**Lecture Notes in Mechanical Engineering** 

Rabibrata Mukherjee · Christoph Janiak · Ziyauddin Khan · Somak Chatterjee · Banasri Roy · Sarbani Ghosh · Krishna Etika *Editors* 

# **Recent Trends in** Nanotechnology for Sustainable Living and Environment **Proceedings of ICON-NSLE 2022**



# Lecture Notes in Mechanical Engineering

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# Recent Trends in Nanotechnology for Sustainable Living and Environment

Proceedings of ICON-NSLE 2022



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Univ., China, Petru Poni Institute, Iasi, Romania, Wuhan University of Technology, China, and Univ. of Angers, France. He is the fellow of the Royal Society of Chemistry (FRSC) and has been awarded the prestigious Heisenberg Fellowship, ADUC Award, Heinz-Maier-Leibnitz Award, Schering Award, Award of the Fonds of the Chemical Industry (FCI), and Fellowship of the Fonds of the Chemical Industry (FCI). He was able to fetch funding for 12 projects in the last 5 years, notable among which are DFG collaborative and individual grant, DFG Chinese-German center grant, DAAD Prime grant, and BMBF network grant.

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**Dr. Banasri Roy** by training is a materials scientist. She completed her Ph.D. in materials engineering from Colorado School of Mines and National Renewable Energy Laboratory (NREL), USA, M.Tech. in materials engineering from IIT-Kanpur, M.Sc. in applied physics from the University of Puerto Rico, USA, B.Tech. in chemical technology and B.Sc. (with honor) in chemistry from Calcutta University. The exercise in multidisciplinary research fields helps her to understand the advanced theory of characterization and data analysis. Dr. Roy has vast expertise in materials synthesis, analytical characterization, and data analysis. She has extensively worked on the development of nanocatalyst systems for renewable energy production from ethanol and biomasses. Her current focus is on the utilization of waste (agricultural and others) to convert to energy sources and other value-added chemicals. She also works on the development of nanoparticles for environmental pollution control and other

applications. Her research interest includes surface modification of different biomaterials to improve biocompatibility. She is one of the SERB-POWER fellowship recipients of 2021 and was awarded the ULAM-NAWA fellowship by the Polish National Agency for Academic Exchange. Two Ph.D. and 14 M.E. students completed their thesis successfully under her guidance, and currently, she is supervising three Ph.D. and two M.E. students. She authored and co-authored 45 peer-reviewed papers in different international journals, achieving around 1280 citations, 28 i-index, and 19 h-index. Currently, she is affiliated with the chemical engineering department of BITS- Pilani, Pilani campus.

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# **Engineering of Self-Assembled Peptide Hydrogels for Antitumor Therapy**



Apurba K. Das, Tanmay Rit, and Tapas Ghosh

#### **1** Introduction

Cancer is one of the deadliest threats to the mankind. Worldwide, it causes more than 8 million deaths annually. Cancer is autonomous and aggressive growth of cells which have gone through epigenetic changes, genetic mutation and hence escape normal cell cycle [1]. Cancer cells hunt oxygen and nutrients from the surroundings during the progression of tumour. The demand of excessive nutrients and oxygen activates the proliferation of adjacent endothelial cells. This phenomenon gives rise to the angiogenesis. Chemotherapy, hormonal therapy and immunotherapy are the common and effective strategies to combat cancer [2]. However, poor bioavailability, limited tumour distribution and accumulation create hindrance for the anti-tumour activity during chemotherapy. Besides, long-term intravenous injection may cause lethal or serious side effects [3]. Cytotoxicity and non-selectivity of chemotherapy causes toxic effects on the healthy labile cells. Over the last decade, there are developments of noteworthy number of novel cancer treatment strategies but very few among them manage to enter in the clinical trial [1, 4]. However, recently nanomaterial based cancer therapy seems promising and productive. Recent studies have disclosed that unlike normal tissue the tumour microenvironment (TME) displays hypoxia, lower pH (6.5–6.8), higher amount of reactive oxygen species (ROS), over production of glutathione (GSH) and alkaline phosphatase (ALP) etc. [3]. Currently, this is achieved by exploiting the TME nanomaterial based anti-cancer therapy has shown exceptional results. Over the last few decades, low molecular weight hydrogelator (LMWHs) based hydrogel as a nanomaterial has been found to be very promising in the field of biomedical sciences. Recently, self-assembled peptide hydrogels have

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gained significant attention due to their bioactivity, biocompatibility and biodegradability. These hydrogels have versatile applications in the field of biomedical sciences such as tissue engineering, 3D bio-printing, wound healing, antimicrobial activity, drug delivery and anti-tumour activity. Peptide hydrogels can be fabricated by physical, chemical and enzymatic cross linking. Physically cross-linked peptide hydrogel is formed via hydrogen bonding, electrostatic interactions, hydrophobic interaction and  $\pi - \pi$  interactions. These hydrogels are developed by the self-assembly of peptides, and the self-assembled structures lead to various secondary structures like  $\alpha$ -helices,  $\beta$ -sheets,  $\beta$ -hairpins and coiled-coils. Among all,  $\alpha$ -helix and  $\beta$ -sheet based peptide hydrogels have been investigated largely. The  $\alpha$ -helical structure of peptides helps during endocytosis and hence plays an important role in drug delivery and anti-tumour activity. On the other hand  $\beta$ -sheets are stacked by the electrostatic interaction and hydrogen bonding gives rise to the parallel structure and finally self-assembles to form the hydrogel. In the case of chemically cross-linked peptide hydrogel, reactive cross-linking agents are being introduced and the nano-fibrillar networks are formed by the reaction between the cross-linking agent and the active functional group of the polypeptide. Enzymatically cross-linked peptide hydrogel is more advantageous as the gelation process can be controlled by external stimuli (enzyme). On the basis of stimuli responsive hydrogelation, peptide hydrogel can be categorized as thermo-sensitive, pH-sensitive, light-sensitive and enzyme-sensitive. Moreover, they have been utilized for the nanomaterial based cancer therapy [5, 6]by exploiting the stimuli responsive behaviour of peptide-based hydrogels.

#### 1.1 Anticancer Drug Loaded and Drug Conjugated Peptide Hydrogel

Controlled drug delivery is very significant during cancer therapy. In this context, peptide hydrogel based anticancer drug delivery has been proved quite impressive. Recently, Ge et al. have developed the peptide hydrogel for the pH responsive delivery of the anti-tumour drug (paclitaxel) via intratumoural injection [7]. They synthesised FER-8 peptide via the solid phase peptide synthesis (SPPS) process and FER-8 formed the hydrogel at pH 7.4. The average size of the fibres of the hydrogel was found below 500 nm by using TEM and DLS analysis. Paclitaxel (PTX) was loaded during the hydrogel formation. The in vitro drug release study of FER-8 peptide hydrogel was performed in the buffer of pH 5.5 for 6 days. The hydrogel exhibited PTX release of 65, 80 and 86% at 24, 72 and 144 h respectively. The in vitro anti-tumour experiment was performed against HepG2 tumour cells and the drug loaded hydrogel was more effective as compared to the bare drug. They checked the biocompatibility of the hydrogel by MTT cell viability assay. Furthermore, they investigated the in vivo anti-tumour activity on H22 tumour bearing mice. In the in vivo studies, a higher amount of drug was found in the tumour tissue and the

retention time was 96 h using intratumoral injection. They explained that the pHresponsive nature of the peptide hydrogel was utilized to release the drug PTX at the tumour site which has acidic pH environment. They successfully developed FER-8 peptide hydrogel for the sustained release of PTX and for the induced inhibition of the tumour [7]. Ashwanikumar et al. reported phenylalanine containing peptidebased hydrogel for the controlled delivery of 5-fluorouracil (5-FU) and leucovorin (LV) against cancer. They synthesized CH<sub>3</sub>-CO-RATARAEFRATARAEA-CONH<sub>2</sub> (RATEA-F8) peptide and the prepared hydrogel in Milli Q water and Tris-HCl (pH 7.4). Both the drugs (5-FU and LV) were incorporated during the preparation of the hydrogel upon mixing peptide-drugs in 20:1 ratio. The CD spectroscopy explained the antiparallel  $\beta$ -sheet structure of the self-assembled peptides and the formation of nanofibrous networks was confirmed from the TEM images. Moreover, the mechanical properties of the RATEA-F8 hydrogel was characterized by the rheology experiment. The effective loading efficiency of 5-FU and LV was determined from the CD spectra and fluorescence spectra. CD spectra revealed that the antiparallel  $\beta$ -sheet structure remained intact in the 5-FU and LV loaded RATEA-F8 hydrogel. In the presence of ANS, fluorescence spectra indicated the formation of hydrophobic core inside the nanofibers of the hydrogel and the drugs (5-FU and LV) were encapsulated in this hydrophobic core. The in vitro cellular uptake of the hydrogel was checked in HCT 116 cell and for this purpose peptides were tagged with FITC. The CLSM images predicted the cellular internalisation of the peptide (RATEA-F8) in HCT 116 cell. The in vitro anticancer activity of bare 5-FU, combined 5-FU + LV and RATES-F8 (5-FU + LV) hydrogel was performed against the HCT-116 cell line. It was observed that the RATES-F8 (5-FU + LV) hydrogel was most effective against HCT-116 after 72 h of incubation. The IC<sub>50</sub> values of 5-FU, 5-FU + LV and RATES-F8 (5-FU + LV) were 66.59, 58.56 and 4.03  $\mu$ M respectively after 72 h and this observation described the synergistic anticancer effect of 5-FU, LV and RATES-F8 peptide [8]. Liu et al. have engineered in situ selfassembled, injectable and pH-sensitive drug-peptide hydrogel for the cancer therapy. They synthesized a drug methotrexate (MTX) attached peptide (KKFKFEFEF) by the solid phase peptide synthesis process. The pH-sensitive moiety 2,3-dimethylmaleic anhydride (DA) was conjugated with the MTX- KKFKFEFEF peptide via amidation reaction. MTX conjugated peptide (MTX-KKFKFEFEF) formed hydrogels at pH 7.4 whereas, DA conjugated MTX-KKFKFEFEF exhibited hydrogelation at pH 6.5 instead of 7.4. Transmission electron microscopy (TEM) exhibited the shortnanofibrillar morphology for MTX-KKFKFEFEF hydrogel whereas regular and entangled nanofiber was observed in case of MTX-KKFKFEFEF(DA) hydrogel. Cell viability test was performed with MTX, KKFKFEFEF, MTX-KKFKFEFEF and MTX- KKFKFEFEF(DA) against 4T1, Hela and B16 cell lines by CCK-8 assay. This showed almost 100% cell viability for the peptide (KKFKFEFEF) of different concentrations against 4T1 cell line at 37 °C after 24 h of incubation. To investigate the cellular uptake ability of the peptide, 4T1 cells were incubated with the FITC-loaded KKFKFEFEF and flow-cytometric analysis and fluorescence intensity confirmed the endocytosis. Further the in vivo cellular uptake study was performed with the help of fluorescence imaging. In this context, cy5.5 was labelled with MTX,

