DEVELOPMENT OF BIO-BASED SILVER NANOPARTICLES FOR APPLICATION IN WATER TREATMENT

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Development of bio-based Silver Nanoparticles for Application in Water Treatment

by

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This thesis is dedicated to

my dearest Parents

Whose love and unwavering support have been the driving force

behind this achievement.

Thank you for being my pillars of strength, my role models,

and my biggest cheerleaders.

This accomplishment is as much yours as it is mine.

Supervisor Certification

This is to certify that the thesis entitled "**Development of bio-based silver nanoparticles for application in water treatment**" being submitted by **Ms. Sadaf Aiman Khan** to the Indian Institute of Technology Delhi and The University of Queensland for the award of degree of **Doctor of Philosophy** is a record of *bonafide* research work carried out by her. **Ms. Sadaf** has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard. The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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Abstract

Access to a safe, clean, and adequate water supply stands as the cornerstone of humanity's sustainability and overall well-being. The crucial process of water disinfection serves to eradicate pathogenic microorganisms from water sources, playing a pivotal role in averting potential waterborne disease outbreaks. Conventional methods like chlorination, ozonation, and UV radiation have been successfully employed for many years to curtail microbial proliferation, but they are not devoid of limitations. One of the prominent concerns associated with these methods lies in the formation of disinfection by-products (DBPs), which, alarmingly, possess carcinogenic properties. The imperative, then, lies in the development of innovative, affordable and effective technologies for water disinfection that can simultaneously counteract these challenges. Notably, the purity of water is affected by more than just microbial contamination. A spectrum of pollutants, ranging from commonplace cosmetic ingredients to novel molecules that display remarkable persistence in water, poses significant threats to both human health and the environment. This emerging concern necessitates the exploration of holistic solutions to ensure the safety and potability of water sources.

A promising avenue for tackling these intertwined challenges revolves around the utilization of silver, a material that has been exploited for its antimicrobial properties since antiquity. The focal point of the research contained in this thesis revolves around the synthesis of silver nanoparticles (AgNPs) through biologically inspired pathways. AgNPs were synthesized using biological extract from *Citrus* fruit peel waste as a reducing and stabilizing agent. This approach ensures the production of stable nanoparticles without the use of toxic chemicals, aligning perfectly with the principles of green chemistry. The synthesized nanoparticles were then assessed for their multifunctional properties, as demonstrated through activities such as efficient catalytic degradation of the toxic nitroaromatic pollutant 4-nitrophenol in water,

colorimetric sensing of mercury (II) ions, and antibacterial efficacy against *Staphylococcus aureus*.

While the biological method can successfully synthesize AgNPs, there are challenges in directly using the formed products, such as nanoparticle agglomeration, the formation of larger particles, and potential leaching into the environment during water treatment applications. To address these limitations, graphene oxide was employed as a support matrix for AgNPs. A nanocomposite comprising AgNPs on the surface of reduced graphene oxide was synthesized through in-situ reduction facilitated by a biological extract. The rGO/AgNPs nanocomposite exhibits significant potential to revolutionize two crucial aspects of water quality management: the photocatalytic degradation of emerging pollutants and the prevention of microbial biofilm formation.

The persistent presence of cosmetic ingredients in water bodies poses a significant ecological threat, potentially disrupting aquatic ecosystems and impacting human health through contaminated drinking water. The rGO/AgNPs nanocomposite was tested for the photocatalytic degradation of methylparaben, an emerging pollutant of concern, using visible light. Remarkably, the nanocomposite demonstrated significantly improved adsorption and photocatalytic degradation efficiency for MeP (97.6%) when compared to rGO or AgNPs individually. The factors influencing the kinetics of the photocatalytic degradation by rGO/AgNPs were thoroughly examined using response surface methodology (RSM), encompassing solution pH, catalyst dose, persulfate concentration, MeP initial concentration, and time. The nanocomposite exhibited high stability and could be employed for multiple cycles without a reduction in activity. Furthermore, the mechanism of the photocatalytic reaction was explored through scavenger tests and density functional theory (DFT) study. Leveraging the capabilities of rGO/AgNPs, this approach facilitates the breakdown of

pollutants into less harmful compounds through photocatalytic reactions, without requiring expensive energy inputs. This presents a promising and effective solution for tackling the challenge posed by emerging pollutants.

