SYNTHESIS AND CHARACTERIZATION OF POLY(METHYL METHACRYLATE)/SILVER/PORPHYRIN NANOPARTICLES AND ITS ANTIBACTERIAL STUDIES ON *ESCHERICHIA COLI* AND *STAPHYLOCOCCUS AUREUS*

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DEDICATION

This thesis is dedicated to my beloved mother, Soheila who taught me that even the largest task can be accomplished if it is done one step at a time and to my dearest brother, Mohammad who motivated me to go on and not to give up.

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ABSTRACT

Preventing the bacterial colonization of different surfaces specially in the biomedical field with a technique that avoids the emergence of resistant bacteria is the key to limiting the spread of infections. The advancement of an antimicrobial coating material with photoactivated properties can be helpful in obviating the misuse or overuse of antibacterial substances and, therefore, prevents the development of superbugs. As a potential light-activated antibacterial material that employs two different antibacterial strategies, poly(methyl methacrylate) (PMMA) nanoparticles were impregnated with silver nanoparticles and cationic 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)porphyrin (TMPyP) *via* a novel one-pot miniemulsion technique. At first, silver nanoparticles were prepared *via* chemical and physical methods. The resultant colloids were compared based on the particle size and yield of the reaction. Chemical reduction of silver was carried out using aniline and sodium borohydride ($NaBH_4$) as different reducing agents. The effect of various parameters was optimized such as the order of mixing the reactants, presence of a stabilizer and time on stability, as well as size and concentration of the silver nanoparticles which were studied by UV-Vis. As a comparison, the physical technique was performed with ablation of a silver plate in distilled water with Q-switched Nd:YAG laser. The effect of ablation time and presence of a stabilizer on the production and stability of silver nanoparticles were optimized by using UV-Vis. Afterwards, the silver nanoparticles prepared *via* $NaBH_4$ reduction method were incorporated into PMMA *via* a novel miniemulsion method. The obtained products were then studied using UV-Vis DR, FTIR, ^1H NMR, FESEM, and TEM to investigate and optimize the polymerization, size of the particles and presence of silver in the samples. In the next phase, cationic porphyrin of TMPyP was synthesized from tetra pyridinyl porphyrin (TPyP) which was initially prepared *via* Alder-Longo condensation method. The obtained porphyrins were then characterized with UV-Vis, ^1H NMR, and FTIR. Consequently, PMMA/TMPyP and PMMA/TMPyP/silver nanoparticles were synthesized *via* our established miniemulsion method and were studied using UV-Vis DR and TEM to investigate the presence of porphyrin and silver in the samples. The antibacterial activities for all samples were evaluated by Kirby-Bauer test in dark against Gram-negative *E. coli* and Gram-positive *S. aureus.* Samples containing porphyrin were further tested under illumination to study the photoactivation of porphyrin. Silver nanoparticles studies showed that the silver nanoparticles prepared *via* reduction with $NaBH_4$ produced the highest yield with the size ranged between 7-25 nm and hence it was used in the production of polymer nanoparticles. Moreover, it was observed that in the physical technique, the production of silver nanoparticles increased by the time of ablation however, due to blockage of laser beam by silver nanoparticles the production was limited. The results of miniemulsion synthesis showed the successful production of PMMA/silver, PMMA/TMPyP, and PMMA/TMPyP/silver nanoparticles with high yields. The antibacterial test revealed that the use of two different antibacterial strategies improved the antibacterial properties of the polymer nanoparticles.

