

**CONTROLLED GREEN SYNTHESIS OF SILVER  
NANOPARTICLES USING LOCALLY AVAILABLE PLANTS  
FOR IN-SITU PREPARATION OF DURABLE MULTI-  
FUNCTIONAL COTTON FABRICS**

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OCTOBER 2020**

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**Controlled green synthesis of silver  
nanoparticles using locally available plants  
for in-situ preparation of durable multi-  
functional cotton fabrics**

by

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***Submitted***

*in fulfillment of the requirements of the degree of Doctor of Philosophy*

*to the*



**Indian Institute of Technology Delhi  
OCTOBER 2020**

*Dedicated to*  
My Parents Late Mr. R.K. Sharma and Mrs.  
Pawan Sharma

# Certificate

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This is to certify that the thesis entitled “**Controlled Green Synthesis of Silver Nanoparticles using Locally Available Plants for In-situ Preparation of Durable Multi-functional Cotton Fabrics**” being submitted by Ms. Ashu Jain to the Indian Institute of Technology Delhi for the award of “**Doctor of Philosophy**” is a record of bonafide research work carried out by her. She has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis. To the best of our knowledge the results contained in this thesis have not been submitted in part or full to any other university or institute for award of any degree or diploma.

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# Acknowledgements

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My PhD supervisors Prof. Anushree Malik and Prof. Hitendra Kumar Malik have been always there for me, helped me overcome the numerous obstacles that came my way during the course of my PhD, for being patient with me and for expecting nothing less than excellence from me. Thank you, because I owe it all to you!

I am grateful to my children, Deepanshi, Kriteesha, Yash and Bicky for encouraging me out of frustrating moments during PhD. I will never forget your screams of joy whenever I reached a milestone. I am extremely grateful to my husband, Mr. Sannat Jain who supported me emotionally and took pride in my slightest of achievements. My mother, Mrs. Pawan Sharma who lived her dreams through me always keen to know how I was proceeding; although I am sure she never really was able to grasp what it was all about. My sister, Anuja Bhardwaj who is my anchor, my lifecoach, my sounding board and my cheerleader for life!

A very special gratitude goes out to Prof. Bhupendra Singh Butola, Department of Textile Technology, IIT Delhi for his immense help in my research work.

I would like to thank my fellow labmates from the Applied Microbiology Lab and from Plasma Science and Technology Lab; Dr. Megha Mathur, Dr. Arghya Bhattacharya, Dr. Raashi Vishwakarma, Ms. Farhat, Ms. Farha Naaz, Mr. Saurabh Samoochiwal, Mr. Rahul Jain, Ms. Harshita Nigam, Ms. Shweta Kalia, Mr. Rahul Kumar, Mr. Saptarishi Dey, Mr. Vivek Dalvi, Dr. Dimple Sharma, Mr. Rajat Dhawan, Mr. Manish Dwivedi, Mr. Sonu Kumar, Mr. Dhanajay Verma, Mr. Sandeep Singh, Mr. Munish, Ms. Sheetal Punia, Ms. Tammanna Punia, Dr. Aparna Sharma, Mr. Yetendra Prasad Jha , Mr. Mohit Kumar, Mr. Subhajit Bhaskar for their encouragement, motivation, cooperation and of course friendship. It was a fantastic experience of working in midst of you all. It was really great sharing laboratory with you all during my PhD years.

I would specially like to mention Ms. Mayuri Srivastava who helped me with experimentation at Textile Chemistry Lab and for her last minute favors.

I would also like to thank Dr. Nitin Chauhan and Dr. Deepak Gola, my senior from AML for sharing their dissertation woes, and assuring me of post-dissertation normalcy.

A special mention to DST for supporting my work and for funding my research through Women Scientist Scheme A.

Thank you all for your encouragement!



Ashu Jain

# Abstract

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Nanotechnology is the dominant technology in today's world because of the scope of tailoring of the functionalities by altering the size, shape or constitution of nanomaterials. Silver nanoparticles (SNPs) are amongst the most widely researched nanoparticles because of their wide applicability and because of their ease of synthesis. Green nanotechnology is getting a lot of attention owing to environmental concerns but the green synthesis method for SNPs is yet to be adopted commercially because of lack of control over synthesis. The present study describes the screening process for shortlisting of leaf extract to be used for controlled SNPs synthesis. The leaf extracts of *Murraya koenigii*, *Carica papaya*, *Eucalyptus hybrida*, *Azadirachta indica*, *Ocimum sanctum* and *Chenopodium album* were chosen for the screening on the basis of their reported efficiency in synthesizing stable, spherical and monodisperse SNPs on review of literature. Leaf extracts of selected plants were reacted with AgNO<sub>3</sub> under identical conditions and the synthesized SNPs were analyzed for uniformity in size and shape and for stability on the basis of UV-absorption spectra and TEM images. The SNPs synthesized using leaf extract of *Azadirachta indica* remained stable within the observation duration of 24 hours. Optimization of synthesis parameters for the selected leaf extract of *Azadirachta indica* was carried out and stable SNPs having a narrow size range and an average size of 6 nm and 24 nm and of spherical shape were synthesized having a zeta potential of -16.8 mV and -16.2 mV, respectively.

