EMULSION TEMPLATED POROUS SCAFFOLDS FOR SUSTAINABLE VALORIZATION OF POLYPROPYLENE WASTE

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by

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Submitted

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CERTIFICATE

This is to certify that the thesis titled "**Emulsion Templated Porous Scaffolds for Sustainable valorization of Polypropylene Waste**", being submitted by **Sweety Rani** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by her. She has worked under my guidance and fulfilled the requirements for submission of the thesis which has attained the standard required for a Ph.D. degree of this Institute.

The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

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ABSTRACT

The increasing amount of waste generated from polypropylene (PP) protective gears used during and post COVID outbreak has exacerbated plastic waste management challenges. This thesis explored novel opportunities for valorization of waste PP to address environmental concerns and develop efficient materials for advanced applications. At the beginning an emulsion templated, mesoporous PP scaffold of specific surface area exceeding 170 m^2/g, confirmed by BET and SAXS analyses, was developed for oil adsorption to address oil spill management. The emulsion-templated porous scaffolds demonstrated a high oil adsorption capacity of 7.5 g/g for petrol, which was comparable to commercial nonwoven PP absorbent pads. To further enhance practical applications of the material a 3D printed funnel was fabricated using sacrificial templating 3D printing, achieving a separation efficiency of 99.8% for petrol/water mixtures over ten cycles without any decline in performance, hydrophobicity, or structural integrity. Subsequently to address the dual challenges of pollution from heavy metals and plastic waste, a waste PP-based reversible sensor was fabricated to selectively detect copper ions (Cu^{2+}) in blood and water from various sources. The sensor was fabricated as an emulsion-templated porous scaffold decorated with benzothiazolinium spiropyran (BTS), which produced a reddish color upon Cu^{2+} exposure. Detection capabilities were confirmed through naked-eye observation, UV-Vis spectroscopy, and current measurement via a DC probe station. The sensor maintained consistent performance in diverse environments, including blood, various water sources, and acidic or basic conditions and exhibited a detection limit of 1.3 ppm for Cu^{2+}, in agreement with WHO recommendations. Its reversible nature was validated through cyclic exposure to visible light and XPS analysis through Cu^{2+}-Cu^{+} exchange.

Further advancing the applications of waste PP, the scaffold was functionalized with chemically modified calixarene (CMC) *via* Fenton reaction for efficient strontium ion (Sr^{2+}) adsorption, to meet the concerns related to radioactive pollutants from nuclear reactors. Adsorption isotherms were studied using Langmuir and Freundlich models, with the maximum adsorption capacity determined to be 131.74 mg/g, favoring the physisorption process due to the scaffold's porous nature. The pseudo-second-order kinetic model, based on data fitting, suggested chemisorption of Sr^{2+} ions by the hydroxyl groups of the CMC grafted on the PP scaffold. Lastly, an antimicrobial PP scaffold was synthesized by grafting acrylic acid (AA) onto PP scaffold *via* a Fenton reaction. Green synthesis of silver nanoparticles (AgNPs) using the root extract of *Nyctanthes arbortristis* was employed, and the AgNPs were immobilized onto the grafted PP scaffold to form PP-g-AA-Ag composites. The composites exhibited significant antibacterial activity against *E. coli* and *S. aureus*, with smaller AgNPs demonstrating higher efficacy (99.35% for *E. coli* and 99.55% for *S. aureus*) compared to larger AgNPs (97.55% for *E. coli* and 98.05% for *S. aureus*). The antibacterial performance was confirmed by bacterial reduction percentages and zone of inhibition (ZOI) values, affirming the enhanced antimicrobial properties of the PP-g-AA-Ag scaffolds. The combination of porous PP, acrylic acid grafting, and green-synthesized AgNPs offered a versatile platform for mitigating bacterial growth, contributing to global health challenges in addition to plastic waste management.

Overall, this research demonstrated innovative approaches to repurpose waste PP into functional materials for environmental remediation and health applications. The findings highlighted the potential for commercial scalability and broader applicability in plastic waste valorization, providing a significant contribution to sustainable development and environmental protection.