MTX-KKFKFEFEF and MTX-KKFKFEFEF(DA) and checked after 72 h. Cv5.5labelled MTX-KKFKFEFEF(DA) showed the signal with highest intensity while the signal from cv5.5-labelled MTX and cv5.5-labelled MTX-KKFKFEFEF disappeared after 4 h. This observation indicated that the MTX-KKFKFEFEF(DA) peptide formed hydrogels in tumour microenvironment (acidic pH) and remained intact for a long period of time. The in vivo anti-tumour activity of MTX, MTX-KKFKFEFEF and MTX-KKFKFEFEF(DA) was investigated on 4T1 tumour bearing BALB/c mice (female, 8 weeks). All the samples were injected into the tumour site on the 1st and 4th day respectively. The MTX and MTX-KKFKFEFEF exhibited almost 50% tumour inhibition, on the other hand MTX-KKFKFEFEF(DA) showed tumour inhibition rate of  $80 \pm 0.78\%$ . They have successfully developed pH-sensitive in situ self-assembled peptide based hydrogels with good tumour-proliferation and anti-tumour activity [3]. Hauser et al. have reported anticancer drug ligated self-assembled ultrashort peptides for anticancer therapy. They synthesized propiolic acid functionalized peptides. namely LIVAGK-NH2, IVK-NH2, LIVAGD-OH and IVD-OH by SPPS method and azide group containing oxaliplatin analogue. They attached alkyne-functionalized peptides with oxaliplatin analogue via the click reaction in the presence of Cu(I) catalyst. Peptide-oxaliplatin analogue conjugates were soluble in water and did not form hydrogel whereas, alkyne-conjugated peptides formed gel at a concentration of 29 mg mL $^{-1}$ . This could be attributed due to the bulky triazole group which might obstruct the self-assembly phenomenon by introducing the hydrophilic nature at the N-terminus of the peptides. A hybrid hydrogel was formed when the parent peptide and drug derived peptide were mixed together in water and it was believed that the parent peptide was utilized as matrix during hydrogelation. The gelation process was faster and the critical gelation concentration was lower in phosphate buffered saline (PBS) as compared to water. Cytotoxicity test of the synthesized compounds was carried out against Hela and SW480 cell lines. The in vitro anticancer activity was checked against Hela, SW480 and 4T1 cell lines and IC<sub>50</sub> value for the peptide-drug conjugate hydrogel was evaluated. All the oxaliplatin-peptide conjugated hydrogels were found to be most active against SW480 cells with IC<sub>50</sub> value 1.5–2.3  $\mu$ M and showed least activity against Hela cells with IC<sub>50</sub> value  $3.4-7.7 \,\mu$ M. Furthermore, the pathway of anticancer activity of the compounds was investigated in 4T1 and SW480 cell lines and oxaliplatin was taken as control. It was found that all the compounds successfully arrested both the cell lines in G2/M phase and stopped the cells from crossing G2/M DNA damage check point. They measured the caspase 3 and caspase 7 activity and demonstrated that all the compounds along with the control induce the apoptosis through caspase 3 and 7 pathway. Further they checked the in vivo anticancer activity of the oxaliplatin derived peptide hybrid hydrogels on female BALB/ c mice. The compounds and control were injected into seven day old tumour and the half dose was injected again on day 21. The size of the tumour was measured on day 7, 14, 21, and 28. The hybrid hydrogel containing Ac-LIVAGK-NH<sub>2</sub> peptide and oxaliplatin—LIVAGK-NH<sub>2</sub> conjugate peptide showed the most significant antitumour activity [9]. Liu et al. have developed peptide-based hydrogels consisting of chlorambucil (CRB) and peptide drug YSV for cancer combination therapy. They synthesized CRB-FFE-YSV peptide-drug conjugates via SPPS method and prepared

the hydrogel in PBS (pH 7.4) by heating and cooling method. The hydrogel was characterized by rheometer and CD spectroscopy. TEM image revealed the formation of nanofiber networks in the hydrogel. The stability of bare YSV and CRB-FFE-YSV hydrogel in the presence of enzyme (proteinase K) was determined and it was observed that free YSV fully degraded within 1 h of incubation while 50% of the CRB-FFE-YSV hydrogel degraded after 4 h of incubation. This result clearly indicated that the fibrillar networks of the hydrogel protected the peptide drug (YSV) from rapid degradation in the presence of proteinase K. FITC was incorporated into the hydrogel (CRB-FFE-YSV) to evaluate the cellular uptake and higher fluorescence intensity was observed as compared to bare FITC. Furthermore, they incubated free YSV and CRB-FFE-YSV hydrogel with HepG2, MCF-7 and BEL-7402 cell lines for 4 h and there was 2-threefold increase of intracellular CRB-FFE-YSV hydrogel concentration as compared to YSV. The in vitro anticancer activity of CRB-FFE-YSV hydrogel was measured against HepG2, MCF-7 and BEL-7402 cell lines. The IC<sub>50</sub> values of CRB-FFE-YSV hydrogel were 28.9, 47.5 and 25.7 µM respectively and the observed IC<sub>50</sub> values were lower than that of the free YSV and CRB. This observation clearly depicted the potentiality of the CRB-FFE-YSV hydrogel for anticancer therapy. Along with in vitro activity, in vivo anti-tumour activity was performed in HepG2-tumour bearing BALB/c mice. The YSV, CRB, YSV + CRB, CRB-FFE-YSV were injected separately into the tumour of mice at an equivalent dose on days 1, 4, 7 and 10. After 28 days of treatment, the relative volume of the tumour was 728, 491, 514, and 356% corresponding to the YSV, CRB, YSV + CRB and CRB-FFE-YSV, respectively. It was observed that during the in vivo biocompatibility test, CRB-FFE-YSV hydrogel did not harm any vital organs of the tumour bearing mice, hence it was biocompatible [10]. Another work on the supramolecular peptide based anticancer hydrogel was reported by Liu et al. They synthesized the chemotherapeutic drug (Taxol) conjugated peptide (EYSV) and prepared the hydrogel in PBS (pH 7.4). An anticancer drug Taxol was conjugated with the anticancer peptide YSV to introduce the combinational anticancer activity. Glutamic acid (E) was attached to increase the solubility of Taxol-EYSV and along with anticancer activity YSV reversed the anticancer drug resistivity by inhibiting the activity of P-gp efflux pumps. The hydrogel was characterised by rheological experiment and the nanofibrillar networks were found in TEM image. Moreover, the cellular uptake study revealed the higher intracellular concentration of the Taxol-EYSV hydrogel  $(2.7 \,\mu\text{M})$  as compared to the free Taxol (<0.5  $\mu$ M) in A2780 cell. The in vitro anticancer activity of the Taxol, YSV and Taxol-EYSV hydrogel was performed against Hela and A2780 cell lines. This result showed the lower IC<sub>50</sub> value for Taxol-EYSV as compared to free Taxol and YSV. This observation indicated the enhanced cellular uptake and the combinational effect of Taxol and YSV. The in vivo anticancer efficiency of Taxol-EYSV was measured on A2780 tumour bearing mice via injecting the hydrogel. The tumour inhibition rate of YSV, Taxol, Taxol-EVSY and Taxol-YSV was 15, 33, 30 and 55%, respectively. Furthermore, H&E staining assays of the main organs of mice were performed to confirm the in vivo biocompatibility. They have successfully engineered a carrier-free Taxol-EYSV peptide hydrogel for combinational anticancer therapy to defeat drug resistance [11]. Recently, our group has reported benzoselenadiazole (BSe)-capped peptide hydrogels with inherent anticancer and anti-inflammatory activity. We synthesized two BSe-peptide conjugated compounds namely, BSeLYF and BSeLYW via the solution phase peptide synthesis method. The BSeLYF fabricated the hydrogel in the phosphate buffer (PB) of pH 7.4 whereas BSeLYW formed the hydrogel in PB of pH 6.8. Both the hydrogels were characterised by rheological test and TEM images confirmed the formation of nanofiber networks in the gel. The in vitro anticancer activities of those hydrogels were evaluated against MCF-7 and HEK293T cell lines by dose dependent MTT assay. The IC<sub>50</sub> values of BSeLYF and BSeLYW hydrogels against MCF-7 cell were 3.26 and 2.97 mM, respectively. However, at lower concentrations (1-2 mM) of hydrogels no toxicity was observed against HEK293T cells. We measured the production of reactive oxygen species (ROS) in MCF-7 cells after applying BSeLYF and BSeLYW hydrogels separately. Overproduction of intracellular ROS led to the oxidative stress in the cell and finally apoptosis. Along with ROS detection, we performed quantitative real time-polymerase chain reaction (qRT-PCR) analysis to determine the involvement of intrinsic (CytC, Caspase-9, Bax, Apaf-1) and extrinsic (Caspase-8, Fadd) pathways of cancer cell apoptosis. ROS and qRT-PCR experiments depicted that the BSeLYF and BSeLYW induced ROS overproduction and turned on the intrinsic apoptosis pathway [12] (Fig. 1).