The SNPs synthesized using leaf extract of *Carica papaya* were spherical but not of uniform size. In the present study, *Carica papaya* leaf extract was used for the synthesis of silver nanoparticles (Pa-SNPs). The SNPs yield was increased by optimization of parameters such as temperature and pH. The spherical shape of synthesized Pa-SNPs was clearly seen in the TEM micrographs with size ranging from 10 - 70 nm. The presence of silver in the sample was highlighted by the EDS analysis. Zeta potential and DLS were performed in order to analyze the stability and average size of Pa-SNPs. The high stability of the synthesized SNPs was indicated by the zeta potential which showed the value of -12 mV. The average size of the Pa-SNPs as indicated by DLS was 68 nm. Further, the antimicrobial activity of the Pa-AgNPs along with few antibiotics (penicillin, kanamycin and chloramphenicol) was evaluated against *E. coli* and *S. aureus*. A synergistic effect was observed with AgNPs combined with antibiotics in Zone of inhibition assay. In the dye degradation assay, ability of Pa-AgNPs was studied for Blue CP and Yellow 3RS. The results showed effective degradation ability of Pa-AgNPs with 90% and 83 % removal for Blue CP and Yellow 3RS, respectively, at 50 mg/l of dye concentration.

Precision in synthesis requires a very precise understanding of the kinetics involved in the nucleation and the growth kinetics involved in the formation of the nanoparticles. Even though the green synthesis of SNPs has been extensively reported in literature, however, in terms of understanding of crystallization kinetics it is a dark zone primarily because of the lack of understanding of the reduction and the stabilization mechanism involved in the formation of silver nanoparticles. In this study, a hypothesis regarding the kinetics involved in nucleation and growth of SNP was developed on the basis of data reported in literature and on the basis of experimental results recorded by us. The hypothesis was to be used as a basis for design of engineered synthesis to enable size specific synthesis of SNP. According to the developed hypothesis, the synthesis conditions during nucleation for synthesis of uniform size nuclei and the conditions to ensure their growth into SNP of uniform size and shape were different. A mathematical model was developed for seed mediated multistep green synthesis using *Azadirachta indica* leaf extract, using which SNPs of required size could be synthesized. The size of the SNPs synthesized was close to the size predicted by the model.

In the last part of the thesis, cotton fabrics were coated with silver nanoparticles by an environment friendly method using in-situ reduction of silver nitrate with leaf extract of *Azadirachta indica*. For improving the wash durability of silver nanoparticle coating, mercerization of cotton fabrics was used as a pre-treatment followed by in-situ synthesis of nanoparticles under hydrothermal conditions of 120 °C temperature of and 15 psi pressure. The coated fabrics were characterized by Scanning Electron Microscopy, Inductively Coupled Plasma Mass Spectroscopy and Colorimetric analysis. Antibacterial activity of the silver nanoparticle treated fabrics was determined both against Gram-positive and Gram-negative bacteria by colony counting method. The UV protection factor of the fabric samples was measured on a UV spectrophotometer via transmittance data in the range of 290 – 400 nm. The impact of density of silver nanoparticle deposition on the mechanical strength of the fabric was also evaluated. The microscopic images of the fabrics showed dense and uniform coating of silver nanoparticles. All the samples showed excellent antimicrobial activity and UV-protection that varied from very good to excellent (UPF 33.4 - 89.9). There was no degeneration of mechanical strength of the fabrics after treatment with silver nanoparticles. The silver nanoparticle treatment to fabric also showed excellent durability against repeated laundering. The cost analysis of the SNPs treatment at a cottage industry scale showed its commercial viability also.

## सार

नैनो तकनीक आज की दुनिया में एक प्रमुख तकनीक है क्योंकि नैनोमेट्रिक्स के आकार, आकृति या संरचना में परिवर्तन के कारण नैनो संरचना की कार्यात्मकता में परिवर्तन की जा सकती है। चाँदी के नैनोकणों (एसएनपी) सबसे व्यापक रूप से शोध किए गए नैनोकणों में से हैं, क्योंकि इनकी व्यापक प्रयोज्यता और संश्लेषण सरल है। ग्रीन नैनोटेक्नोलॉजी में पर्यावरण संबंधी चिंताओं के कारण बहुत अधिक ध्यान दिया जा रहा है, लेकिन एसएनपी के लिए हरी संश्लेषण विधि को अभी तक व्यावसायिक रूप से अपनाया जाना है क्योंकि संश्लेषण पर नियंत्रण नहीं है। वर्तमान अध्ययन में नियंत्रित एसएनपी संश्लेषण के लिए उपयोग किए जाने वाले पत्ती के अर्क का चयन करने के लिए स्क्रीनिंग प्रक्रिया का वर्णन है। साहित्य की समीक्षा पर स्थिर, गोलाकार और एकरूप एसएनपी को संश्लेषित करने में उनकी वर्णित दक्षता के आधार पर करी पत्ता (*Murraya koenigii*), पपीता (*Carica papaya*), यूकेलिप्टस हाइब्रिडा (*Eucalyptus hybrida*), नीम (*Azadirachta indica*), तुलसी (*Ocimum sanctum*) और बथुआ (*Chenopodium album*) के पत्ते के अर्क को चुना गया। चयनित पौधों के पत्तों के अर्क को समान परिस्थितियों में  $\text{AgNO}_3$  के साथ प्रतिक्रिया दी गई और संश्लेषित एसएनपी का आकार और आकृति में एकरूपता के लिए और यूवी-अवशोषण स्पेक्ट्रा और टीईएम छवियों के आधार पर स्थिरता के लिए विश्लेषण किया गया। नीम के पत्ती के अर्क के उपयोग से संश्लेषित एसएनपी 24 घंटे के अवलोकन की अवधि के भीतर स्थिर रहा। नीम के चयनित पत्ती निकालने के लिए संश्लेषण के मापदंडों का अनुकूलन किया गया था और एक संकीर्ण आकार सीमा एवं 6 nm और 24 nm के औसत आकार और गोलाकार आकार वाले स्थिर सिल्वर नैनोकणों संश्लेषित किए गए थे। ज़ीटा पोटेंशियल क्रमशः -16.8 mV और -16.2 mV था।