ABSTRAK

Pelindungan pelbagai permukaan daripada pembentukan koloni bakteria terutamanya dalam bidang bioperubatan dengan teknik yang menghalang peningkatan kerintangan bakteria merupakan kunci utama dalam mengawal perebakan jangkitan. Kemajuan bahan pelapis antimikrobial dengan sifat yang diaktifkan secara cahaya dapat membantu dalam mengatasi masalah penyalahgunaan atau terlebih guna bahan antibakteria, justeru menghalang pembentukan bakteria. Sebagai bahan antibakteria teraktif cahaya yang berpotensi menggunakan dua strategi antibakteria, nanopartikel poli(metil metakrilat) (PMMA) telah diisitepukan bersama nanopartikel perak dan porfirin kationik 5,10,15,20-tetrakis(*N*-metilpiridinium-4-il)porfirin (TMPyP) menggunakan kaedah baharu satu pot mini-emulsi. Untuk permulaan, nanopartikel perak telah disediakan menggunakan kaedah kimia dan kaedah fizikal di mana hasil koloid dibandingkan berdasarkan saiz partikel dan jumlah hasil tindak balas. Tindakbalas penurunan terhadap perak dijalankan menggunakan anilina dan sodium borohidrida ($NaBH_4$) yang bertindak sebagai agen penurun. Pengoptimuman parameter dilakukan berdasarkan aturan pencampuran reaktan, kehadiran penstabil dan masa penstabilan serta saiz dan kepekatan nanopartikel perak dengan menggunakan kaedah UV-Vis. Sebagai perbandingan, teknik fizikal ablasi dilaksanakan terhadap plat perak dalam air suling menggunakan laser Q-bersuis Nd: YAG. Kesan masa ablasi dan kehadiran penstabil terhadap nanopartikel perak dioptimumkan menggunakan kaedah UV-Vis. Seterusnya, nanopartikel perak yang disediakan menggunakan kaedah penurunan $NaBH_4$ telah digabungkan dengan PMMA menggunakan kaedah baharu mini-emulsi. Hasil gabungan telah dikaji menggunakan UV-Vis DR, FTIR, ^{1}H NMR, FESEM, dan TEM bagi mengkaji dan mengoptimumkan proses pempolimeran, saiz partikel dan kehadiran perak dalam sampel. Dalam fasa seterusnya, porfirin kationik TMPyP telah disintesis daripada tetra piridinil porfirin (TPyP) yang terlebih awal disediakan daripada tindak balas kondensasi Adler-Longo. Semua hasil porfirin dicirikan menggunakan UV-Vis, ^{1}H NMR, dan FTIR. Kemudian, nanopartikel PMMA/TMPyP dan PMMA/TMPyP/perak telah disintesis menggunakan kaedah mini-emulsi yang telah dibangunkan dan seterusnya dikaji menggunakan kaedah UV-Vis DR dan TEM bagi menentukan kehadiran porfirin dan perak dalam sampel. Aktiviti antibakteria semua sampel telah dijalankan menggunakan ujian Kirby-Bauer dalam keadaan gelap terhadap bakteria gram negatif *E. coli* dan gram positif *S. aureus*. Sampel yang mengandungi porfirin dikaji seterusnya dalam keadaan cahaya bagi mengkaji kesan fotoaktif porfirin. Kajian menunjukkan nanopartikel perak yang disediakan melalui kaedah penurunan menggunakan $NaBH_4$ mempunyai hasil yang tinggi dengan saiz di antara 7-25 nm, justeru digunakan untuk penghasilan polimer nanopartikel. Malah, penghasilan nanopartikel dengan kaedah fizik juga meningkat dengan peningkatan masa ablasi, namun masih terhad kerana sinar laser dihalang oleh nanopartikel perak. Keputusan sintesis miniemulsi menunjukkan kejayaan penghasilan nanopartikel PMMA/perak, PMMA/TMPyP, and PMMA/TMPyP/perak dengan hasil yang tinggi. Ujian antibakteria pula mengesahkan dengan menggunakan dua strategi antibakteria berbeza dapat meningkatkan sifat antibakteria nanopartikel polimer.

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LIST OF ABBREVIATIONS

AMR	-	Antimicrobial resistance
aPDT	-	Antibacterial photodynamic therapy
ATP	-	Adenosine triphosphate
CA	-	Cetyl alcohol
CTAB	-	Cetrimonium Bromide
DCM	-	Dichloromethane
DDM	-	Dodecyl mercaptan
DMSO	-	Dimethyl sulfoxide
DNA	-	Deoxyribonucleic acid
DSD	-	Droplet size distribution
EDTA	-	Ethylenediaminetetraacetic acid
F	-	Fluorescence emission
FESEM	-	Field Emission Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared Spectroscopy
HAIs	-	Hospital acquired infections
HBV	-	Hepatitis B virus
HD	-	Hexadecane
HDP-P	-	High density polyethylene
HIV	-	Human immunodeficiency virus
^{1}HNMR	-	Proton Nuclear Magnetic Resonance
ISC	-	Intersystem crossing
J	-	Coupling constant
KPS	-	Potassium persulfate
LAL	-	Laser ablation/irradiation in liquid
LB	-	Luria-Bertani Agar
LPS	-	Lipopolysaccharides
LUMO	-	Lowest unoccupied molecular orbital
MDR	-	Multidrug-resistance
MHA	-	Mueller-Hinton Agar
MMA	-	Methyl methacrylate