#### 1.2 Enzyme-Instructed Self-Assembled Peptide Hydrogel

Xu et al. have engineered an enzyme-instructed peptide-taxol self-assembled hydrogel for cancer therapy. They synthesized the NapFFKYp peptide and the drug Taxol was tagged with the peptide via a linker (succinic acid). They dissolved Taxol-NapFFKYp in water (pH 7.3) with the help of sonication, but no gel was formed. 5 µL of alkaline phosphatase (10 U/µL) was added to the solution of Taxol-NapFFKYp and kept for overnight. The hydrogel was formed. In the presence of alkaline phosphatase (ALP) dephosphorylation of tyrosine took place and self-assembly of the Taxol-NapFFKY peptide started which led to the formation of the hydrogel. The CD spectra of the hydrogel revealed the  $\beta$ -sheet-like structure of self-assembled Taxol-NapFFKY peptide and the formation of nanofiber networks was investigated with the help of SEM and TEM images. The in vitro anticancer activity of Taxol-NapFFKYp and Taxol-NapFFKY was evaluated on Hela cell lines and Taxol was used as control. The IC<sub>50</sub> values of Taxol-NapFFKYp and Taxol-NapFFKY were comparable with the value of free Taxol and this indicated that the anticancer activity of Taxol remained intact in the hydrogel matrix [13]. Yang et al. have reported a peptide self-assembled nanosphere structured hydrogel for the delivery of Taxol. They synthesized folic acid (FA) functionalized phosphorylated peptide (GpYK) and tagged this peptide (FA-GpYK) with Taxol via succinic acid linkage. FA-GpYK-Taxol was dissolved in PBS (pH 7.4) followed by the addition of phosphatase solution (final concentration 90 U



**Fig. 1** a Graphical presentation of anti-tumour activity of the peptide hydrogel at the tumour environment (Reproduced with the permission of Ref. no [3]), **b** Schematic presentation of selfassembled peptide nanofibers (Reproduced with the permission of Ref. no [8]), **c** Inverted fluorescence microscopy images of HepG2 cells treated with free FITC or FITC-loaded CRB – FFE – YSV hydrogel after incubation at equivalent FITC concentration (10 µg/mL) for 4 h (green, FITC; blue, DAPI). The in vivo anti-tumour efficacy in the H22 tumour bearing mice model (Reproduced with the permission of Ref. no [10]), **d** Curve of the tumour volume growth, **e** Photographs of tumours excised at the end of treatment. Values are shown as the ± standard deviation of the mean. \**p*-Value < 0.05, \*\**p*-value < 0.01. NS: normal saline, free-PTX: free paclitaxel solution, and HG-PTX: paclitaxel-loaded FER-8 peptide hydrogel (Reproduced with the permission of Ref. no [7]), **f** The in vivo bioluminescence images of MTX-based peptides at the tumour environment after injection (Reproduced with the permission of Ref. no [3])

mL<sup>-1</sup>) and kept for few minutes at room temperature (22–25 °C). The dephosphorylation of the peptide (FA-GpYK-Taxol) by phosphatase and the formation of FA-GYK-Taxol led to the formation of a self-assembled hydrogel. Morphological analysis by AFM revealed the nanospherical structure of the hydrogel (FA-GpYK-Taxol). They explained that the FA part of the conjugated peptide formed a tetramer via intermolecular H-bonding and these tetramers self-assembled in a higher order to form the nanosphere structure. The mechanical strength of the hydrogel was measured by rheological experiments. Furthermore, in vitro anticancer activity of FA-GYK-Taxol and FA-GpYK-Taxol was performed on the HepG2 cell line. The IC<sub>50</sub> values of FA-GYK-Taxol and FA-GpYK-Taxol were comparable with the bare Taxol and the anticancer activity of Taxol remained unaltered in the hydrogel [14]. Li et al. reported enzyme-triggered hydrogelation of the platinum prodrug-peptide conjugate via supramolecular self-assembly for the anti-tumour therapy. They synthesized the phosphorylated peptide and conjugated the anticancer drug cis-platin via succinic acid. Thus they developed Pt (IV)-peptide prodrug which self-assembled in the presence of alkaline phosphatase (tumour cell environment) and released Pt (II) drug in the redox condition of the tumour cell. The Pt (IV)-peptide prodrug was dissolved in

PBS (pH 7.4) followed by the addition of alkaline phosphatase, which gave rise to the formation of a translucent hydrogel. The CD spectra of the hydrogel revealed the  $\beta$ sheet-like structure of the self-assembled Pt (IV)-peptide prodrug and the formation of nano fibrous networks were investigated by TEM and AFM analysis. The rheological experiments depicted the mechanical characteristics of the hydrogel. The drug release profile revealed that the release of Pt (II) drug was induced by various concentrations of glutathione in PBS (10 mM, pH 7.4). At the higher concentration of GSH (5 mM), which is comparable with the concentration of cancer cells, the drug release was quite steady. The in vitro anti-tumour activity was performed on Hela and 4T1 cell lines. The Pt (IV)-peptide showed IC<sub>50</sub> values of 4.6 and 3.4  $\mu$ M for Hela and 4T1 cells respectively after 72 h of incubation. Further, to investigate the in vivo anti-tumour activity, 4T1 tumour bearing mice were injected with cisplatin and Pt (IV)-peptide separately within the interval of every 48 h. After 8 days of treatment, the volume of tumours for cisplatin and Pt (IV)-peptide were  $11.21 \pm 3.5$  mm<sup>3</sup> and  $23.80 \pm 9.8 \text{ mm}^3$ , respectively. This observation signified that the ant-itumour activity of cisplatin remained unaltered in the Pt (IV)-peptide hydrogel. The histological analysis showed no harmful effect of Pt (IV)-peptide on the major organs of mice, hence the hydrogel was biocompatible [15] (Fig. 2).



**Fig. 2** a Graphical description of the enzyme-triggered supramolecular self-assembly of prodrug 1 (Pt (IV)-peptide) for accumulation and controlled drug release in the presence of stimuli (alkaline phosphatases and ROS in tumour cells), **b** Live-cell fluorescent apoptosis imaging in HeLa cells pre-treated with prodrug 1 in the presence or absence of caspase-3 inhibitors. Blue: nuclear staining dye (DAPI); red: caspase-3 probe (sulforhodamine-DEVD-FMK) (Scale bar = 75  $\mu$ m), **c** The in vivo tumour volume changes of 4T1 breast cancer xenografts after treatment with PBS buffer, cisplatin and 1, **d** Representation of H&E staining images of tumours and major organs, collected from 4T1 tumour-bearing mice treated with PBS buffer, cisplatin and 1. Error bars represent standard deviations, Scale bar = 100  $\mu$ m (Reproduced with the permission of Ref. no [15])

#### 1.3 Peptide Hydrogel for Photodynamic Therapy (PDT)

Yan et al. have developed a photosensitive drug loaded peptide hydrogel for photodynamic therapy against tumour. They prepared the Fmoc-diphenylalanine (Fmoc-FF) and poly-L-lysine (PLL) based hydrogel in Tris-HCl solution at a pH of 7.8 and the photosensitive drug Chlorin e6 (Ce6) was incorporated into the fibrillar hydrogel matrix. Rheological characterisations of the bare Fmoc-FF/PLL hydrogel and Ce6 incorporated hydrogel were performed and the data indicated that the mechanical properties of the Fmoc-FF/PLL hydrogel remained intact after encapsulation of the Ce6 drug molecule. The in vivo drug release efficacy and the anti-tumour activity of the Ce6 incorporated Fmoc-FF/PLL hydrogel were determined in the MCF-7 tumour bearing mouse model. Free Ce6 and Ce6-Fmoc-FF/PLL hydrogel were injected in the tumour site and the release of the drug was monitored by fluorescence imaging. The fluorescence intensity of the Ce6 solution diminished after 24 h of injection whereas in case of the Ce6-Fmoc-FF/PLL hydrogel, the drug was found even after 8 days of injection. Hence, this observation depicted the controlled release of Ce6 from the nanofibers of the Fmoc-FF/PLL hydrogel. Fmoc-FF/PLL hydrogel and Ce6-Fmoc-FF/PLL hydrogel were injected in the tumour site of MCF-7 containing mice to check the efficacy of photodynamic therapy. The Ce6-Fmoc-FF/PLL hydrogel was injected in the tumour site and irradiated with laser (wavelength 635 nm, power of 100 mW cm<sup>-2</sup>) for 2 times, 4 times and 6 times consecutively. The observed result revealed that the tumour volume decreased significantly and vanished after two weeks of treatment. Thus, photodynamic therapy of the Ce6 incorporated Fmoc-FF/PLL hydrogel was proved to be a significant therapy against tumour. Furthermore, in vivo biocompatibility test (H&E strain experiment) of the hydrogel was performed and there was no significant damage of major organs like heart, liver, lung and kidney of the mice, hence the hydrogel was biocompatible [16]. Another work on the selfassembled bola-dipeptide hydrogel for the photodynamic therapy against tumour has been reported by Yan et al. They synthesized bola-dipeptide (DFF) and prepared the DFF hydrogel and prodrug 5-aminovulinic acid (5-ALA) containing DFF hydrogel in DMSO/H<sub>2</sub>O. The formation of the nano-fibrillar networks in the hydrogel was confirmed by SEM, TEM and AFM images. Further, the sensitivity of the hydrogels (DFF and DFF/5) towards glutathione (GSH) and trypsin was identified and from the TEM, AFM and CD spectroscopy data degradation of hydrogels was confirmed. The in vivo anti-tumour activity was performed on tumour bearing mice by injecting the DFF/5 hydrogel at the tumour site. Two different groups of mice were injected with DFF/5 and 5-ALA separately. Then the laser (635 nm and 200 mW cm<sup>-2</sup>) is irradiated at the tumour site after 6 h of injection. Another group of mice were only irradiated with laser without injecting DFF/5 and 5-ALA. The result depicted the complete suppression of the tumour after 21 days by using DFF/5 and laser combined therapy. They explained that the prodrug 5-ALA transformed into protoporphyrin IX (PpIX) via the biosynthetic process and absorbed laser radiation to show PDT. The in vivo distribution of 5-ALA and DFF/5 hydrogel was monitored by fluorescence imaging. The images showed that the DFF/5 hydrogel was tumour specific but 5-ALA was