पपीता के पत्ती के अर्क से संश्लेषित एसएनपी गोलाकार थे लेकिन समान आकार के नहीं थे। वर्तमान अध्ययन में पपीता के पत्ती के अर्क निकालने का उपयोग चाँदी के नैनोकणों (पा-एसएनपी) के संश्लेषण के लिए किया गया था। तापमान और पीएच जैसे मापदंडों के अनुकूलन से एसएनपी की उपज में वृद्धि हुई थी। संश्लेषित पा-एसएनपी के गोलाकार आकार को TEM माइक्रोग्राफ में 10 - 70 nm की सीमा में आकार के साथ स्पष्ट रूप से देखा गया था। नमूने में चाँदी की उपस्थिति को ईडीएस विश्लेषण द्वारा उजागर किया गया था। पा-एसएनपी की स्थिरता और औसत आकार का विश्लेषण करने के लिए ज़ीटा पोटेंशियल और डीएलएस का प्रदर्शन किया गया। संश्लेषित एसएनपी की उच्च स्थिरता को ज़ीटा पोटेंशियल द्वारा इंगित किया गया था, जो -12 mV के मूल्य को दर्शाता है। डीएलएस द्वारा दर्शाए गए पा-एसएनपी का औसत आकार 68 nm था। इसके अलावा, *Escheichia coli* और *Staphylococcus aureus* के खिलाफ कुछ एंटीबायोटिक दवाओं (पेनिसिलिन, केनामाइसिन और क्लोरैम्फेनिकॉल) के साथ पा-एसएनपी की रोगाणुरोधी गतिविधि का मूल्यांकन किया गया था। निषेध परख के क्षेत्र में एंटीबायोटिक दवाओं के साथ संयुक्त AgNPs के साथ एक सहक्रियात्मक प्रभाव देखा गया। डाई क्षरण परख में, ब्लू सीपी और येलो 3 आरएस के लिए पा एसएनपी की क्षमता का अध्ययन किया गया था। परिणामों में 90% और ब्लू सीपी और येलो 3RS के लिए क्रमशः 83% हटाने, डाई एकाग्रता के 50% और 83% के साथ Pa-AgNPs की प्रभावी गिरावट देखी गई।

संश्लेषण में परिशुद्धता को न्यूक्लियेशन में शामिल बलगति विज्ञान और नैनोकणों के निर्माण में शामिल विकास बलगति विज्ञान की बहुत सटीक समझ की आवश्यकता होती है। भले ही एसएनपी के पर्यावरण के अनुकूल संश्लेषण को साहित्य में बड़े पैमाने पर बताया गया है, परन्तु क्रिस्टलीकरण बलगति विज्ञान की समझ के संदर्भ में यह मुख्य रूप से कमी और चाँदी नैनोकणों के गठन में शामिल स्थिरीकरण तंत्र की समझ की कमी के कारण एक रहस्य है। इस अध्ययन में, एसएनपी के न्यूक्लियेशन और विकास में शामिल बलगति विज्ञान के बारे में एक परिकल्पना को साहित्य में रिपोर्ट किए गए आँकड़ों के आधार पर और हमारे द्वारा दर्ज किए गए प्रयोगात्मक परिणामों के आधार पर विकसित किया गया था। एसएनपी के विशिष्ट आकार का व्यवस्थित संश्लेषण को सक्षम करने के लिए आधार के रूप में परिकल्पना का उपयोग किया गया था। विकसित परिकल्पना के अनुसार समान आकार के एसएनपी के संश्लेषण के लिए न्यूक्लियेशन के दौरान संश्लेषण की स्थिति और समान आकार और आकार के एसएनपी में उनके विकास को सुनिश्चित करने के लिए स्थितियाँ अलग थीं। एसएनपी के विशिष्ट आकार का व्यवस्थित संश्लेषण के लिए एक गणितीय मॉडल विकसित किया गया था जिसका उपयोग नीम के पत्ती के अर्क का उपयोग करके किया गया है, जिसके उपयोग से आवश्यक आकार के एसएनपी का संश्लेषण किया जा सकता है। संश्लेषित एसएनपी का आकार मॉडल द्वारा अनुमानित आकार के करीब था।