Furthermore, the antibiofilm properties of rGO/AgNPs were investigated against single and mixed species of microbes. Both minimum inhibitory concentrations and biofilm prevention concentrations were determined for single species of *S. aureus*, *Streptococcus mutans*, *Pseudomonas aeruginosa, Candida albicans* and mixed species of *C. albicans- S. aureus, C. albicans- S. mutans, C. albicans- P. aeruginosa*. rGO/AgNPs displayed significant antimicrobial activity against vegetative cells as well as reduction in biofilm biomass (50-70%). This outcome was corroborated through scanning electron imaging analysis of treated and untreated biofilms. Biofilm prevention by nanocomposites ensures waterborne pathogens are eliminated as they are unable to escape from killing agents by forming a resistant biofilm, thus mitigating the risk of disease outbreaks. This application holds particular significance in regions where conventional disinfection methods fall short or give rise to unintended by-products. This study paves new pathways to utilize greener and alternative approaches to design antimicrobials and utilize for antifouling applications.

Overall, this research represents a pioneering and sustainable approach to water treatment practices. The synthesis of nano-silver particles through biologically inspired pathways, particularly the biosynthesis based on biowaste, is instrumental in reducing waste from food and agriculture. This innovative method holds the promise of revolutionizing water disinfection and pollutant degradation, contributing to the overarching goal of ensuring a sustainable and healthy future for all.

संक्षेप

सुरक्षित, स्वच्छ और पर्याप्त जल आपूर्ति तक पहुंच मानवता की स्थिरता और समग्र कल्याण की आधारशिला है। जल कीटाणुशोधन की महत्वपूर्ण प्रक्रिया जल स्रोतों से रोगजनक सूक्ष्मजीवों को खत्म करने का काम करती है, जो संभावित जलजनित रोग के प्रकोप को रोकने में महत्वपूर्ण भूमिका निभाती है। माइक्रोबियल प्रसार को कम करने के लिए क्लोरीनीकरण, ओजोनेशन और यूवी विकिरण जैसे पारंपरिक तरीकों को कई वर्षों से सफलतापूर्वक नियोजित किया गया है, लेकिन वे सीमाओं से रहित नहीं हैं। इन तरीकों से जुड़ी प्रमुख चिंताओं में से एक कीटाणुशोधन उप-उत्पादों (डीबीपी) के निर्माण में निहित है, जो चिंताजनक रूप से कैंसरकारी गुणों से युक्त होते हैं। तो फिर, अनिवार्यता जल कीटाणुशोधन के लिए नवीन, सस्ती और प्रभावी प्रौद्योगिकियों के विकास में निहित है जो एक साथ इन चुनौतियों का मुकाबला कर सकती हैं। विशेष रूप से, पानी की शुद्धता केवल माइक्रोबियल संदूषण से अधिक प्रभावित होती है। प्रदूषकों का एक स्पेक्ट्रम, सामान्य कॉस्मेटिक अवयवों से लेकर नए अणुओं तक, जो पानी में उल्लेखनीय दृढ़ता प्रदर्शित करते हैं, मानव स्वास्थ्य और पर्यावरण दोनों के लिए महत्वपूर्ण खतरा पैदा करते हैं। इस उभरती चिंता के कारण जल स्रोतों की सुरक्षा और पीने की क्षमता सुनिश्चित करने के लिए समग्र समाधानों की खोज की आवश्यकता है।

इन परस्पर जुड़ी चुनौतियों से निपटने का एक आशाजनक रास्ता चांदी के उपयोग के इर्द-गिर्द घूमता है, एक ऐसी सामग्री जिसका उपयोग प्राचीन काल से अपने रोगाणुरोधी गुणों के लिए किया जाता रहा है। इस थीसिस में निहित शोध का केंद्र बिंदु जैविक रूप से प्रेरित मार्गों के माध्यम से सिल्वर नैनोकणों (एजीएनपी) के संश्लेषण के इर्द-गिर्द घूमता है। एजीएनपी को कम करने वाले और स्थिर करने वाले एजेंट के रूप में खट्टे फलों के छिलके के कचरे से जैविक अर्क का उपयोग करके संश्लेषित किया गया था। यह दृष्टिकोण हरित रसायन विज्ञान के सिद्धांतों के साथ पूरी तरह से संरेखित होकर, जहरीले रसायनों के उपयोग के बिना स्थिर नैनोकणों का उत्पादन सुनिश्चित करता है। तब संश्लेषित नैनोकणों का उनके बहुक्रियाशील गुणों के लिए मूल्यांकन किया गया था, जैसा कि पानी में जहरीले नाइट्रोएरोमैटिक प्रदूषक 4-नाइट्रोफेनॉल के कुशल उत्प्रेरक क्षरण, पारा (II) आयनों के वर्णमिति संवेदन और स्टैफिलोकोकस ऑरियस के खिलाफ जीवाणुरोधी प्रभावकारिता जैसी गतिविधियों के माध्यम से प्रदर्शित किया गया था।