**Fig. 3** a Schematic presentation of photosensitive drug (Ce6) encapsulated injectable peptidebased fibrous hydrogels for antitumor photodynamic therapy (Reproduced with the permission of Ref. no [16]), **b** Schematic representation of bola-dipeptide-based injectable hydrogels for the prodrug (5-aminolevulinic acid hydrochloride, 5-ALA) delivery and enhanced photodynamic antitumor therapy (Reproduced with the permission of Ref. no [17]), **c** Photographs of the resected tumours after 2 weeks, **d** In vivo fluorescence images of mice after intratumour injection of Ce6 or Fmoc-FF/PLL hydrogel encapsulated with Ce6 by an equal amount over time (Reproduced with the permission of Ref. no [16])

distributed in different organs along with the tumour site. Hence, the developed DFF/5 hydrogel efficiently released prodrug 5-ALA and showed enhanced PDT for antitumour activity [17] (Fig. 3).

#### 2 Conclusion

Since the last decade an enormous advancement has been observed in the peptide hydrogel based cancer therapy. It is worth mentioning that the self-assembling nature of the peptide and the formation of nanostructures help to incorporate the anticancer drugs in the hydrogel matrix easily. The stimuli responsive nature of the peptide based hydrogel ensures the controlled and sustained delivery of the drugs. Furthermore, enzyme-instructed peptide based hydrogels are more specific to the tumour site due to their stimuli-responsiveness in the presence of GSH, ROS and ALP. Besides, peptide hydrogel based photothermal and photodynamic therapy have combined effect to combat cancer. There are so many reports on the peptide based hydrogel for anticancer therapy but the clinical trial approval has not been given yet due to some shortcomings of these hydrogels. One of the vital obstacles is the immunogenicity of the hydrogel. The injected hydrogel can cause inflammation or other harmful effects on the health cells surrounding the cancer cells. Apart from this, the mechanism of the stimuli-responsive drug delivery or anticancer therapy has not been understood

well. This is expected that the drawbacks will be conquered very soon and the peptide based hydrogel will lead to the successful development of anticancer therapy in the near future.

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# A Sustainable Approach to Counteract Dampness in Building



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#### **1** Introduction

Dampness is the presence of moisture in various parts of a building, such as the floor, walls, and roof. Dampness is caused by either outside moisture intrusion or condensation within the building. The dampness in the building causes an unpleasant and unsanitary environment for the occupants [1-3]. As a result, adequate precautions must be taken to avoid such situations. Dampness is caused primarily by rainwater, groundwater, and pipe leaks. Rainwater may enter the building if the roof is not waterproofed, and an improper slope may result in ponding of water, which can cause dampness from the wall top [4]. Buildings are built on soil, and moisture may enter the foundation due to capillary action or an increase in the groundwater table, resulting in dampness at the floor level and also the effect over the steel can be seen because considering that ambient humidity and oxygen are necessary for steel corrosion, and any decrease in their penetration into the concrete will slow the process down if it has already started [5]. As a result, the dampness formation has been a persistent issue for construction engineers, fueling their eagerness to find a solution. The quest for sustainable and environmentally friendly materials is taking center stage in the emerging world of materials. The following materials have been reported in the scientific literature as common damp proofing materials: (1) bitumen; (2) mastic asphalt; (3) bricks; (4) stones; (5) metal sheets; and (6) plastic sheets [6].

Mortar is a cement-based construction material that is widely accepted and used all over the world [7]. Because of the bad material, corrosion in steel, and water absorption on the walls, mortar used in construction can harm the environment as well as human health. The structure loses its allure as water is drawn to the walls. Water seeping into a structure causes the mortar or paint to peel and flake off, reducing

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the structure's lifespan. Waterproofing agents have been mixed into the cement to mitigate these effects. To reduce moisture transmission, admixture and the moisture-reducing agent have been widely used. To make the mortar surface impermeable, mixtures with large surface areas and high durability, such as micromaterials or nanomaterials with organic materials, must be confined to organic nanomaterials.

Several chemicals and other admixtures have been used for surface water-proofing and coating materials over the last few decades [8]. Despite being reported to be toxic to human health and the environment, these chemicals were effective in reducing moisture intrusion into the building surface. Many attempts have been made to reduce the interaction between water and building materials by using organic materials at the micro and nanoscale. The poor durability of concrete materials, which can lead to premature failure and serviceability issues, may complicate the construction of property infrastructure systems [9]. It is critical to have a thorough understanding of the concept of concrete durability and the proper specification of materials for infrastructure projects if the structure is to be protected from the potentially harmful effects of exposure to the outside environment on its long-term durability.

In the present investigation, we utilized extract from Colocasia esculenta as an additive to the mortar cement to examine the effectiveness of eliminating the interaction of water with the building surface. Wettability and water absorption tests were performed to interpret the interaction of extract coating and the water over time.

#### 2 Materials and Methods

#### 2.1 Materials

For the investigation, the plant Colocasia was collected from the vegetation fields. Chloroform was used as a solvent, to extract the material procured from Thermo Fisher Scientific India Pvt. Ltd. Portland Pozzolana cement (PPC) of Indian Standard 1489 (part 1):1991 is used in this experiment. The raw materials used in this cement contain fly ash and Portland cement clinker concerning the chemical requirement and other admixture added with a limit of not more than 1% [10]. As per the IS 4031(part 5):1988, the initial setting time is a minimum of 30 min and the final setting time is a maximum of 600 min tested by the Vicat apparatus method. The fine aggregate of size 0.075–0.425 mm is used as the binder material in the mortar sample for durability and strength with the required water-cement ratio.

#### 2.2 Methods

#### 2.2.1 Extraction of Material from Plant Colocasia Esculenta

The following steps were followed to get an extract of the plant Colocasia esculenta leaf:

- a. Taro roots were collected from different vegetation sites
- b. Leaves were cleaned from running water and dried in an air oven at 80  $^{\circ}\mathrm{C}$  for 3–4 h
- c. After drying, leaves were crushed manually by applying mechanical pressure to make fine powder
- d. The powder was then dissolved in the volatile solvent (Chloroform)
- e. Stirred using a magnetic stirrer at 40 °C for 20 min
- f. The solution was then filtered through a filter paper to fetch the extract from the leaves

#### 2.2.2 Preparation of Samples for Investigation

The ASTM Standard (C109) mold has a size of 50 mm  $\times$  50 mm  $\times$  50 mm. Before casting the cement mix mortar into the mold, a small coating of release agent should be added to the inside sides of the mold to generally allow the cube to depart from the mold [11]. After this, the samples were maintained for 3, 7, and 28 days to cure to the allowable strength. After curing, each batch of samples was dipped into the extract for around 12 h to produce an equal coating on the sample surface.

#### 2.2.3 Wettability Test

Wettability is a preference of a liquid/fluid to physically adhere to any surface and can be quantified by measuring the contact angle [12]. This test was performed to check the water interaction with the prepared samples. A coated mortar block was placed on the sample bed of (Kruss DSA25E, Germany). A 0.5  $\mu$ L water droplet was formed through the needle of injection and dropped on the surface of the mortar cube to check the water contact angle. The resolution of the camera system was 1920  $\times$  1200 px and the frame rate was 2300 fps.

#### 2.2.4 Water Penetration Test and Compressive Strength Test

A water absorption test was carried out to validate the hydrophobic nature of the provided coating on the mortar samples. Samples were immersed in the water over a definite period of 7–28 days to record the water interaction with the sample. The water absorption capacity was measured as:

$$C_W = \frac{M_2 - M_1}{M_1} \times 100$$

where  $C_W$  is the water absorption capacity of the sample,  $M_2$  is the final weight of the sample after absorption, and  $M_2$  is the initial weight of the sample before absorption.

Compressive strength is the major parameter that needs to be taken into the consideration. Compressive strength was measured to validate the hypothesis for hydrophobic coating over the mortar surface to eliminate dampness. A compressive strength testing machine (HE-SPL H09403) was utilized to record the compressive strength.

#### **3** Results and Discussions

#### 3.1 Effect of Extract on the Wettability of Mortar Sample

The interaction of water and materials, as well as the dynamic behavior of water on the surface or within the materials, are always included in hydrophobicity assessment and testing methodologies for materials. Water wettability is one of the most typical characteristics of a solid surface. Additionally, due to the hydrophobic nature of materials based on cement, capillary adsorption, concentration-driven diffusion, and pressure-driven infiltration are three examples of the types of mechanisms that can be used to evaluate different types of materials. Water absorption and impermeability are also based on water migration and transport [13]. The hydrophobicity of the surface can be classified as hydrophilic if the contact angle is <90°; hydrophobic if the contact angle is  $>90^\circ$ ; superhydrophobic if the contact angle is  $>150^\circ$ . The central thought of hydrophobic properties is to impart water repulsiveness to the plaster for the reduction of the perforation of water into the interior and exterior walls. The figure shows the wettability of the mortar surface with respect to the water. The mortar sample coated with the extract of the Colocasia esculenta showed a contact angle of around 100° at a mean temperature of  $20 \pm 2$  °C. However, the drop is retained for about 400–600 s and afterward it slowly starts penetrating the contact angle after still remaining for 96–98° [14]. The wetting characteristics as shown in the Fig. 1 signifies that the leaf extract can provide the mortar cement with hydrophobic surface. The result signifies the leaf extract can provide the mortar cement with a hydrophobic surface.