शोध ग्रन्थ के अंतिम भाग में, सूती कपड़े को चाँदी के नैनोकणों के साथ एक पर्यावरण के अनुकूल विधि द्वारा लेपित किया गया था, जिसमें नीम के पत्ती के अर्क के साथ  $\text{AgNO}_3$  की स्वस्थानी प्रतिक्रिया द्वारा कपड़े पर निक्षेप के लिए उपयोग किया गया था। चाँदी के नैनोकणों के निक्षेप के टिकाऊपन में सुधार के लिए, सूती कपड़ों के mercerization का उपयोग एक पूर्वोपचार के रूप में किया गया, जिसके बाद 120 C तापमान और 15 psi दबाव के हाइड्रोथर्मल स्थितियों के तहत नैनोकणों का स्वस्थानी संश्लेषण किया जाता है। लेपित कपड़े को स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी, इंडिकली कपल्ड प्लाज़्मा मास स्पेक्ट्रोस्कोपी और Colorimetric विश्लेषण के द्वारा परखा गया। सिल्वर नैनोकणों से उपचारित कपड़ों की जीवाणुरोधी गतिविधि को कॉलोनी की गिनती विधि द्वारा ग्राम-सकारात्मक और ग्राम-नकारात्मक बैक्टीरिया दोनों के विरुद्ध निर्धारित किया गया था। कपड़े के नमूनों का यूवी संरक्षण कारक एक यूवी स्पेक्ट्रोफोटोमीटर पर 290 - 400 nm की सीमा में transmittance डेटा के माध्यम से मापा गया था। कपड़े की तन्य शक्ति पर चाँदी के नैनोकणों के जमाव के घनत्व के प्रभाव का भी मूल्यांकन किया गया था। कपड़ों की सूक्ष्म छवियों ने चाँदी के नैनोकणों की घनी और समान कोटिंग दिखाई। सभी नमूनों ने उत्कृष्ट रोगाणुरोधी गतिविधि और यूवी-संरक्षण दिखाया जो कि बहुत अच्छे से उत्कृष्ट (UPF 33.4 - 89.9) परिधि में था। चाँदी नैनोकणों के साथ उपचार के बाद कपड़े की तन्य शक्ति का कोई अधःपतन नहीं था। कपड़े के लिए सिल्वर नैनोपार्टिकल उपचार ने नित्य धुलाई के विरुद्ध उत्कृष्ट स्थायित्व दिखाया। कुटीर उद्योग के पैमाने पर कपड़े के एसएनपी उपचार के लागत विश्लेषण ने इसकी व्यावसायिक व्यवहार्यता को भी उजागर किया।

# Table of Contents

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	Page No
Certificate	i
Acknowledgments	ii
Abstract	iii-iv
Table of Contents	v-xii
List of Figures	xiii-xvi
List of Tables	xvii-xviii
Nomenclature	xix
<b><i>Chapter 1: Introduction and Literature Review</i></b>	<b>1-18</b>
1.1 Introduction	1
1.2 Application of silver nanoparticles (SNPs)	1
1.2.1 Agriculture	1
1.2.1.1 Silver nanoparticles based biosensors	2
1.2.1.2 Nanofertilizers and nanopesticides	2
1.2.2 Medical Sciences	3
1.2.2.1 Therapeutic Applications	4
1.2.2.2 Bio-imaging	5
1.2.2.3 Biosensing applications	5
1.2.2.4 Drug delivery	6
1.2.3 Multifunctional finishing on textiles	7
1.2.4 Environmental remediations	7
1.2.4.1 Removal of pollutants	8
	8

1.2.4.2 Detection of pollutants	8
1.3 Synthesis of silver nanoparticles	8
1.3.1 Top down synthesis of silver nanoparticles	9
1.3.2 Bottom up synthesis of silver nanoparticles	10
1.4 Review of Literature	10
1.4.1 Green synthesis of Silver nanoparticles using medicinal Indian plants	11
1.4.2 Kinetics of formation of nanoparticles by wet synthesis	13
1.4.3 In-situ synthesis of silver nanoparticles on fabrics	13
1.5 Motivation for the thesis work	15
1.6 Synopsis of the thesis	19-42
<b><i>Chapter 2: Screening of Plants for Synthesis of Stable and Spherical Silver Nanoparticle and Optimization of Silver Nanoparticle Synthesis by Selected Plants</i></b>	20
2.1 Screening of plants for controlled synthesis of SNP	20
2.1.1 Plants chosen for screening	20
2.1.1.1 <i>Murraya koenigii</i>	21
2.1.1.2 <i>Carica papaya</i>	21
2.1.1.3 <i>Ocimum sanctum</i>	22
2.1.1.4 <i>Azadirachta indica</i>	23
2.1.1.5 <i>Eucalyptus hybrida</i>	24
2.1.1.6 <i>Chenopodium album</i>	24
2.1.2 Materials and Methods	24
2.1.2.1 Materials	25
2.1.2.2 Methods	25
2.1.2.2.1 Preparation of leaf extract	25