सारांश

कोविड-19 महामारी के दौरान और बाद में उपयोग किए गए पॉलीप्रोपिलीन (पीपी) सुरक्षात्मक गियर से उत्पन्न अपशिष्ट की बढ़ती मात्रा ने प्लास्टिक अपशिष्ट प्रबंधन की चुनौतियों को बढ़ा दिया है। इस शोध में पर्यावरणीय चिंताओं का समाधान करने और उन्नत अनुप्रयोगों के लिए कुशल सामग्री विकसित करने के लिए अपशिष्ट पीपी के मूल्यवर्धन के लिए नए अवसरों की खोज की गई। शुरुआत में, तेल रिसाव प्रबंधन के लिए एक इमल्शन टेम्पलेटेड, मेसोपोरस पीपी स्कैफोल्ड विकसित किया गया, जिसका विशिष्ट सतह क्षेत्र 170 m^2/g से अधिक था, जिसकी पुष्टि बीईटी और एसएक्सएस विश्लेषण द्वारा की गई थी। इमल्शन-टेम्पलेटेड छिद्रदार स्कैफोल्ड्स ने पेट्रोल के लिए 7.5 g/g की उच्च तेल अधिशोषण क्षमता प्रदर्शित की, जो वाणिज्यिक नॉनवोवन पीपी अवशोषक पैड के बराबर थी। सामग्री के व्यावहारिक अनुप्रयोगों को और बढ़ाने के लिए, बलिदानिक टेम्पलेटिंग 3D प्रिंटिंग का उपयोग करके एक 3D मुद्रित फ़नल तैयार किया गया, जो बिना किसी प्रदर्शन, जलविरोधीता या संरचनात्मक अखंडता में गिरावट के दस चक्रों में पेट्रोल/पानी के मिश्रण के लिए 99.8% की पृथक्करण दक्षता प्राप्त करता है। बाद में भारी धातुओं और प्लास्टिक अपशिष्ट से प्रदूषण की दोहरी चुनौतियों का समाधान करने के लिए, विभिन्न स्रोतों से रक्त और पानी में तांबा आयनों (Cu^{2+}) का चयनात्मक रूप से पता लगाने के लिए अपशिष्ट पीपी-आधारित प्रतिवर्ती सेंसर तैयार किया गया। सेंसर को बेंजोथियाज़ोलिनियम स्पाइरोपाइरान (बीटीएस) से सजाए गए इमल्शन-टेम्पलेटेड छिद्रदार स्कैफोल्ड के रूप में तैयार किया गया था, जो Cu^{2+} के संपर्क में आने पर लाल रंग का उत्पादन करता था। पता लगाने की क्षमताओं की पुष्टि नग्न आंख अवलोकन, यूवी-वीआईएस स्पेक्ट्रोस्कोपी और डीसी प्रोब स्टेशन के माध्यम से वर्तमान मापन द्वारा की गई थी। सेंसर ने रक्त, विभिन्न जल स्रोतों और अम्लीय या क्षारीय स्थितियों सहित विभिन्न वातावरणों में लगातार प्रदर्शन बनाए रखा और डब्ल्यूएचओ की सिफारिशों

के अनुसार Cu^{2+} के लिए 1.3 ppm की पता लगाने की सीमा प्रदर्शित की। इसकी प्रतिवर्ती प्रकृति को दृश्य प्रकाश के चक्रीय संपर्क और Cu^{2+}- Cu^{+} एक्सचेंज के माध्यम से एक्सपीएस विश्लेषण द्वारा मान्य किया गया था।