जबकि जैविक विधि AgNPs को सफलतापूर्वक संश्लेषित कर सकती है, लेकिन निर्मित उत्पादों का सीधे उपयोग करने में चुनौतियाँ हैं, जैसे नैनोकणों का समूहन, बड़े कणों का निर्माण, और जल उपचार अनुप्रयोगों के दौरान पर्यावरण में संभावित लीचिंग। इन सीमाओं को संबोधित करने के लिए, ग्राफीन ऑक्साइड को AgNPs के लिए एक समर्थन मैट्रिक्स के रूप में नियोजित किया गया था। कम ग्राफीन ऑक्साइड की सतह पर एजीएनपी युक्त एक नैनोकम्पोजिट को जैविक अर्क द्वारा इन-सीटू कमी के माध्यम से संश्लेषित किया गया था। आरजीओ/एजीएनपी नैनोकम्पोजिट जल गुणवत्ता प्रबंधन के दो महत्वपूर्ण पहलुओं में क्रांति लाने की महत्वपूर्ण क्षमता प्रदर्शित करता है: उभरते प्रदूषकों का फोटोकैटलिटिक क्षरण और माइक्रोबियल बायोफिल्म निर्माण की रोकथाम।

जल निकायों में कॉस्मेटिक अवयवों की लगातार उपस्थिति एक महत्वपूर्ण पारिस्थितिक खतरा पैदा करती है, संभावित रूप से जलीय पारिस्थितिकी तंत्र को बाधित करती है और दूषित पेयजल के माध्यम से मानव स्वास्थ्य को प्रभावित करती है। आरजीओ/एजीएनपी नैनोकंपोजिट का परीक्षण दृश्य प्रकाश का उपयोग करके चिंता के उभरते प्रदूषक मिथाइलपरबेन के फोटोकैटलिटिक क्षरण के लिए किया गया था। उल्लेखनीय रूप से, व्यक्तिगत रूप से आरजीओ या एजीएनपी की तुलना में नैनोकम्पोजिट ने एमईपी (97.6%) के लिए काफी बेहतर सोखना और फोटोकैटलिटिक गिरावट दक्षता का प्रदर्शन किया। आरजीओ/एजीएनपी द्वारा फोटोकैटलिटिक गिरावट के कैनेटीक्स को प्रभावित करने वाले कारकों की प्रतिक्रिया सतह पद्धति (आरएसएम) का उपयोग करके पूरी तरह से जांच की गई, जिसमें समाधान पीएच, उत्प्रेरक खुराक, परसल्फेट एकाग्रता, एमईपी प्रारंभिक एकाग्रता और समय शामिल है। नैनोकम्पोजिट ने उच्च स्थिरता प्रदर्शित की और गतिविधि में कमी के बिना कई चक्रों के लिए नियोजित किया जा सकता है। इसके अलावा, मेहतर परीक्षणों और घनत्व कार्यात्मक सिद्धांत (डीएफटी) अध्ययन के माध्यम से फोटोकैटलिटिक प्रतिक्रिया के तंत्र का पता लगाया गया था। आरजीओ/एजीएनपी की क्षमताओं का लाभ उठाते हुए, यह दृष्टिकोण महंगे ऊर्जा इनपुट की आवश्यकता के बिना, फोटोकैटलिटिक प्रतिक्रियाओं के माध्यम से प्रदूषकों को कम हानिकारक यौगिकों में तोड़ने की सुविधा प्रदान करता है। यह उभरते प्रदूषकों द्वारा उत्पन्न चुनौती से निपटने के लिए एक आशाजनक और प्रभावी समाधान प्रस्तुत करता है।