2.1.2.2.2 Synthesis of silver nanoparticles	26
2.1.2.2.3 Characterization of SNPs and analysis	26
2.1.2.2.3.1 UV-vis Spectra Analysis	26
2.1.2.2.3.2 Transmission Electron Microscopy	26
2.1.2.2.3.3 Analysis of stability of SNP against aggregation	26
2.1.3 Results	26
2.1.3.1 Analysis of UV-vis absorbance spectra	29
2.1.3.2 Transmission electron microscope images	31
2.1.3.3 Stability of SNP in colloidal solution	31
2.2 Optimization of SNP synthesis using <i>Azadirachta indica</i> leaf extract	32
2.2.1 Materials and Methods	32
2.2.1.1 Materials	32
2.2.1.2 Methods	32
2.2.1.2.1 Preparation of leaf extract	32
2.2.1.2.2 Optimization of SNP synthesis using <i>Azadirachta indica</i> leaf extract	32
2.2.1.2.2.1 Optimization of leaf extract preparation: cut versus crushed leaves	32
2.2.1.2.2.2 Optimization of reaction pH of SNP synthesis	32
2.2.1.2.2.3 Optimization of Leaf extract concentration for SNP synthesis	33
2.2.1.2.2.4 Optimization of AgNO <sub>3</sub> concentration for SNP synthesis	
2.2.1.2.3 Characterization	33
	33

2.2.1.2.3.1 UV-vis absorbance spectra	33
2.2.1.2.3.2 Transmission electron microscope images	33
2.2.1.2.3.3 Zeta Potential	33
2.2.2 Results	33
2.2.2.1 Optimization of leaf extract preparation	33
2.2.2.2 Optimization of reaction pH	36
2.2.2.3 Optimization of leaf extract concentration for SNP synthesis	37
2.2.2.4 Optimization of AgNO <sub>3</sub> concentration for SNP synthesis	38
2.2.3 SNP synthesis under optimized conditions	38
2.2.3.1 Optimized SNP synthesis at reaction pH 7	39
2.2.3.2 Optimized SNP synthesis at reaction pH 12	40
2.2.4 Conclusions	43
<i>Chapter 3: Analysis of Antibacterial Activity and Photocatalytic Dye Degradation Activity of Silver Nanoparticles Synthesized using Papaya Leaf Extract</i>	44
3.1 Materials and methods	44
3.1.1 Preparation of aqueous leaf extract of <i>C. papaya</i>	44
3.1.2 Chemicals	44
3.1.3 Antimicrobial efficacy of silver nanoparticles and antibiotics	44
3.1.4 Assessment of increase in fold area	45
3.1.5 Photo-catalytic activity of Pa-SNPs for dye degradation	45
3.1.6 Characterization of Pa-SNPs	45
3.1.6.1 Ultraviolet-Visible spectroscopy	45
3.1.6.2 Zeta Potential-Dynamic light scattering	45
3.1.6.3 Transmission Electron Microscopy (TEM) and Energy	45

dispersive spectrometer (EDS)	45
3.2 Results and Discussion	45
3.2.1 Ultraviolet-Visible spectroscopy of Pa-SNPs	46
3.2.2 Transmission Electron Micrograph of Pa-SNPs	47
3.2.3 Energy-dispersive X-ray spectroscopy Micrograph	48
3.2.4 Zeta Potential & Dynamic light scattering	49
3.2.5 Dynamic light scattering measurements	50
3.2.6 Antimicrobial efficacy of silver nanoparticles and antibiotics	55
3.3 Conclusions	57-62
<b><i>Chapter 4: Development of Hypothesis for Kinetics of Formation of Silver Nanoparticles using Leaf Extracts</i></b>	57
4.1 The role of leaf extract to Ag <sup>+</sup> ratio	59
4.2 The kinetics of formation of SNP	59
4.2.1 Nucleation of SNP during green synthesis	61
4.2.2 Growth of SNP during green synthesis	61
4.3 Shape controlled growth of SNP	61-74
4.4 Conclusions	
<b><i>Chapter 5: Development of Mathematical Model for Size Specific Silver Nanoparticle Synthesis by Seeded Growth Method</i></b>	63
5.1 Material and methods	63
5.1.1 Material	63
5.1.2. Preparation of leaf extract	
5.1.3. Characterization of silver nanoparticles	63
5.1.3.1. UV-vis Spectra analysis	64
	64

5.1.3.2. Transmission Electron Microscopy	64
5.1.4. Synthesis of SNP seeds	64
5.1.5. Stepped Growth of SNP seeds	64
5.1.6. Development of the mathematical model	65
5.2. Results and Discussion	69
5.2.1. Preparation of SNP seeds	69
5.2.2. Using the mathematical model for size-specific synthesis	71
5.3 Conclusions	73-96
<b><i>Chapter 6: Development of Antimicrobial, UV-protect Cotton Fabric with Increased Washing Durability by In-situ Geen Synthesis of Silver Nanoparticles</i></b>	75
6.1 Methodology	75
6.1.1 Materials and Chemicals	75
6.1.2 Procedure	76
6.1.2.1 Preparation of leaf Extract	76
6.1.2.2 Mercerization of cotton fabrics	77
6.1.2.3 Hydrothermal conditions	77
6.1.2.4 In-situ synthesis of silver nanoparticles on Cotton Fabric	77
6.1.2.4.1 Synthesis at different pH: Impact on silver content of SNP treated fabric	77
6.1.2.4.2 Synthesis with different AgNO <sub>3</sub> concentrations: Impact on silver content of treated fabric	78
6.1.2.4.3 Synthesis with mercerization pre-treatment and under hydrothermal conditions: Impact on washing durability	78
	78
	78