Fig. 1 Contact angle of PPCM surface with respect to the water

Table 1       Compressive         strength on different curing days	Sample code	Curing time (days)	Gained compressive strength (MPa)
	PPCM1	3	2.66
	PPCM2	7	2.8
	PPCM3	28	3.24

# 3.2 Effect of Extract on Water Penetration and Compressive Strength

The compressive strength of Portland Pozzolana Cement mortar gained the compressive strength (MPa) as shown in Table 1, when cured for 3, 7, and 28 days. The compressive strength recorded after the curing was 2.66, 2.8, and 3.24 MPa. After the curing process, the cement mortar samples were coated with taro-root leaves extract by dip coating. Furthermore, coated and without coating, mortar cement samples were investigated for water uptake. The coated and non-coated mortar cement samples are shown in Fig. 2. A water penetration test was performed on the mortar cement samples. The compressive strength gained by the mortar cement samples over time is shown in Table 1.



Fig. 2 Mortar cement samples; a non-coated; b coated



Fig. 3 Effects of water interaction on the compressive strength of PPCM sample (with or without coating)

Figure 3 demonstrates the effect of water penetration on sample compressive strength (with and without coating). The coating of the extract on the PPCM reduced water interaction with the surface of the PPCM samples while demonstrating no change in compressive strength, according to the data. The compressive strength of the PPCM samples without extract coatings, on the other hand, is lowered. The coating's durability was further tested by immersing the sample in water for 10–15 days. As a result, the coating was not damaged and retains its hydrophobic nature. The insignificant interaction with water might eliminate/reduce dampness issues in constructing buildings.

#### 4 Conclusion

In this present investigation, we endeavored to provide a natural extract coating over the cement surface to prevent it from dampness. The theme of this investigation was to validate whether the natural extract coating can induce non-wetting characteristics to the surface and can prevent dampness and its adverse effects. The following conclusion can be drawn from the present study:

- The coating of Colocasia esculenta leaves extract on PPCM offered a hydrophobic surface.
- The contact angle was measured to be greater than 100° which confirmed the hydrophobicity.

• Moisture is known to reduce the strength of cement over time, which can shorten the life of the structure. The use of a hydrophobic material as a coating prevents water molecules from interacting with the cement. As a result, it can help to reduce dampness while also maintaining compressive strength.

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# Photometric Investigation of Eu<sup>3+</sup> Doped BaGd<sub>2</sub>O<sub>4</sub> Phosphor for Solid-State Lighting Devices



Manisha and S. K. Sharma

#### **1** Introduction

Rare earth (RE) based oxide phosphors are the most important trichromic (Red, Green, and blue) luminescent materials. The green and red emissions developed from the f–f transitions of Tb<sup>3+</sup> and Eu<sup>3+</sup> ions while the blue emission developed from the f–d transitions of Eu<sup>2+</sup> ions [1]. Luminescent materials play an important role for white light emitting diode (WLED) application. There are two ways to produce white light: (i) mixing of primary colours such as red, green and blue. This process is accomplished by using combination of multi-chip (mc-LEDs) (ii) coating of yellow phosphor on blue LED called phosphor converted (pc-LED). White LEDs based on excitations of yellow phosphor by the blue emission of another phosphor have certain advantages such as: low power consumption, high efficiency, eco-friendly and long-persistent over the conventional light sources [2].

RE based oxide materials ARE<sub>2</sub>O<sub>4</sub> (A = Ba, Ca, Sr, and RE = trivalent rare earth ions) exhibit CaFe<sub>2</sub>O<sub>4</sub> type structure, which crystallizes in to orthorhombic structure with space group Pnma. In the series BaY<sub>2</sub>O<sub>4</sub>, SrY<sub>2</sub>O<sub>4</sub>, CaY<sub>2</sub>O<sub>4</sub>, SrGd<sub>2</sub>O<sub>4</sub>, BaGd<sub>2</sub>O<sub>4</sub> have been extensively investigated [3–7]. The same valence state and ionic radii (Eu<sup>3+</sup> = 1.07 Å, and Gd<sup>3+</sup> = 1.05 Å) promoted the embodiment of Eu<sup>3+</sup> ions at Gd<sup>3+</sup> site, which have Eu<sup>3+</sup> ions are an excellent activator to yield red emission from BaGd<sub>2</sub>O<sub>4</sub> host [8].

In the present work, we have discussed the crystal structure, optical band gap, morphology of the particle and photoluminescence properties that are characterized by XRD, UV–Vis-NIR spectroscopy, FESEM and Micro-Raman spectroscopy. To best of our knowledge, there is no report on photometric parameters of Eu<sup>3+</sup>

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doped BaGd<sub>2</sub>O<sub>4</sub> phosphors. The results obtained in the present work are useful in applications, such as, fabrication of field emission display (FED) and LED devices.

#### 2 Experimental Details

#### 2.1 Sample Preparation

Eu<sup>3+</sup> doped BaGd<sub>2</sub>O<sub>4</sub> (BaGd<sub>2-x</sub>Eu<sub>x</sub>O<sub>4</sub>;  $0.00 \le x \le 0.18$ ) were synthesized by the high temperature solid-state reaction method. The starting raw materials BaCO<sub>3</sub> (CDH, 99.9%), Gd<sub>2</sub>O<sub>3</sub> (CDH, 99.9%), and Eu<sub>2</sub>O<sub>3</sub> (CDH, 99.9%) were weighted in stoichiometric ratio and grounded by agate mortar and pestle. The mixture was put in an alumina crucible and placed in a tube furnace. It was calcined at 1050 °C for 4 h and then cooled up to room temperature before grinding the mixture. The mixture was put in an alumina crucible and finally sintered at 1300 °C for 6 h Eu<sup>3+</sup> doped BaGd<sub>2</sub>O<sub>4</sub> phosphors.

#### 2.2 Measurement and Characterization

The structural property was studied by X-Ray Diffractometer (Rigaku, Smartlab) with  $\text{Cu}-\text{K}_{\alpha}$  ( $\lambda = 1.54$  Å) radiation. The surface morphology studies of synthesized phosphors were carried out using Field Emission Electron Microscope (Zeiss, Supra 55). Diffuse reflectance spectra were recorded by UV–Vis-NIR Spectrophotometer (Cary 5000, Agilent). Photoluminescence emission spectra were recorded by Micro-Raman spectrometer (LabRAM HR-UV-Open, HORIBA Scientific) at an excitation wavelength of 325 nm using He–Cd laser. Photometric parameters were calculated by ColorCalculator (*ver*. 6.35, Commission Internationale de l'Elcairage).

#### **3** Result and Discussion

#### 3.1 X-Ray Diffraction

The X-Ray diffraction pattern of BaGd<sub>2-x</sub>O<sub>4</sub>: xEu<sup>3+</sup> is shown in Fig. 1. The results are in agreement with the standard XRD pattern described in JCPDS card no.# 00-082-2320. The peaks are indexed with standard JCPDS data in order to identify (h k l) planes. The inter-planer spacing (d) is calculated by using Bragg's law  $(2d_{hkl}sin\theta_{hkl} = \lambda)$ . The crystal structure belongs to orthorhombic structure, in which 'a', 'b', and 'c' are unequal. The relation between interplanar spacing (d), miller indices (h k l) and lattice constant (*a b c*) for the orthorhombic crystal structure is as in Eq. (1).



Fig. 1 XRD pattern of Eu<sup>3+</sup> doped BaGd<sub>2</sub>O<sub>4</sub> phosphors

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \tag{1}$$

The calculated lattice parameters are:  $a \approx 10.4887$  Å,  $b \approx 12.2618$  Å and  $c \approx 3.5160$  Å. Further, no impurity peak in the XRD pattern after doping shows the successful doping of Eu<sup>3+</sup> ions in BaGd<sub>2</sub>O<sub>4</sub>.

#### 3.2 Surface Morphology Studies

The FESEM technique is utilized to investigate the surface morphology of the  $BaGd_2O_4$  and  $Eu^{3+}$  doped  $BaGd_2O_4$  samples and the corresponding images are shown in Fig. 2. FESEM image show that the synthesized samples exhibit spherical morphology. The particles show very little agglomeration with size of the voids decreasing after doping with  $Eu^{3+}$  ions.

#### 3.3 Reflectance Spectroscopy

The diffuse reflectance spectra for the Eu<sup>3+</sup> doped BaGd<sub>2</sub>O<sub>4</sub> phosphors have been recorded in the UV–Vis wavelength range of 200–800 nm. The reflectance spectra for undoped and Eu<sup>3+</sup> doped BaGd<sub>2</sub>O<sub>4</sub> phosphors are shown in Fig. 3. The reflectance spectra of the synthesized samples exhibit an absorption band at  $\approx$ 230 nm, which

Fig. 2 FESEM image of undoped and  $Eu^{3+}$  doped  $BaGd_2O_4$  phosphors

might be originating due to charge transfer band of  $Eu^{3+} - O^{2-}$  and comparatively weak absorption bands at 362, 395, 465, 539, and 593 nm, corresponding to the f–f transitions of  $Eu^{3+}$  ions. The transitions corresponding to above absorption bands are  ${}^{7}F_{0}-{}^{5}G_{3}$ ,  ${}^{7}F_{0}-{}^{5}L_{6}$ ,  ${}^{7}F_{0}-{}^{5}D_{2}$ ,  ${}^{7}F_{1}-{}^{5}D_{1}$ ,  ${}^{7}F_{1}-{}^{5}D_{0}$  respectively [9, 10]. For the peak at around 274 nm, it can be observed that  $Eu^{3+}$  doping concentration does not have any effect on its intensity which indicates that the peak is originating due to a Gd<sup>3+</sup> transition.