इसके अलावा, रोगाणुओं की एकल और मिश्रित प्रजातियों के खिलाफ आरजीओ/एजीएनपी के एंटीबायोफिल्म गुणों की जांच की गई। न्यूनतम निरोधात्मक सांद्रता और बायोफिल्म रोकथाम सांद्रता दोनों एस. ऑरियस, स्ट्रेप्टोकोकस म्यूटन्स, स्यूडोमोनास एरुगिनोसा, कैंडिडा एल्बिकैंस और सी. एल्बिकैंस- एस. ऑरियस, सी. एल्बिकैंस- एस. म्यूटन्स, सी. एल्बिकैंस की मिश्रित प्रजातियों की एकल प्रजातियों के लिए निर्धारित की गई थीं। पी. एरुगिनोसा. आरजीओ/एजीएनपी ने वनस्पति कोशिकाओं के खिलाफ महत्वपूर्ण रोगाणुरोधी गतिविधि के साथ-साथ बायोफिल्म बायोमास (50-70%) में कमी प्रदर्शित की। उपचारित और अनुपचारित बायोफिल्म के स्कैनिंग इलेक्ट्रॉन इमेजिंग विश्लेषण के माध्यम से इस परिणाम की पुष्टि की गई। नैनोकम्पोजिट द्वारा बायोफिल्म की रोकथाम यह सुनिश्चित करती है कि जलजनित रोगजनकों का खात्मा हो जाए क्योंकि वे एक प्रतिरोधी बायोफिल्म बनाकर हत्या करने वाले एजेंटों से बचने में असमर्थ हैं, जिससे रोग फैलने का खतरा कम हो जाता है। यह अनुप्रयोग उन क्षेत्रों में विशेष महत्व रखता है जहां पारंपरिक कीटाणुशोधन विधियां कम पड़ जाती हैं या अनपेक्षित उप-उत्पादों को जन्म देती हैं। यह अध्ययन रोगाणुरोधकों को डिजाइन करने और दूषणरोधी अनुप्रयोगों के लिए उपयोग करने के लिए हरित और वैकल्पिक तरीकों का उपयोग करने के लिए नए मार्ग प्रशस्त करता है।

कुल मिलाकर, यह शोध जल उपचार प्रथाओं के लिए एक अग्रणी और टिकाऊ दृष्टिकोण का प्रतिनिधित्व करता है। जैविक रूप से प्रेरित मार्गों के माध्यम से नैनो-सिल्वर कणों का संश्लेषण, विशेष रूप से बायोवेस्ट पर आधारित जैवसंश्लेषण, भोजन और कृषि से अपशिष्ट को कम करने में सहायक है। यह नवोन्वेषी पद्धति जल कीटाणुशोधन और प्रदूषक क्षरण में क्रांति लाने का वादा करती है, जो सभी के लिए एक स्थायी और स्वस्थ भविष्य सुनिश्चित करने के व्यापक लक्ष्य में योगदान करती है।

Declaration by author

This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly authored works that I have included in my thesis.

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Publications included in this thesis

1. **Khan S.A**., Jain, M., Ziora, Z.M., Blaskovich, M.A.T., Pant, K. K. 2023. Photocatalytic degradation of methylparaben using green nanosilver supported on reduced graphene oxide. Industrial and Engineering Chemistry Research, 62 (17), 6646-6659.

2. **Khan S.A.**, Jain, M., Pant, K. K., Ziora, Z.M., Blaskovich, M.A.T. 2024. Photocatalytic degradation of parabens: A comprehensive meta-analysis investigating the environmental remediation potential of emerging pollutant

3. **Khan S.A.**, Jain, M., Pandey, A., Ziora, Z.M., Blaskovich, M.A.T., Pant, K. K., Shetti, N.P., Aminabhavi, T.M. 2022. Leveraging the potential of silver nanoparticles-based materials towards sustainable water treatment. Journal of Environmental Management, 319, 115675.

4. **Khan S.A.,** Zeng J., Jain, M., Pant, K. K., Ziora, Z.M., Blaskovich, M.A.T., Seneviratne, J.C. 2024. Facile fabrication of multifunctional silver nanoparticles utilizing biowaste for efficient pollutant degradation, heavy metal sensing, and bactericidal activity, Materials Chemistry and Physics, 129606

Other publications during candidature

- Jain, M., Sahoo, A., Mishra, D., **Khan S.A**., Ziora, Z.M., Blaskovich, M.A.T., Pant, K. K. 2024. Modelling and statistical interpretation of phenol adsorption behaviour of 3-dimensional hybrid aerogel of waste-derived carbon nanotubes and graphene oxide, Chem. Engg. J, 151351.

- Jain, M., **Khan, S.A.**, Sharma, K., Jadhao, P.R., Pant, K.K., Ziora, Z.M. and Blaskovich, M.A., 2022. Current perspective of innovative strategies for bioremediation of organic pollutants from wastewater. Bioresource Technology, 344, p.126305.

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Contributions by others to the thesis

All chapters

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Chapter 3 and 6

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Statement of parts of the thesis submitted to qualify for the award of another degree

No works submitted towards another degree have been included in this thesis.

Research involving human or animal subjects

No animal or human subjects were involved in this research.

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