m-py	-	Meta-pyridine
MRSA	-	Methicillin-resistant *Staphylococcus aureus*
MW	-	Microwave irradiation
MWD	-	Molecular weight distribution
NADES	-	Natural deep eutectic solvents
NPs	-	Nanoparticles
o-py	-	Ortho-pyridine
P	-	Phosphorescence emission
PDT	-	Photodynamic therapy
PMMA	-	Poly methyl methacrylate
PNP	-	Polymer nanoparticle
p-py	-	Para-pyridine
PS	-	Photosensitizer
PSD	-	Particle size distributions
PSf	-	Polysulfone
PVP	-	Polyvinylpyrrolidone
R_f	-	Retention factor
RAFT	-	Reversible addition-fragmentation chain-transfer
RESOLV	-	Rapid expansion of a supercritical solution into a liquid solvent
RESS	-	Rapid expansion of supercritical solution
ROS	-	Reactive oxygen species
RSV	-	Respiratory syncytial virus
SCF	-	Supercritical fluid technology
SLS	-	Sodium Lauryl sulfate
TEM	-	Transmission Electron Microscopy
TFA	-	Trifluoroacetic acid
TMPyP	-	5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)porphyrin
TPP	-	Tetraphenylporphyrin
TPyP	-	5,10,15,20-Tetra(4-pyridyl)porphyrin
UV-Vis	-	Ultraviolet-visible spectroscopy
UV-Vis DR	-	Ultraviolet-visible Diffuse reflectance spectroscopy

LIST OF SYMBOLS

β	-	Beta
°C	-	Degree Celsius
υ	-	Frequency
γ	-	Gamma
g	-	Gram
Hz	-	Hertz
h	-	Hour
mol	-	Mole
M	-	Mole/litter
mJ	-	Milijoule
mL	-	Mililitter
nm	-	Nanometer
ns	-	Nanosecond
ppm	-	Part per million

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Microbial contamination on surfaces of different wound dressings, medical devices, food packages, industrial pipes, and separation membranes is a serious concern worldwide that poses a great threat to their efficiency and lifetime. In general, bacteria can adhere on these surfaces and grow under suitable environmental conditions to form biofilms. These surface-associated bacterial communities are very hard to eradicate due to different factors such as slow growth of bacteria in the biofilms, poor penetration of antimicrobials into the biofilm matrix, spatial heterogeneity in biofilm structure, formation of persisted cells, and drug tolerant physiology of the cells. The effective way to inhibit the biofilm-induced infection or contamination is by completely remove the contaminated devices or items and replace them with new ones, which is extremely costly and inconvenient. Therefore, there is a great necessity to design high-performance antibacterial surface coatings that can prevent biofilm formations by either destroying the bacteria or strongly resisting bacterial adhesions (Guo *et al.*, 2013 and Sathya *et al.*, 2019).

Nanomaterials play an important role in antibacterial applications particularly due to their large surface area and size-dependent physiochemical properties. Among various materials, polymeric materials are great candidates to form nanocomposites with different biocidal agents for antibacterial coatings due to their flexibility, tailorability, and availability of various techniques for polymer immobilization (Mauter *et al.*, 2011 and Duncan, 2011). These nanocomposite materials have strikingly upgraded properties which can be interestingly achieved at low nanoparticle concentrations. Polymers can act as surface topping specialist when nanoparticles are implanted in them (Puišo *et al.*, 2013). Incorporation of biocidal agents into polymeric nanomaterials has been commercially applied in drug and pesticide delivery, textiles, household goods, surgical implants and other biomedical devices (Sawant et el., 2013).

Poly (methyl methacrylate) PMMA is a biocompatible, low-cost, light-weight, mechanically strong, and transparent polymer, most frequently used in medical, pharmaceutical, and food packaging industries. In the medical field, PMMA has been used as implants, intra ocular lenses, synovial joints, drug delivery agents, dentures and wound dressings (Kanie *et al.*, 2004, and Tihan *et al.*, 2009). There have been numerous reports on synthesis of PMMA/antibacterial agent nanocomposites for active coatings to prevent biofilm formations on different surfaces. For instance, PMMA has been loaded with gentamycin in bone cements, PMMA/chitosan nanoparticles have been synthesized as coating materials for latex gloves, and PMMA/silver nanocomposites have been prepared as a bioactive water filter (Arpornwichanop *et al.*, 2014, Alvarez-Paino *et al.*, 2017 and Awad *et al.*, 2019). Among various antimicrobial agents, silver nanoparticles are the most widely used as polymer additives due to their physiochemical properties and area of use (Siddiqui *et al.*, 2015).