The optical band gap  $(E_g)$  of a material is related to its absorption coefficient  $(\alpha)$  by well-known Tauc's equation as in Eq. (2) [11].

$$\alpha hv = C \left( hv - E_g \right)^n \tag{2}$$

100 80 Reflectance % 0.0 mol% Eu<sup>3+</sup> 60 0.5mol% Eu3+ 1.0 mol% Eu<sup>3+</sup> 4( 2.0 mol% Eu<sup>3+</sup> 3.0 mol% Eu<sup>3+</sup> 5.0 mol% Eu3+ 20 - 7.0 mol% Eu<sup>3+</sup> - 9.0 mol% Eu<sup>3+</sup> 200 300 400 500 600 700 800 Wavelength (nm)



where,  $h\nu$  is the incident photon energy, *C* is a proportionality constant, and *n* denotes the nature of electronic transition involved. The optical band gap calculation for Eu<sup>3+</sup> doped BaGd<sub>2</sub>O<sub>4</sub> phosphors was performed by employing Kubelka–Munk theory (Eq. (3)) [12].

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S}$$
(3)

where, F(*R*), *R*, *K* and *S* are Kubelka–Munk function, reflectance, absorption and scattering coefficients respectively. BaGd<sub>2</sub>O<sub>4</sub> exhibits direct allowed transition i.e., n = 1/2. The absorption coefficient  $\alpha$  is proportional to the Kubelka–Munk function (F(*R*)), and hence, in Tauc's equation (Eq. (2))  $\alpha$  is replaced with F(R). So, the final equation can be written as in Eq. (4).

$$[F(R)hv]^2 = C(hv - E_g)$$
<sup>(4)</sup>

The optical band gap can be obtained by extrapolating  $[F(R)hv]^2$  versus hu curve to zero of  $[F(R)hv]^2$  axis. The Tauc's plot using Kubelka–Munk function for undoped and Eu<sup>3+</sup> doped BaGd<sub>2</sub>O<sub>4</sub> phosphors are shown in Fig. 4. The optical band gaps for the phosphors using the above-mentioned procedure have been determined to be  $\approx$ 5.85 eV [13].



Fig. 4 Tauc's plot for the determination of optical band gap of undoped and  $Eu^{3+}$  doped  $BaGd_2O_4$  phosphors





#### 3.4 Photoluminescence Emission Spectra

The PL emission spectra of Eu<sup>3+</sup> doped BaGd<sub>2</sub>O<sub>4</sub> phosphors excited by 325 nm (He– Cd) laser source are shown in Fig. 5. Six emission peaks centred around 582, 595, 610, 612, 625, and 706 nm are ascribed to 4f–4f transitions of Eu<sup>3+</sup> ions from the  ${}^{5}D_{0}-{}^{7}F_{j}$  (j = 0, 1, 2, 3, 4) respectively. The PL emission spectra show the presence of intense red emission at 610 and 612 nm corresponding to the  ${}^{5}D_{0}-{}^{7}F_{2,3}$  transition of Eu<sup>3+</sup> ions [14]. The PL intensity increases with increase in Eu<sup>3+</sup> concentration and at 7 mol% the maximum intensity is observed. After this, the intensity decreases. Hence, 7 mol% Eu<sup>3+</sup> concentration is considered as optimum in the present work.

#### 3.5 Photometric Parameters

The emitted color from the phosphors was quantified by calculating the photometric parameters using color calculator software. The CIE diagram was plotted for Eu<sup>3+</sup> doped BaGd<sub>2</sub>O<sub>4</sub> phosphors and shown in Fig. 6. It is observed that the color coordinates traverse a path from yellowish white to red region with increase of Eu<sup>3+</sup> ions concentration. The results suggest that the tuning of the red color emission is possible by the variation of Eu<sup>3+</sup> ions concentration. The CCT (color correlated temperature) and color purity values are listed in Table 1. The CCT values lie in the range of 3357–1331 K. In general, CCT <4000 K and CCT >4000 K indicate the warm and cool light respectively [15]. Color purity of the synthesized phosphors lies in the range of 15.7–80.5%.



Fig. 6 CIE diagram of Eu<sup>3+</sup> doped BaGd<sub>2</sub>O<sub>4</sub> phosphors

Eu <sup>3+</sup> concentration (mol%)	Color coordinates		CCT (K)	Color purity (%)
	X	Y		
0.5	0.3879	0.3311	3357	15.7
1	0.4037	0.3366	3012	22.1
2	0.4316	0.3385	2494	31.1
3	0.4547	0.3470	2246	34.5
5	0.4956	0.3322	1732	49.1
7	0.5639	0.3359	1331	80.5
9	0.5255	0.3367	1550	76.2

Table 1 Photometric parameters of Eu<sup>3+</sup> doped BaGd<sub>2</sub>O<sub>4</sub> phosphors

#### 4 Summary and Conclusions

In summary, a series of  $Eu^{3+}$  doped  $BaGd_2O_4$  phosphors is developed by the solid-state reaction method. Phase and structural studies of phosphors confirm the orthorhombic crystal structure with space group Pnma. The FESEM images indicate similar type of spherical morphology and exhibit a slight agglomeration with reduction in size of the voids after  $Eu^{3+}$  doping. The diffuse reflectance spectra show the

optical band gap of the undoped and  $Eu^{3+}$  doped  $BaGd_2O_4$  are around 5.85 eV. The PL emission spectra exhibit the intense red emission with prominent peak at 612 nm and assigned to the  ${}^5D_0 - {}^7F_2$  transition of  $Eu^{3+}$  ions. The calculation of photometric parameters for the synthesized  $Eu^{3+}$  doped  $BaGd_2O_4$  phosphors have shown that with an excitation of UV light (excitation wavelength = 325 nm), there is a tuning of emission wavelength from yellowish white to red with increase in  $Eu^{3+}$  concentration. This property of the synthesized phosphors suggests that they can be applied for assisting the artificial photosynthesis in plants as well as can be highly suitable for fabrication of solid-state lighting devices, like, LEDs.

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# Analysis of Vapour Compression Refrigeration System with Refrigerants R22, R134a, R1234ze (E) and R1234yf—An Exergy Approach



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# Abbreviations

COP	Coefficient of Performance
ODP	Ozone Depletion Potential
GWP	Global Warming Potential
VCRS	Vapor Compression Refrigeration System
LVHE	Liquid Vapor Heat Exchanger
SFEE	Steady Flow Energy Equation
HFO <sub>S</sub>	Hydro Fluoro Olefins
HCFC <sub>S</sub>	Hydro Chloro Fluoro Carbons
HFC <sub>S</sub>	Hydro Fluoro Carbons
RACs	Refrigeration and Air- Conditioners
VCR	Vapor Compression Refrigeration
TR	Ton of Refrigeration

# **Symbols**

Ėx	Exergy rate, kW
ex	Specific exergy, kJ/Kg
ṁ	Mass flow rate of refrigerant, kg/s
ËD	Exergy destruction in component, kW
$\eta_{\rm ex}$	Exergetic efficiency

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h	Specific enthalpy, kJ/kg
Т	Temperature, K
S	Specific entropy, kJ/Kg.K
T <sub>e</sub>	Evaporator temperature, K
$\dot{W}_{el}$	Actual compressor work, kW
Tc	Condenser temperature, K
Ср	Specific heat, kJ/kg k

# Subscript

Evaporator
Condenser
Compressor
Expansion valve
Dead state

# 1 Introduction

Refrigerating machine is a device which is used to abstract the heat from the storage space in order to provide and maintain a lower temperature than that of ambient temperature [1], highly crucial in home and commercial sectors for cooling and food preservation applications, blood plasma storage in blood banks, dry ice manufacture, petroleum gas liquefication and pharmaceuticals manufacturing [2]. The first operational vapor-compression refrigeration system has been developed in 1834 [3]. In 1987, the United Nations Environment Programme (UNEP) held a summit in Montreal (Canada) where the Montreal Treaty was signed to phase out  $CFC_s$  the ozone depleting substances (ODS), the most successful protocol ever [4]. The  $CFC_s$ and HCFCs refrigerants have high GWPs and high ODPs. So HFCs are used as its alternatives having low ODPs but later it was found that HFCs have high GWPs [5]. The global warming and ozone depletion is one of the biggest threats of climate change and the COP-26 UNFCCC in 2021 aims to maintain net zero emissions. With global carbon emissions on the rise a determined effort to limit global temperature rise to 1.5 °C by 2050 is aimed at. INDIA has committed to achieving net zero emissions by 2070 [6].

Many researchers got encouraged to find new refrigerants having very Low GWP<sub>s</sub> and zero ODP<sub>s</sub> without compromising thier performance in the system [7–10]. Analysis of a VCRS by refrigerants R507A, R502 and R404A was done theoretically by Arora et al. [11], where the study concludes from the perspective of exergy destruction LVHE which is the efficient component and the condenser is the worst component.

Akash et al. [12], in his experiment used LPG as a replacement for R-12 in a household refrigerator. They utilize LPG by mass combinations of 50, 80 and 100 g and it was observed that 80 g gives a better result. Ahmed et al. [13] did a review on exergy analysis of VCRS and concluded that with the increase in discharge and suction temperature of the compressor exergy losses also increased. Sun et al. [14], found that COP and exergetic efficiency decreased by 9 and 14% respectively for R513a as a R134a drop-in replacement, to get better exergetic efficiency compressor that should be redesigned first. Roy et al. [15], analyzed low GWP<sub>s</sub> refrigerants and found that optimum results of R1234ze and R600a are very close to R152a. Arshad et al. [16], analyzed that exergetic efficiency of R22 lies between R11 and R134a.