6.2 Measurements	80
6.2.1 Color measurements	80
6.2.2 Evaluation of silver content	80
6.2.3 Mechanical strength	80
6.2.4 Scanning Electron Microscopy	81
6.2.5 Washing Process	81
6.2.6 Determination of washing durability of SNP treatment	82
6.2.7 Antibacterial tests for SNP treated cotton fabrics	82
6.2.8 Ultraviolet radiation blocking Efficacy	82
6.3 Results and discussion	84
6.3.1 Effect of synthesis pH on silver content of treated fabrics	87
6.3.2 Effect of AgNO <sub>3</sub> concentration on silver content of treated fabrics	
6.3.3 Effect of SNP content on mechanical strength of SNP treated fabrics	88
6.3.4 Effect of silver content on antibacterial activity of SNP treated fabrics	89
6.3.5 Effect of SNP content on UV- blocking efficiency of SNP treated fabrics	90
6.3.6 Effect of mercerization and Hydrothermal treatment on washing durability of SNP treatment to cotton fabric	93
6.3.7 Effect of mercerization and in-situ synthesis under hydrothermal conditions on washing durability of SNP treated fabrics	94
6.3.8 Economic analysis of SNP treatment on scarves (gamchha)	96
6.3.8.1 For the entrepreneur	96
6.3.8.2 For the consumer	
	97-100
6.4 Conclusions	97

<b><u>Chapter 7: Summary and Conclusions</u></b>	<b>98</b>
7.1 Screening of plants and optimization of synthesis parameters for leaf extract of <i>Azadirachta indica</i> .	99
7.2 Analysis of antibacterial and photocatalytic dye degradation activity of silver nanoparticles synthesized using papaya leaf extract	99
7.3 Development of hypothesis for kinetics of formation of SNP using leaf extracts	100
7.4 Development of mathematical model for size specific silver nanoparticle synthesis by seeded growth method	100
7.5 Development of antimicrobial, UV-protect cotton fabric with increased washing durability by In-situ green synthesis of silver nanoparticles	101-126
7.6 Future prospects	
References	
<b>Brief Bio-data of Author</b>	<b>127-129</b>

# List of Figures

---

**Figure 1.1:** Biomedical applications of silver nanoparticles

**Figure 1.2:** Synthesis of silver nanoparticles

**Figure 2.1:** *Murraya koenigii*

**Figure 2.2:** *Carica papaya*

**Figure 2.3:** *Ocimum sanctum*

**Figure 2.4:** *Azadirachta indica*

**Figure 2.5:** *Eucalyptus hybrida*

**Figure 2.6:** *Chenopodium album*

**Figure 2.7:** Preparation of leaf extract

**Figure 2.8:** UV-vis absorbance spectrum of SNP synthesized using aqueous leaf extract of *Murraya koenigii*

**Figure 2.9:** UV-vis absorbance spectrum of SNP at 50% dilution synthesized using aqueous leaf extract of *Carica papaya*

**Figure 2.10:** UV-vis absorbance spectrum of SNP synthesized using aqueous leaf extract of *Eucalyptus hybrida*

**Figure 2.11:** UV-vis absorbance spectrum of SNP at 50% dilution synthesized using aqueous leaf extract of *Azadirachta indica*

**Figure 2.12:** UV-vis absorbance spectrum of SNP synthesized using aqueous leaf extract of *Ocimum sanctum*

**Figure 2.13:** UV-vis absorbance spectrum of SNP synthesized using aqueous leaf extract of *Chenopodium album*

**Figure 2.14:** Transmission electron microscope images of SNP synthesized using leaf extracts of *Murraya koenigii* (A), *Carica papaya* (B), *Eucalyptus hybrida* (C), *Azadirachta indica* (D), *Ocimum sanctum* (E) & *Chenopodium album* (F)

**Figure 2.15:** (A) Stable SNP colloidal solution. (B) Precipitated SNP

**Figure 2.16:** UV-vis absorbance spectra of SNP synthesized diluted to 25% using 20% (w/v) cut and crushed leaf extract with 2mM AgNO<sub>3</sub> in 1:9 ratio at room temperature at pH 7 after 60 minutes of starting the reaction.

**Figure 2.17:** UV-vis absorbance spectra of SNP synthesized diluted to 25% using 20% (w/v) leaf extract with 2mM AgNO<sub>3</sub> in 1:9 ratio at room temperature at pH 5, 7 and 12 after 60 minutes of starting the reaction.

**Figure 2.18:** UV-vis absorbance spectra of SNP synthesized diluted to 25% using 20% (w/v) leaf extract with 2mM AgNO<sub>3</sub> in 1:9 ratio at room temperature at pH 8, 9, 10 and 11 after 60 minutes of starting the reaction.