अपशिष्ट पीपी के अनुप्रयोगों को और आगे बढ़ाते हुए, परमाणु रिएक्टरों से रेडियोधर्मी प्रदूषकों से संबंधित चिंताओं को पूरा करने के लिए, स्कैफोल्ड को फेंटन प्रतिक्रिया के माध्यम से रासायनिक रूप से संशोधित कैलिक्सरेन (सीएमसी) के साथ कार्यात्मक बनाया गया था, ताकि स्ट्रोंटियम आयन (Sr^{2+}) का कुशल अधिशोषण किया जा सके। लैंगमुइर और फ्रेंडलिच मॉडल का उपयोग करके अधिशोषण आइसोथर्म का अध्ययन किया गया, जिसमें अधिकतम अधिशोषण क्षमता 131.74 mg/g निर्धारित की गई, जो स्कैफोल्ड की छिद्रपूर्ण प्रकृति के कारण भौतिक अधिशोषण प्रक्रिया का पक्षधर है। छद्म-दूसरे क्रम के गतिज मॉडल, डेटा फिटिंग के आधार पर, पीपी स्कैफोल्ड पर ग्राफ्ट किए गए सीएमसी के हाइड्रॉक्सिल समूहों द्वारा Sr^{2+} आयनों के रासायनिक अधिशोषण का सुझाव दिया गया। अंत में, एक एंटीमाइक्रोबियल पीपी स्कैफोल्ड का संश्लेषण फेंटन प्रतिक्रिया के माध्यम से पीपी स्कैफोल्ड पर एक्रिलिक एसिड (एए) को ग्राफ्टिंग करके किया गया। नायटैंथस अर्बोरट्रिस्टिस के जड़ निकालने का उपयोग करके चांदी के नैनोकणों (AgNPs) का हरा संश्लेषण किया गया था, और AgNPs को पीपी-जी-एए-एजी कंपोजिट बनाने के लिए ग्राफ्टेड पीपी स्कैफोल्ड पर स्थिर किया गया था। कंपोजिट्स ने ई. कोली और एस. ऑरेस के खिलाफ महत्वपूर्ण जीवाणुरोधी गतिविधि प्रदर्शित की, जिसमें छोटे एजीएनपी बड़े एजीएनपी की तुलना में उच्च प्रभावकारिता (ई कोली के लिए 99.35% और एस ऑरेस के लिए 99.55%) प्रदर्शित करते हैं (ई कोली के लिए 97.55% और एस ऑरेस के लिए 98.05%)। जीवाणुरोधी प्रदर्शन की पुष्टि बैक्टीरिया की कमी प्रतिशत और निषेध क्षेत्र (ZOI) मानों द्वारा की गई, जो पीपी-जी-एए-एजी स्कैफोल्ड के बढ़े हुए जीवाणुरोधी

गुणों की पुष्टि करता है। छिद्रपूर्ण पीपी, एक्रिलिक एसिड ग्राफ्टिंग और हरे-संश्लेषित AgNPs के संयोजन ने बैक्टीरिया के विकास को कम करने के लिए एक बहुमुखी मंच की पेशकश की, जो प्लास्टिक अपशिष्ट प्रबंधन के अलावा वैश्विक स्वास्थ्य चुनौतियों में योगदान देता है।

कुल मिलाकर, इस शोध ने पर्यावरणीय उपचार और स्वास्थ्य अनुप्रयोगों के लिए अपशिष्ट पीपी को कार्यात्मक सामग्री में पुन: उपयोग करने के लिए नवीन दृष्टिकोण प्रदर्शित किए। निष्कर्षों ने प्लास्टिक अपशिष्ट मूल्य वर्धन में व्यावसायिक स्तर पर और व्यापक अनुप्रयोग क्षमता की संभावना पर प्रकाश डाला, जो सतत विकास और पर्यावरण संरक्षण में महत्वपूर्ण योगदान प्रदान करता है।

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List of Symbols

®	Registered trademark symbol
%	Percentage
°	Degrees
±	Plus, or minus
2θ	2 times theta
h	Hours
nm	Nanometers
mm	Millimeters
cm	Centimeters
cm^{-1}	Centimeters inverse
A^{-1}	Angstrom inverse
°C	Degrees Celsius
min	Minutes
°C/min	Degrees Celsius per minute
g	Grams
mg	Milligrams
mL	Milliliters
µm	Micrometers
mL/min	Milliliters per minute
eV	Electron volts
kg	Kilograms
M_w	Weight-average molecular weight
M_n	Number- average molecular weight

M_z	Z-average molecular weight
g/mol	Grams per mole
V	Volts
mV	Millivolts
kV	Kilovolts
Hz	Hertz
MHz	Megahertz
pH	Potential of hydrogen
ppm	Parts per million
g/10 min	Grams per 10 minutes
~	Approximately
mA	Milliampere
J/g	Joules per gram
g/cc	Grams per cubic centimeter
g/g	Grams per gram
cP	Centipoise
mg/L	Milligrams per litre
mg/g	Milligrams per gram
L	Litres
m^2/g	Square meters per gram
cc/g	Cubic centimeters per gram
ϕ_d	Volume fraction of dispersed phase
L/g	Litres per gram
L/mg	Litres per milligram
cfu/mL	Colony forming units per millilitre