In the compressor major losses takes place. Malwe et al. [17], observed that R245fa, R152a, R141b offers better performance than R1234yf and R1234ze (E), but these refrigerants have high GWP values. Exergy analysis is used to depict the system's real performance in terms of Second Law efficiency or exegetic efficiency and quantifies the effect of exergy destruction of components in the refrigeration system [11]. Heat transfer takes place at finite temperature difference between the system and surrounding environment, which is one of the major causes of irreversibility and degrades the system's performance. In the investigation of thermal systems, the energy approach (first law of thermodynamics) is still widely utilized [18]. The first law is focused with energy conservation. It doesn't clarify how, where or how much performance is affected. In contrast to energetic approach an exergy approach is often used which is based on the first law and second law of thermodynamics, a well-known technique for analyzing thermodynamic cycle to understand better and evaluate the irreversibility linked with any process quantitatively, thus offering a hint where designers should focus more to improve the performances in the refrigeration system or any thermal systems [19].

The objective of this investigation is to examine the theoretical performance and analysis of the selected four refrigerants based on the concept of exergy. Refrigerant R1234ze(E), R1234yf, which is HFO<sub>S</sub> having low GWP and ODP, R134a which is HFC<sub>S</sub> and R22 which is HCFC<sub>S</sub> refrigerant. In the present work the mass flow rate of the refrigerant (0.02768 kg/s) that is obtained by having 1TR at  $T_e = -25$  °C and  $T_c = 40$  °C for R134a without LVHE is taken for VCRS incorporated with LVHE. The different performance parameters are exergetic efficiency; COP, refrigerating effect and total exergy destruction that are evaluated while varying the evaporator and condenser temperature. There effects are also studied while incorporating LVHE.

#### 2 System Descriptions

Figure 1 represents the VCRS cycle and its components compressor, condenser, expansion valve and evaporator, state points 1 and 5 represent the saturated vapor and saturated liquid state respectively. Figure 2 shows the schematic diagram of temperature versus entropy of the VCRS cycle. *The VCRS cycle incorporated with LVHE is depicted in Fig. 3 due to which superheating and subcooling of refrigerants is* 

achieved from state points 1–2 and 6–7 respectively. Figure 4 shows the temperature versus entropy diagram of VCRS incorporated with LVHE, here state points 1 and 6 are at saturated vapor and saturated liquid state respectively.

The saturated vapor with low temperature and low pressure is allowed to pass through LVHE (1–2) for superheating than it enters to compressor (2–3) where the refrigerant vapor converts to high pressure and high temperature refrigerant after which the condenser (3–6) rejects heat  $\dot{Q}_c$  to ambient in which the refrigerant looses heat to the ambient and is converted to saturated liquid. After being rejected the heat refrigerant passes through LVHE (6–7) for subcooling which reduces flashing of



Fig. 1 Vapor compression refrigeration system without LVHE



Fig. 2 Temperature versus entropy of VCRS without LVHE



Fig. 3 Vapor compression refrigeration system with LVHE



Fig. 4 Temperature versus entropy of VCRS with LVHE

*liquid*, during expansion after which the subcooled refrigerant is passed through the throttling valve (7–8) in which pressure and temperature drop takes place and this low temperature refrigerants is allowed to pass through the evaporator Section (8–1) to absorb heat  $\dot{Q}_e$  from the refrigerated space and this cycle is repeated which produces the net refrigerating effect.

# 3 Mathematical Modeling

In the present work exergetic analysis of a VCRS is incorporated with LVHE by using four different refrigerants R22, R134a, R1234ze (E) and R1234yf with effectiveness of LVHE, compressor isentropic efficiency, electrical efficiency and mechanical efficiency for different ranges of evaporator temperature. The compressor work, total exergy destruction of components along with systems, COP and exegetic efficiency are also explored. A coding on the computer is written while using EES Software [23] Professional V. 10.561-3D to calculate the different thermodynamic properties of the refrigerants at different states in the VCRS cycle incorporated with LVHE.

The following relevant assumptions are used in exergy analysis of VCRS incorporated with LVHE.

- 1. All the components in VCRS are operating at a steady state.
- Exit of refrigerants in the evaporator and condenser at saturated vapor and saturated liquid conditions respectively.
- 3. Pressure drops in the evaporator and condenser are neglected.
- 4. Entry of air at 0 °C to evaporator.
- 5. Heat losses from components and pipelines are ignored.
- 6. The value of reference entropy  $(s_0)$  and enthalpy  $(h_0)$ , of the refrigerant is calculated corresponding to dead state temperature  $(T_0)$  and atmospheric pressure  $(P_0)$ .

# 3.1 Exergy Analysis

The maximum work potential of a system is represented by its exergy or availability at any given state. As a result exergy loss is a significant criterion for determining a system's thermodynamic performance [1]. Exergy is the maximum amount of work that a stream of matter, heat or work may create when it reaches equilibrium with a reference environment. Exergy always decreases due to thermodynamic irreversibility [20].

Vapor compression refrigeration system block diagrams are shown in Figs. 1 and 3. The operating parameters of VCRS incorporated with LVHE for EES simulation are listed in Table 1.

Table 1         Operating           parameters of VCRS	Parameters	Symbol	Value
incorporated with LVHE for EES simulation	Refrigerants	(R\$)	R22, R134a, R1234yf and R1234ze (E)
	Refrigerant's mass flow rate	( <i>m</i> )	0.02768 kg/s
	Range of evaporator temperature	$(T_e)$	$-25 \text{ to} + 40 ^{\circ}\text{C}$
	Condenser temperature	$(T_c)$	40 °C
	Ambient temperature	$(T_0)$	25 °C
	Effectiveness of LVHE	( <i>e</i> )	80%
	Refrigerating capacity without LVHE	$(\dot{Q}_e)$	1 TR
	Isentropic efficiency of compressor	$(\eta_c)$	85%
	Mechanical efficiency of compressor	$(\eta_m)$	84%
	Electrical efficiency of compressor	$(\eta_{el})$	90%

#### 3.1.1 Specific Exergy

The exergy of flowing fluid in the system at a point is given as [22],

$$ex = (h - h_o) - T_0(s - s_0)$$
(1)

where,  $h_0$  is the reference enthalpy, and  $s_0$  is the entropy of refrigerants corresponding to dead state temperature  $T_0$  at 25 °C.

#### 3.1.2 Exergy Flow Rate

$$\dot{\mathbf{E}}\mathbf{x} = \dot{\mathbf{m}}(\mathbf{e}\mathbf{x}) \tag{2}$$

The general exergy balance equation in rate form for the control volume undergoing the steady state process is given as [17].

$$\sum \dot{Q} \left(1 - \frac{T_o}{T}\right)_{in} + \sum \dot{W}_{in} + \dot{E}x_{in}$$

$$= \sum \dot{Q} \left(1 - \frac{T_o}{T}\right)_{out} + \sum \dot{W}_{out} + \dot{E}x_{out} + \dot{E}D_I$$
(3)

ED shows the rate at which the exergy is destroyed in the process. EX, EX represents the exergy of streams entering and leaving the control volume.  $\sum \dot{Q}(1 - \frac{T_0}{T})_{in}$ ,  $\sum \dot{Q}(1 - \frac{T_0}{T})_{out}$  represents the exergy associated heat transfer from the source maintained at a constant temperature T.  $\sum \dot{W}_{in}$  and  $\sum \dot{W}_{out}$ , represent the transfer of mechanical work to or from the control volume.

Exergy destruction for each component in VCRS incorporated with LVHE.

#### (a) Evaporator

Evaporator absorbs the heat ( $\dot{Q}e$ ) from the storage space which is maintained at temperature T<sub>e</sub> and is given by.

$$\dot{\mathbf{Q}}\mathbf{e} = \dot{\mathbf{m}}(\mathbf{h}_1 - \mathbf{h}_8) \tag{4}$$

m-Mass flow rate of refrigerants (kg/s),  $h_1$ —enthalpy at the outlet of the evaporator (kJ/kg),  $h_8$ —enthalpy at the inlet of the evaporator (kJ/kg).

Exergy destruction for evaporator

$$\begin{split} \dot{E}_{eva}^{D} &= \dot{Q}e \left( 1 - \frac{T_{o}}{T_{e}} \right) + \dot{E}x_{8} - \dot{E}x_{1} \\ &= \dot{Q}e \left( 1 - \frac{T_{o}}{T_{e}} \right) + \dot{m}(h_{8} - T_{o}S_{8}) - \dot{m}(h_{1} - T_{o}S_{1}) \end{split}$$
(5)

#### (b) Compressor

The isentropic work  $(\dot{W}_c)$  input to the compressor is given by

$$\dot{W}_{es} = \dot{m}(h_4 - h_2) \tag{6}$$

and the compressor work  $(\dot{W}_c)$  is specified

$$\dot{W}_{c} = \frac{Wcs}{\eta c}$$
(7)

where,  $(\dot{W}_{el})$ —actual compressor work.

$$\dot{W}_{el} = \frac{Wc}{\eta el * \eta m}$$
(8)

#### Exergy destruction for compressor

$$\mathop{\rm ED}_{\rm comp} = \dot{W}_{\rm el} + \dot{E}x_2 - \dot{E}x_3 = \dot{W}_{\rm el} + \dot{m}(h_2 - T_0S_2) - \dot{m}(h_3 - T_0S_3) \tag{9}$$

#### (c) Condenser

The heat rejected  $(\dot{Q}_c)$  to the atmosphere by the condenser is given as.

$$\dot{Q}_c = \dot{m}(h_3 - h_6)$$
 (10)

#### Exergy destruction for condenser

$$ED_{cond} = \dot{E}x_3 - \dot{E}x_6 = \dot{m}(h_3 - T_0S_3) - \dot{m}(h_6 - T_0S_6)$$
(11)

#### (d) Expansion valve

In expansion valve, the enthalpy remains constant.