**Figure 2.19:** UV-vis absorbance spectra of SNP synthesized diluted to 25% using 10%, 20% and 30% (w/v) leaf extract with 2mM AgNO<sub>3</sub> in 1:9 ratio at room temperature at pH 7 after 60 minutes of starting the reaction.

**Figure 2.20:** UV-vis absorbance spectra of SNP synthesized diluted to 25% using 20% (w/v) leaf extract with 1mM, 2mM, 3mM and 4mM AgNO<sub>3</sub> in 1:9 ratio at room temperature at pH 7 after 60 minutes of starting the reaction.

**Figure 2.21:** Transmission electron microscope images of room temperature synthesized SNP using 20% (w/v) cut leaf extracts of *Azadirachta indica* at pH 7. The leaf extract was reacted with 2mM AgNO<sub>3</sub> in a ratio of 1:9

**Figure 2.22:** Zeta potential of room temperature synthesized SNP using 20% (w/v) cut leaf extracts of *Azadirachta indica* at pH 7. The leaf extract was reacted with 2mM AgNO<sub>3</sub> in a ratio of 1:9

**Figure 2.23:** Transmission electron microscope image of room temperature synthesized SNP using 20% (w/v) cut leaf extracts of *Azadirachta indica* at pH 12. The leaf extract was reacted with 2mM AgNO<sub>3</sub> in a ratio of 1:9

**Figure 2.24:** Zeta potential of room temperature synthesized SNP using 20% (w/v) cut leaf extracts of *Azadirachta indica* at pH 12. The leaf extract was reacted with 2mM AgNO<sub>3</sub> in a ratio of 1:9

**Figure 3.1:** UV-visible absorption spectrum of SNPs biosynthesized by the reduction of AgNO<sub>3</sub> solution with the *C. papaya* leaf extract

**Figure 3.2:** TEM micrograph of biosynthesized Pa-SNPs

**Figure 3.3:** Energy dispersive spectrometer (EDS) of Pa-SNPs

**Figure 3.4:** Zeta potential of SNPs (-12.1 mV) produced by *C. papaya* leaf extract

**Figure 3.5:** Dynamic light scattering micrograph of Pa-SNPs, average size-68 nm

**Figure 3.6:** Initial concentration, final concentration and percentage degradation of dyes and dye mixture by SNPs after 30 min (Ci- Initial concentration; Cf- final concentration).

**Figure 4.1:** UV-vis absorbance spectra of SNP synthesized diluted to 25% using 10%, 20% and 30% (w/v) leaf extract with 2mM AgNO<sub>3</sub> in 1:9 ratio at room temperature at pH 7 after 60 minutes of starting the reaction.

**Figure 4.2:** Transmission electron microscope images of SNP synthesized at (A) pH 5, (B) pH 7 and (C) pH 12. 20% (w/v) *Azadirachta indica* leaf extract was reacted with 2mM AgNO<sub>3</sub> in a mixing ratio of 1:9 at room temperature.

**Figure 4.3:** Process of green synthesis of SNP by use of leaf extracts

**Figure 5.1:** Seeded growth of silver nanoparticles using *Azadirachta indica* leaf extract

**Figure 5.2:** UV absorbance spectrum of silver nanoparticles seed solution at 50% dilution

**Figure 5.3:** Transmission Electron Microscope image of silver nanoparticle seeds

**Figure 5.4:** TEM image of silver nanoparticles at different stages of growth (a) n=0, (b) n=5, (c) n=10, (d) n=15 & (e) n=20

**Figure 5.5:** UV-absorbance spectra of silver nanoparticle colloidal solution after various growth steps

**Figure 6.1:** Schematic of antimicrobial UV-protect cotton fabric by in-situ green synthesis of SNPs

**Figure 6.2:** Schematic showing hydrothermal treatment cycle for cotton fabrics

**Figure 6.3:** Concentration of deposited silver and K/S values of fabric samples treated at different pH

**Figure 6.4:** K/S values of SNP treated fabrics synthesized with different concentration of AgNO<sub>3</sub> at room temperature at pH 7.1

**Figure 6.5:** UV-VIS absorbance spectra of exhaust bath after in-situ SNP synthesis on fabric samples with different AgNO<sub>3</sub> concentrations

**Figure 6.6:** Scanning Electron Microscope images of SNP treated fabrics. (A) No treatment. (B) 1 mM AgNO<sub>3</sub>, pH 5 (C) 2 mM AgNO<sub>3</sub>, pH 5. (D) 1 mM AgNO<sub>3</sub>, pH 7.1. (E) 2 mM AgNO<sub>3</sub>, pH 7.1. (F) 2 mM AgNO<sub>3</sub>, pH 12

**Figure 6.7:** Impact of SNP content of treated fabrics on their strength. Sample A(no treatment), Sample B(23.99µg/g), Sample C(37.55µg/g), Sample D(45.22µg/g), Sample E(76.55µg/g), Sample F(85.46µg/g)

**Figure 6.8:** Antibacterial efficacy of SNP treated fabrics against *S.aureus* (i-vi) & *E.coli*(vii-xii) SAMPLE A(no treatment), SAMPLE B(1mM AgNO<sub>3</sub>, pH 5), SAMPLE C (2mM