η	Bactericidal efficiency
ΔH_f	Heat of fusion of the sample
ΔH_f^o	Heat of fusion of 100% crystalline sample
p/p_0	Pressure ratio
q	Scattering vector
Cu^+	Cuprous ion
Cu^{2+}	Cupric ion
Fe^{2+}	Ferrous ion
$FeCl_2$	Ferrous chloride
NaOH	Sodium hydroxide
$CaCO_3$	Calcium carbonate
HNO_3	Nitric acid
HCl	Hydrochloric acid
SiO_2	Silicon dioxide
CO_2	Carbon dioxide
Mg^{2+}	Magnesium ion
Ca^{2+}	Calcium ion
Na^+	Sodium ion
K^+	Potassium ion
^{90}Sr	Strontium-90
^{137}Cs	Cesium-137
TiO_2	Titanium dioxide
As	Arsenic
Cr	Chromium
Pb	Lead

$CDCl_3$	Deuterated chloroform
C-O	Carbon-oxygen single bond
C=O	Carbon-oxygen double bond
C-N	Carbon-nitrogen single bond
C=C	Carbon- carbon double bond
C-C	Carbon-carbon single bond
$-CH_3$	Methyl group
$>CH_2$	Methylene group
T_g	Glass transition temperature
T_m	Melting temperature
T_c	Crystallization temperature
δ	Chemical shift
α	Alpha

List of Abbreviations

UNESCO	United nations educational, scientific and cultural organization
USEPA	United States environmental protection agency
CSE	Centre for science and environment
WHO	World health organization
IUPAC	International union of pure and applied chemistry
FDA	Food and drug administration
RT	Room temperature
HLB	Hydrophilic-lipophilic balance
w/o	water-in-oil
o/w	oil-in-water
o/w/o	oil-in-water-in-oil
w/o/w	water-in-oil-in-water
HIPS	High impact polystyrene
ZOI	Zone of inhibition
3D	Three dimensional
MSW	Municipal solid waste
USD	United States dollar
DNA	Deoxyribose nucleic acid
a.u.	Arbitrary units
RGB	Red, green, and blue
GO	Graphene oxide
PVC	Polyvinyl chloride
LDPE	Low-density polyethylene

HDPE	High-density polyethylene
PUR	Polyurethane
PS	Polystyrene
PET	Polyethylene terephthalate
PP	Polypropylene
PE	Polyethylene
HIPE	High internal phase emulsion
CHP	Cumene hydroperoxide
DCM	Dichloromethane
LOD	Limit of detection
CMC	Chemically modified calixarene
AgNPs	Silver nanoparticles
PPE	Personal protective equipment
COVID 19	Coronavirus disease 2019
E. coli	Escherichia coli
S. aureus	Staphylococcus aureus
BTS	Benzothiazolinium spiropyran
MOF	Metal-organic framework
MWCNT	Multi-walled carbon nanotube
UV	Ultraviolet
TIPS	Thermally induced phase separation
SFF	Solid freefrom fabrication
SLA	Stereolithography
SLS	Selective lase sintering
CAD	Computer aided design

FDM	Fused deposition modeling
3DP	Three-dimensional printing
UV-Vis	Ultraviolet-Visible
TEM	Transmission electron microscopy
SAED	Selected area electron diffraction
DLS	Dynamic light scattering
SAXS	Small angle X-ray scattering
WAXD	Wide angle X-ray diffraction
FTIR	Fourier transform infrared
ATR	Attenuated total reflection
XPS	X-ray photoelectron spectroscopy
NMR	Nuclear magnetic resonance
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
GPC	Gel permeation chromatography
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
EDS	Energy dispersive X-ray spectroscopy
FESEM	Field emission scanning electron microscopy
EG	Ethylene glycol
MFI	Melt flow index
DCB	Dichlorobenzene
DI	Distilled water
LED	Light emitting diode

ABS	Acrylonitrile butadiene styrene
iPP	Isotactic polypropylene
PVA	Polyvinyl alcohol
MMT	Montmorillonite
AA	Acrylic acid
PEO	Poly(ethylene oxide)
CTAC	Cetyltrimethylammonium chloride
SP	Spiropyran
MC	Merocyanin
PLA	Polylactic acid
PPP	Print pause print
BC	Before christ
SPAN 80	Sorbitan monooleate
SPAN 20	Sorbitan monolaurate
Tween 80	Polyoxyethylene sorbitan monooleate