticle hybrid nanocomposite mats prepared by electrospinning *ACS Biomaterials Science and Engineering* **3** 471-486.

[24] Alipilakkotte S, Sreejith L 2018 Green synthesized PLA/Silver nanoparticles probe for sensing of hydrogen peroxide in biological samples *Materials Letters* **217** 33-38.
[25] Tarmizi Z I, Arifin N I, Ali R R, Shameli K, Zhe J C, and Salleh M S N 2021 Preparation and characterization of polysaccharide mediated copper nanoparticle: The effect of time-varying exposure *IOP Conf. Series: Materials Science and Engineering* **1051** 012096
[26] Taib S H M, Shameli K, Ali R R, Izadiyan Z, Tarmizi Z I 2021 Green synthesis of silver nanoparticles using *Hibiscus sabdariffa* leaves extract *Journal of Research in Nanoscience and Nanotechnology* **3** 76-81.