AgNO<sub>3</sub>, pH5, SAMPLE D (1mM AgNO<sub>3</sub>, pH 7.1), SAMPLE E (2mM AgNO<sub>3</sub>, pH 7), SAMPLE F (2mM AgNO<sub>3</sub>, pH 12)

**Figure 6.9:** Effect of SNP content of treated cotton fabrics on their antimicrobial activity on *Escherichia.coli* and *Staphylococcus aureus* as compared to untreated sample. Sample B (Ag content. 23.99µg/g), Sample C (Ag content 35.46µg/g), Sample D(Ag content 45.22µg/g), Sample E(Ag content 76.55µg/g), Sample F(Ag content 97.55µg/g)

**Figure 6.10:** UV protection efficacy of SNP treated fabric with varying concentration of silver nanoparticles. Sample A (No SNP treatment), Sample B (SNP content 23.99µg/g), Sample C (SNP content 35.46µg/g), Sample D (SNP content 45.22µg/g), Sample E (SNP content 76.55µg/g), Sample F (SNP content 97.55µg/g)

**Figure 6.11:** Washing durability of cotton fabric treated by SNP by in-situ synthesis by reacting 2mM AgNO<sub>3</sub> with 20% (w/v) cut *Azadirachta indica* leaf extract in a ratio of 9:1 at pH 7.1. (A) Unmercerized sample. SNP synthesis at room temperature (B) Mercerized sample. SNP synthesis at hydrothermal conditions.

# List of Tables

---

**Table 1.1:** Literature reviewed for green synthesis of SNP using Indian plants

**Table 1. 2:** Literature review regarding kinetics of formation of metal nanoparticles

**Table 1.3:** Literature review regarding treatment of cotton fabrics with green synthesized silver nanoparticles

**Table 2.1:** Time of initiation of precipitation of SNP from colloidal solution after the start of SNP synthesis using leaf extracts

**Table 3.1:** Antibacterial activity of plant extract, AgNO<sub>3</sub> solution (0.002 M), Pa-SNPs alone and in combination with Penicillin against *E. coli* and *S. aureus*

**Table 3.2:** Antibacterial activity of plant extract, AgNO<sub>3</sub> solution (0.002 M), Pa-SNPs alone and in combination with Kanamycin against *E. coli* and *S. aureus*

**Table 3.3:** Antibacterial activity of plant extract, AgNO<sub>3</sub> solution (0.002 M), Pa-SNPs alone and in combination with chloramphenicol against *E. coli* and *S. aureus*

**Table 3.4:** Concentration of dyes and dye mixture at different time interval during degradation process by Pa-SNPs

**Table 5.1:** Predicted silver nanoparticle size at end of each step during growth stage I

**Table 5.2:** Predicted silver nanoparticle size at the end of each step during growth stage II

**Table 6.1:** Colorimetric data of fabric samples with room temperature in-situ synthesis of SNP at different pH (5, 7.1 and 12). The samples were first dipped in AgNO<sub>3</sub> and then in leaf extract for 10 minutes.

**Table 6.2:** Colorimetric data of SNP treated fabrics using different concentration of AgNO<sub>3</sub> at pH 7.1 at room temperature. Fabrics were first dipped in AgNO<sub>3</sub> and then *A.indica* leaf extract for 10 minutes each

**Table 6.3:** UPF Values and Blocking for UV-A (290-315 nm) and UV-B (315-400 nm) for pristine cotton fabric and different samples of Cotton Fabrics treated with Silver nanoparticles

**Table 6.4:** K/S values of cotton fabric treated with SNP under different conditions

**Table 6.5:** Washing durability of cotton fabric treated with SNP under different conditions

**Table 6.6:** Capital cost for cottage industry with daily capacity of treating 80 gamchhas per day

**Table 6.7:** Capital cost for cottage industry with daily capacity of treating 80 gamchhas per day

# Nomenclature

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ADL	Atomic Layer Deposition
CVD	Chemical Vapor Deposition
DLS	Dynamic Light Scattering
EDS	Energy-dispersive X-ray spectroscopy
LFA	Lateral Flow Assays
ML ratio	Material to Liquor ratio
LSPR	Local Surface Plasmon Resonance
SEM	Scanning Electron Microscope
SNP	Silver Nanoparticles
SPR	Surface Plasmon Resonance
TEM	Transmission Electron Microscope
w/v	Weight by volume
ZOI	Zone of Inhibition
$n_s$	Number of atoms in a silver nanoparticle seed
$R_s$	Radius of silver nanoparticle seed
$R_{Ag}$	Radius of silver atom
$N_s$	Number of silver nanoparticle seeds
$N_A$	Avogadro's number
$M_{AgNO_3}$	Molar concentration of $AgNO_3$
$V_{AgNO_3}$	Volume of $AgNO_3$ solution
$N_s'$	Number of seeds introduced in growth medium
$V_{LB}$	Volume of Leaf broth
$V_g$	Volume of $AgNO_3$ added for growth
$M_g$	Molar concentration of $AgNO_3$ added for growth
$R_n$	Radius of silver nanoparticle after 'n' growth steps
UPF	Ultraviolet Protection Factor