Silver nanoparticles are well-known antibacterial agents that have been used in the biomedical field to prevent infectious disease or colonization of biomedical devices by pathogenic microorganisms (Carlos *et al.*, 2020). Due to large surface area per mass, silver nanoparticles exhibit remarkable antibacterial activity, even at low concentration. Moreover, they are low-cost and have shown limitation of developing resistant microbial strains, low cytotoxicity and immunological response (Yin *et al.*, 2020). Materials impregnated with silver nanoparticles may preserve their antibacterial activity over a long-time period, hence, combination of polymeric materials with silver nanoparticles provides excellent composites for prefect antimicrobial coatings (Lyutakov *et al.*, 2015).

Incorporation of silver nanoparticles into polymeric matrices has pronounced potential to inhibit aggregation of nanosilver and create uniform surface coatings on various substrates. Moreover, these materials can control the release of silver for sustained antimicrobial effects, decrease cytotoxicity and more importantly, can be designed to resist adhesion of bacteria and enhance bactericidal properties. Therefore, it is highly beneficial to combine silver nanoparticles and polymer matrices to produce multifunctional nanocomposite coatings for antibacterial applications (Eby *et al.*, 2009 and Sur *et al.*, 2010).

Several chemical approaches have been reported to incorporate silver nanoparticles into polymer matrices. For all of them, in-situ and ex-situ methods are the main route of preparation. In the in-situ approach, either polymerization of monomers takes place in the presence of pre-synthesized silver nanoparticles which are dispersed in the monomeric solution before polymerization or silver ion reduction and polymerization occurs simultaneously. On the other hand, in the ex-situ approach, silver nanoparticles and polymer are synthesized separately and subsequently silver nanoparticles are incorporated into the polymer via either melt compounding or solution blending. The ex-situ synthesis method is more suitable wherever large-scale industrial applications are required but the key challenge related to this technique is preparing nanoparticles that have higher dispersibility in the polymer and long-term stability against aggregation (Tamayo *et al.*, 2019).

In recent years, much effort has been devoted to the studies of in-situ synthesis of metal nanoparticles in polymer matrices. The most important advantage of this technique is that it prevents particle agglomeration and maintains a good spatial distribution of nanoparticles in the polymer matrix whereas, the major drawback of this method is the slight probability of the presence of unreacted educts in the course of reaction. For instance, according to Yin *et al.* polyacrylamide/silver nanocomposites were prepared by simultaneous reduction of silver ions and polymerization of monomers using 60Co γ-ray (Yin *et al.*, 1998). In another work, Huang and Brittain prepared PMMA/layered silicate nanocomposites by in situ suspension polymerization. Similarly, Yeum and Deng synthesized PMMA/silver microspheres by suspension-polymerizing methyl methacrylate in the presence of silver nanoparticles (Yeum & Deng 2005, and Sadasivuni *et al.*, 2019). However, developing an easy and straightforward method to incorporate silver nanoparticles into the polymeric matrices is still a challenge.

The active polymer/silver coatings are mostly based on creating cationic or charged surfaces that release silver nanoparticles or silver ions as antibacterial agents from their structure. However, for most of these systems the antibacterial properties are lost once the silver source is consumed (Zhou *et al*., 2017). Moreover, silver nanoparticles can exhibit different efficiencies towards different kinds of bacteria and furthermore towards one stamp to another. Generally, silver nanoparticles have been shown to be more effective against Gram-negative bacteria, than Gram-positive strains (Lyutakove *et al*., 2014). Therefore, in order to design an effective antibacterial coating that can continuously inactivate both Gram-positive and Gram-negative bacteria, employing another antibacterial strategy to the polymeric nanocomposites can be beneficial.

One of the antibacterial approaches that has recently attracted great attention is antibacterial photodynamic therapy (aPDT). This non-antibiotic treatment modality utilizes photosensitizers and visible light to induce an oxidative damage to microbial pathogens and due to its multi-target process, it is unlikely that it induces resistance in microorganism. As one of the major problems in eradicating biofilms on the surfaces is the emergence of resistant bacteria strains due to the use of conventional antibiotics, employing aPDT can be a useful alternative (Yu *et al*., 2008 and Humblin, 2016).

The concept of photodynamic therapy consists of the action of three components which are photosensitizer (PS), a light source of appropriate wavelength and the presence of oxygen. The interactions between light and PS generates reactive oxygen species (ROS) which then destroy a variety of cellular components like proteins, nucleic acids and lipids, resulting in cytotoxicity (Mahajan *et al.* 2019). Among the photosensitizer molecules, porphyrins are one of the most commonly used photosensitizers in aPDT due to their high frequency, high rate of ROS production and easy chemical modifications (Ghorbani *et al*., 2018).

Generally, porphyrins bind efficiently to Gram-positive bacteria and inactive them, however, Gram-negative bacteria are known to be more resistant to treatment with porphyrin photosensitizers. Studies show that cationic porphyrins exhibit more unique superiority comparing to anionic or neutral porphyrins as they can photoinactivate both Gram-positive and Gram-negative bacteria. The high susceptibility of Gram-positive species to porphyrins photosensitizers is attributed to the presence of a relatively porous layer of peptidoglycan and lipoteichoic acid in their cell wall, which allows the photosensitizer molecules to diffuse to the target sites within the cell. In contrast, due to the presence of negatively charged lipopolysaccharides (LPS) in the cell wall of Gram-negative bacteria, the permeability of neutral or anionic porphyrins in the external environment into the bacterial cell is hindered while cationic porphyrins effectively interact with these negatively charged surfaces of Gram-negative bacteria and photo-inactivate them (Amos-Tautua *et al.*, 2019).

Antibacterial efficacy of porphyrins in PDT can be further exploited through the fixation of these molecules in support materials and the resultant materials appear to be effectively self-sterilizing. Different support materials have been proposed and studied, including polymers, silica, cellulose, and glass where porphyrins may be entrapped, absorbed or covalently attached to the surface of these carriers (Almeida *et al.*, 2009). Porphyrin-containing polymers are a promising class of materials for aPDT. It has been reported that embedding a porphyrin within a well-defined polymer nanoenvironment can greatly decrease aggregation and excited-state quenching, which are deleterious to many photophysical processes (Roberts *et al.*, 2014 & Zhou *et al.*, 2017). For instance, in a study conducted by Zhdanova *et al.* synthesis of a new cationic pyridyl-containing meso-arylporphyrins in polymeric micelles was reported and their antibacterial photodynamic activity against both Gram-negative (*Escherichia coli*) and Gram-positive (*Staphylococcus aureus*) bacteria in solution and biofilm modes was evaluated. Their results showed that the inclusion of the photosensitizers in polymeric micelles of Pluronic F-127 significantly increased their photodynamic activity. Moreover, in vitro experiments showed that the proposed porphyrins quite strongly inhibit the growth of Gram-positive *S. aureus*, however, Gram-negative *E. coli* inhibition was slightly lower (Zhdanova *et al.*, 2020).

Antibacterial surfaces which work with the PDT principle are of great interest due to their preventive character for infections. These surfaces can potentially help to reduce the transmission of pathogens, particularly multi-resistant microorganisms, which are a huge problem especially in hospital hygiene. As the photodynamic process of such surfaces does not necessarily lead to the photosensitizer consumption, self-disinfecting coatings could offer a long-term and constant prevention of microorganism settlement and growth on any surface (Felgentrager *et al.*, 2014).

In order to create an effective antibacterial coating system for different surfaces that battles the emergence of resistant bacteria, in this study, aPDT strategy with the use of 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)porphyrin (TMPyP) as a cationic photosensitizer was combined with silver nanoparticles containing polymeric material via one-pot miniemlusion technique. Integrating these two different antibacterial strategies into one system can create a positive synergic effect and overcome the possible low efficiency of individual treatments.

1.2 Problem Statement

Antimicrobial resistance (AMR) poses a serious threat of growing concern to human, animal, and environment. The challenge of antimicrobial resistance in bacterial pathogens is associated with high morbidity and mortality and this is due to the emergence, spread and persistence of multidrug-resistance (MDR) bacteria (Aslam *et al.*, 2018). Gram-positive and -negative bacteria with multidrug resistance patterns are very difficult to treat and might even be untreatable with conventional antibiotics. Currently, due to a shortage of effective therapies, lack of successful prevention measures, and only a few new antibiotics, there is an urgent need to develop novel treatment options and alternative antibacterial therapies (Frieri *et al.*, 2017). The biofilms grown on solid substrates have shown extraordinary resistance to conventional antibiotic treatments and can present challenges for infection control. As a result, the research has been driven towards the development of novel coatings with superior antimicrobial properties. These may include not only in the medical area such as for surgical tools or implants, but also in a number of technical applications including underwater optics or ship hulls (Zhou *et al.*, 2017).

Silver nanoparticles are widely used in industry, mainly because of their effective antimicrobial properties, with applications in a growing number of medical and consumer products (Diaz *et al.*, 2013). They have also been studied as candidates for coating medical devices, however, the results have been disappointing in clinical tests. This might be due to inactivation of metallic silver when it comes in contact with blood plasma and also the lack of durability of the coatings. Incorporating silver nanoparticles with polymers however, has shown promising antibacterial properties with a sustained release of silver (Kong & Jang, 2007 and Rai *et al.*, 2008).

Poly(methyl methacrylate) (PMMA) is an important polymeric material that has been widely used as additives, coating and polishing agents due to its superior characteristics such as high light transmittancy, colourlessness, chemical resistance, and weathering corrosion resistance (Nuyken & Lettermann, 1992 and Yeum & Deng, 2005). In the past decade, various attempts have been made to incorporate silver nanoparticles into PMMA nanomaterials in order to produce biocidal surfaces and coatings. For instance, Damm and co-workers coated PMMA sheets by silver dispersion techniques using silver nanoparticles stabilized with various polymers (Damm *et al.*, 2006). However, once the silver reservoir in these coatings is consumed, the antimicrobial properties of such surfaces are lost (Zhou *et al.*, 2017). Moreover, it has been reported that silver nanoparticles in general are more effective against Gram-negative bacteria than Gram-positive ones (Lyutakov *et al.*, 2014).

To overcome such problems, antibacterial photodynamic therapy (aPDT) was introduced to PMMA/silver substrate by utilizing porphyrins as photosensitizers in some studies. It was reported that the photodynamic process of porphyrins incorporated into PMMA/silver system does not naturally lead to their consumption, hence, they could offer a long-term antimicrobial effect on any surfaces. However, due to the use of free base tetraphenylporphyrin (TPP) in these studies, the antibacterial properties of the system against Gram-negative bacteria were relatively lower than Gram-positive bacteria (Lyutakov *et al.*, 2014 and Elashnikov *et al.*, 2016) as it has been shown that neutral porphyrins are not very effective against Gram-negative bacteria (Moghnie *et al.*, 2017). Therefore, the challenge of generating a promising antibacterial system that can be effective against both Gram-positive and Gram-negative bacteria remains elusive.

In addition, PMMA/porphyrin/nanosilver materials in the literature have been reported to be fabricated via spin coating or electrospinning techniques in the form of thin films and nanofibers respectively, however, these techniques have certain limitations and drawbacks (Lyutakov *et al*., 2014 and Elashnikov *et al*., 2016). One of the biggest disadvantages of spin coating is its lack of material efficiency. In a typical spin coating process, only 2-5% of the material dispensed onto the substrate is utilized, while the remaining 95-98% is flung off into the coating bowl and disposed and therefore the manufacturing process is costly and not economically feasible (Sahu *et al*., 2009). Electrospinning is also a costly technique with limited application of electro-spun nanofibers due to their friability after calcination (Shi *et al*., 2015). Hence, finding an easy straightforward technique to fabricate PMMA/porphyrin/silver nanomaterials remains a challenge.

1.3 Research Objectives

The objectives of this research are:

i) To synthesize silver nanoparticles via reduction techniques and laser ablation and compare their findings.
ii) To synthesize PMMA/silver nanocomposites via miniemulsion.
iii) To synthesize 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)porphyrin (TMPyP) and fabricate PMMA/TMPyP/silver nanocomposites via miniemulsion.
iv) To investigate the antibacterial activity of the resultant products against *Escherichia coli* and *Staphylococcus aureus* bacteria using Kirby-Bauer disk diffusion technique.

1.4 Scope of Study

This study initially consists of the synthesis of silver nanoparticles via chemical reduction and laser ablation techniques. In the chemical method, $AgNO_3$ was used as a metal salt precursor, CTAB and SLS were the stabilizing agents and aniline and sodium borohydride were used as two different reducing agents. In the reduction with aniline, different modes of mixing of the reagents and the effect of stirring on the size of the nanoparticles were studied. The reduction of silver with sodium borohydride was carried out using different initial $AgNO_3$ concentrations (0.0001 M, 0.0002 M, 0.0005 M and 0.001 M). Colloidal silver obtained from both reductions were then compared based on the size and yield of the nanoparticles. Silver nanoparticles were also prepared via laser ablation technique while silver plate was immersed in the solution of distilled water and SLS and shot with a Q-switched Nd:YAG laser for different durations. Ablation of silver without the use of SLS was also conducted to study the effect of the stabilizer on the production of nanoparticles.

The silver nanoparticles with different concentrations obtained from the reduction with sodium borohydride were then used as the water phase in miniemulsion polymerization of methyl methacrylate and as a result, PMMA/silver nanoparticles with different concentrations of silver were produced. Moreover, the pure polymer nanoparticles were also synthesized via miniemulsion with deionized water as the water phase.

The cationic porphyrin used in this study was 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)porphyrin (TMPyP) which was prepared by methylation of 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)porphyrin (TPyP) using methyl toluenesulfonate. Prior to the methylation, TPyP was prepared by using Adler-Longo method. Different amounts of as-synthesized TMPyP in deionized water were then used as the water phase in the miniemulsion polymerization of MMA to obtain PMMA/TMPyP with different concentrations of TMPyP. The polymer nanoparticles containing both TMPyP and silver nanoparticles were prepared using different amounts of TMPyP solution and different amounts of silver nanoparticles solution as the water phase in the miniemulsion process to produce PMMA nanoparticles with different combinations of TMPyP and silver nanoparticles.

The antibacterial properties of prepared PMMA, PMMA/silver nanoparticles with different concentrations of silver, PMMA/TMPyP nanoparticles containing different amounts of TMPyP and PMMA/TMPyP/silver nanoparticles with different amounts of TMPyP and silver were evaluated using Kirby-Bauer test against *E. coli* and *S. aureus* bacteria in dark. The antibacterial properties of samples containing porphyrin were further investigated under illumination to study the effect of light in the activation of photoinactivation properties of porphyrin.

Silver nanoparticles were characterized and studied using UV-Vis spectroscopy and Transmission Electron Microscope (TEM). Polymer nanocomposites were characterized using UV-Vis DR spectroscopy, ^{1}HNMR, FTIR, FESEM and TEM.

1.5 Significance of Study

Currently, the second leading cause of death worldwide is infectious diseases and this is directly related to the constant growth in the resistance of many pathogens to current antibiotics (Fischbach *et al.*, 2009 and Garcia-Alvarez *et al.*, 2012). Antimicrobial resistance (AMR) in bacterial pathogens is a worldwide problem that leads to high morbidity and mortality and this because of the emergence, spread, and persistence of multidrug- resistance bacteria or “superbugs”. The tenable causes of AMR or “the global resistome” include the excessive use of antibiotics in animals (food, pets, aquatic) and humans, sale of antibiotics without prescription, increased international travels, poor hygiene, and release of nonmetabolized antibiotics or their residues into the environment through manure or feces (Aslam *et al.*, 2018).

The spread of many of these infectious diseases are associated with contaminated surfaces such as medical devices, implants, water filters, and food packages. The growth of bacteria on these surfaces and formation of biofilms are notoriously difficult to be removed as biofilms provide ideal shelters for bacteria to metabolize safely with much tolerance to antibiotics (Yuan *et al.*, 2008 and Lichter *et al.*, 2009). Therefore, there is an expanding interest in the development and design of new coating materials that are effective killing bacteria and preventing the spread of pathogens without creating antibacterial resistance (Vasilev, 2019).

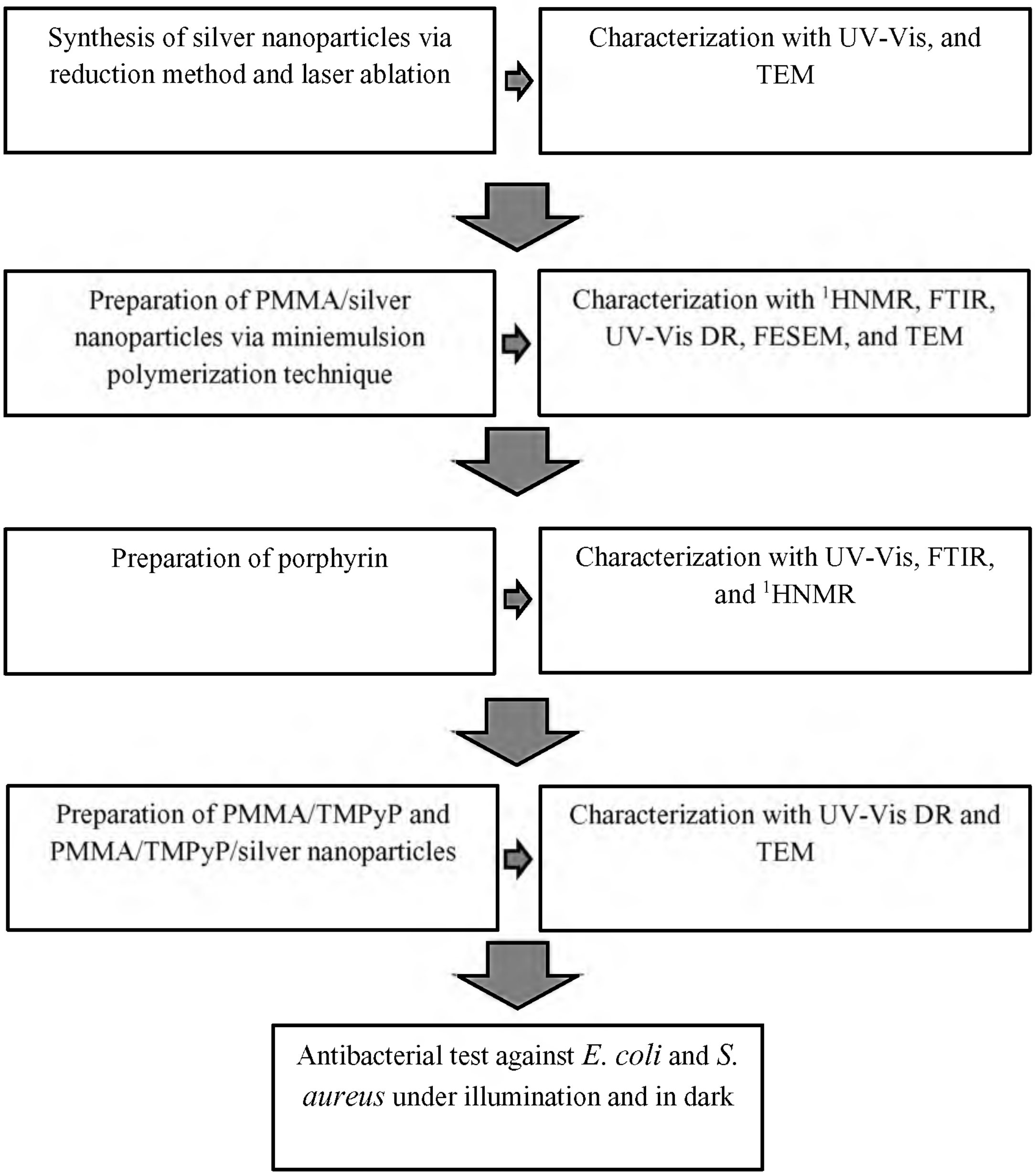
In order to develop an effective antimicrobial material, recent studies have been focused on integrating different biocidal techniques into polymeric matrices in order to take advantage of various approaches at once (Levy *et al.*, 2004). Among the antibacterial agents, silver nanoparticles have been found to be excellent antimicrobial agents due to their effective biocidal ability which makes it hard for bacteria to develop resistance and nontoxicity to human cells (Kong & Jang, 2007). On the other hand, in the field of antibacterial photodynamic therapy (aPDT), cationic porphyrins have received great attentions due to their ability to produce reactive oxygen species and effectively inactivate both Gram-positive and -negative bacteria in the presence of light (Goncalves *et al.*, 2020). Employing these two different antibacterial strategies into a polymeric matrix, can potentially create a more effective antibacterial material for coating applications (Creanga *et al.*, 2013).

In order to accomplish this goal, finding an easy synthetic route that is straightforward is crucial. The miniemulsion technique is a particular heterophase polymerization which allows the formation of functionalized polymers by polymerization or modification of polymers in stable nanodroplets. The use of water rather than organic solvents makes miniemulsion polymerization an environmentally friendly technique. Moreover, miniemulsion is a one-pot synthetic route with high polymer yield that is easy to perform and cost effective (Crespy & Landfester, 2010). The water phase in the miniemulsion enables the use of water-soluble antibacterial agents in the reaction mixture. Therefore, it is a suitable technique to employ for incorporation of antibacterial agents into the polymer matrix.

In this research, in order to combine aPDT strategy with PMMA/silver nanoparticles system, 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)porphyrin (TMPyP) was used as a cationic photosensitizer, as it has been observed that cationic porphyrins can successfully photoinactivate both Gram-positive and Gram-negative bacteria, as well as fungi. Moreover, fabrication of PMMA/silver, PMMA/TMPyP, and PMMA/TMPyP/silver nanoparticles systems was delivered using a one-pot miniemulsion method which is an easy environmentally friendly process that simultaneously polymerizes MMA and incorporates silver nanoparticles and the porphyrin into the polymer nanoparticles. Finally, the switchable antibacterial properties of the resultant nanocomposites were evaluated against *E. coli* and *S. aureus* bacteria in absence and presence of light.

This study enables the development of antibacterial materials that get use of two different strategies against formation of biofilms for coating purposes. In addition, this work can be used as a synthesis model to fabricate new and more effective antimicrobial nanocomposites.

1.6 Project Outline



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