$$\mathbf{h}_7 = \mathbf{h}_8 \tag{12}$$

#### Exergy destruction for expansion valve

$$\mathop{\rm ED}_{\rm exp, valve} = \dot{\rm E}x_7 - \dot{\rm E}x_8 = \dot{\rm m}({\rm h}_7 - {\rm T}_0{\rm S}_7) - \dot{\rm m}({\rm h}_8 - {\rm T}_0{\rm S}_8) \tag{13}$$

#### (e) LVHE

*Effectiveness of LVHE*: It is the ratio of actual heat transfer by the working fluid (refrigerant) to the maximum amount of heat transfer.

$$e = \frac{\text{actual heat transfer}}{\text{maxminum amount of heat transfer}}$$

$$e = \left[\frac{(\dot{m})Cp_{v^*}(T_2 - T_1)}{(\dot{m})Cp_{\min^*}(T_6 - T_1)}\right]$$
(14)

The energy balance of LVHE is given by,

$$h_2 - h_1 = h_6 - h_7$$
  
or  $(\dot{m})Cp_v(T_2 - T_1) = (\dot{m})Cp_L(T_6 - T_7)$  (15)

Exergy destruction for LVHE

# 3.2 Total Exergy Destruction

Total exergy destruction in the system is defined as the sum of each component's exergy destruction in the VCRS cycle.

$$\underset{total}{ED} = \underset{eva}{ED} + \underset{eva}{ED} + \underset{cond}{ED} + \underset{exp,valve}{ED} + \underset{LVHE}{ED}$$

# 3.3 Exergetic Efficiency

The exergetic efficiency of VCRS is defined as the ratio of exergy recovered to the exergy supplied [20].

$$\eta_{\rm ex} = \left[\frac{\dot{\rm W}el - ED}{\dot{\rm W}el}\right] * 100 \tag{18}$$

The exergetic efficiency of a VCR system is defined as the ratio of the exergy of heat absorbed in the evaporator from the space to be cooled at temperature Te to the actual compressor work input ( $\dot{W}_{el}$ ) [11].

$$\eta_{\text{ex}} = \left[\frac{\left|\dot{Q}e^{\circ}\left(1 - \frac{T_{o}}{T_{e}}\right)\right|}{\dot{W}el}\right] * 100$$
(19)

# 3.4 Coefficient of Performance (COP)

The coefficient of performance of vapor compression refrigeration system with LVHE is given by [13].

$$COP = \left[\frac{\dot{Q}e}{\dot{W}el}\right]$$
(20)

# 4 Results and Discussion

In the exergy analysis of VCRS with LVHE all the performance parameters such as COP, exergetic efficiency, total exergy destruction and refrigerating capacity are discussed theoretically with the help of EES software [23].

# 4.1 Coefficient of Performance (COP)

Figure 5 depicts the variation of evaporator temperature on the VCRS cycle incorporated with LVHE, while varying the evaporator temperature in the range of 248–313 K and at a fixed condenser temperature 40 °C, which results in decrease in pressure ratio across the compressor that reduces thw compressor work which results in increase in volumetric efficiency and refrigerating effect. The combined effect of these two factors enhances the overall COP [11]. For the given range of evaporator temperature R1234ze(E) offers relatively a higher COP value than R134a, however R1234yf and R22 have slightly lower COP value than R134a. COP value of VCRS with LVHE for R1234ze(E), R1234yf, R134a is 12.63, 17.70, 7.15% more and for R22 it is 5.02% less than COP value of VCRS without LVHE respectively.

Apart from the influence on the evaporator temperature the COP for refrigerants R1234ze(E), R1234yf, R134a and R22 decreases with enhancement in the condenser temperature as seen in Fig. 6 in the range of 313–340 K for a fixed evaporator temperature -25 °C because it results in the increment in pressure ratio across the compressor that increases the compressor work and decrement in volumetric efficiency which lowers COP. The COP value of R1234ze records higher than other



Fig. 5 Variation of COP with evaporator temperature



Fig. 6 Variation of COP with condenser temperature

refrigerants R1234yf, R134a, R22, however the COP value of R1234yf and R22 is lower than R134a and COP value of R1234ze(E) is 7.13% higher than R22.

#### 4.2 Exergetic Efficiency

Figure 7 represents the effect of the evaporator temperature on exergetic efficiency. The value of exergetic efficiency reduces as the temperature of the evaporator increases; the highest exergetic efficiency occurs only at the optimum evaporator temperature [13]. The exergetic efficiency for R 1234ze(E), R1234yf, R134a is relatively higher by 12.62, 17.69, 7.10% and for R22 it is lower by 0.52% while considering the vapor compression refrigeration cycle with LVHE in comparison to the vapor compression refrigeration cycle without LVHE at fixed condenser temperature of 40 °C and varying evaporator temperature of 248–313 K. The increase or decrease in exergetic efficiency depends on two parameters (Eq. 19)—the first one is the exergy associated with the cooling capacity  $\dot{Q}e(1 - \frac{T_0}{T_e})$ .  $\dot{Q}e$  increases with increase in Te but another factor  $(1 - \frac{T_0}{T_e})$  reduces as Te increases. The second parameter is  $\dot{W}_{el}$ , actual compressor work which decreases with increase in Te. The combined effect of these factors will increase the overall  $\eta_{ex}$  and is maximum at optimum Te after that  $\eta_{ex}$  will decrease.

The exergetic efficiency shows the decreasing trend while varying the condenser temperature in the range of 313–340 K as shown in Fig. 8 while keeping the evaporator temperature fixed at -25 °C. Refrigerants R1234ze(E) record the highest exergetic efficiency followed by R134a, R1234yf and R22.The exergetic efficiency of R1234ze(E) is 7.132% more than R22.



Fig. 7 Variation of exergetic efficiency with evaporator temperature



Fig. 8 Variation of exergetic efficiency with condenser temperature

# 4.3 Total Exergy Destruction

Figure 9 represents the relationship between the evaporator temperature and total exergy destruction for refrigerants R22, R1234ze(E), R134a, and R1234yf. The pattern in this analysis shows that the total exergy destruction in VCRS cycles with LVHE decreases as the evaporator temperature rises, total exergy destruction for R22 is 1.107 kW which is highest, for R1234ze(E), R134a, for R1234yf it is 24.21, 12.63, 29.42% lower than R22 respectively. *As the finite temperature difference between* 



Fig. 9 Variation of total exergy destruction with evaporator temperature

the surrounding refrigerated space and evaporator temperature decreases then the chance of irreversibility also reduces [21].

For all the selected refrigerants the total exergy destruction shows an increasing trend as in Fig. 10 with increase in the condenser temperature. For refrigerants R22 and R 1234yf the total exergy destruction is more and least respectively. For refrigerants R22 and R134a the total exergy destruction is 31.94, 23.70% higher than R1234ze(E) but for R1234yf it is 6.86% lower than R1234ze(E) at T<sub>e</sub> = 248.2 K and T<sub>c</sub> = 313.1 K. There is increment in total exergy destruction in the temperature range of T<sub>c</sub> = 313.2–324.5 K at T<sub>e</sub> = 248 K of R1234ze(E), R1234yf, R134a and R22 atl 41.25, 40.89, 45.89 and 40.27\% respectively.

# 4.4 Refrigerating Capacity

Figure 11 reveals the effect on refrigerating capacity with respect to the evaporator temperature, while increase in the evaporator temperature up to 283.5 K the *refrigerating capacity for refrigerants R22, R1234ze(E), R134a increases because of reduction in the flashing of refrigerant liquid which ensures the reduction in vapor formation as the specific heat of vapor is very low due to which the refrigerating effect increases. After that it decreases and for refrigerant R1234yf the refrigerating effect increases up to 275.5 K by keeping the condenser temperature fixed at 313 K.* 

But while keeping the evaporator temperature fixed at 248.2 K as in Fig. 12 and increasing the condenser temperature the refrigerating capacity for refrigerants R22, R1234ze(E), R134a and R1234yf decreases. For R1234ze(E) the cooling capacity is relatively more than R1234yf in both cases. There is decrement in the refrigerating capacity from  $T_c = 313.1-324.5$  K at Te = 248.2K of R1234ze(E), R1234yf, R134a



Fig. 10 Variation of total exergy destruction with condenser temperature



Fig. 11 Variation of refrigerating capacity with evaporator temperature

and R22 at 5.52, 6.38, 5.59 and 5.21% respectively. For refrigerant R1234ze(E) the refrigerating capacity is 13.65% more than R1234yf.



Fig. 12 Variation of refrigerating capacity with condenser temperature

# 5 Validation and Comparison of Work

Validation of present work (VCRS) with Arshad et al. [16], at Te = -25 °C and T<sub>c</sub> = 40 °C is depicted in Fig. 13. Here the authors have *incorporated a LVHE which* results in superheating and subcooling of the refrigerants simultaneously, hence the performance parameters get improved with respect to VCRS without LVHE, Fig. 14a, b depict the enhancement of performance parameters like refrigerating capacity and exegetic efficiency respectively. The refrigerant R1234ze(E) shows an excellent performance parameter as compared to other three refrigerants R22, R134a and R1234yf.





Fig. 14 a Refrigerating capacity of VCRS with LVHE and without LVHE, **b** Exergetic efficiency of VCRS with LVHE and without LVHE

# 5.1 Conclusions

Based on the above theoretical analysis of the VCRS cycle incorporated with LVHE by keeping the mass flow rate of the refrigerant constant for 1TR for R134a of VCRS, and by using four different refrigerants R22, R134a, R1234yf and R1234ze(E) the following conclusions are summarized as below-

- Refrigerating effect increases for refrigerants R1234ze(E), R1234yf, R134a, and R22.For refrigerants R1234ze(E) enhancement is 22.55% while including LVHE at the evaporator temperature of -25 °C and condenser temperature of 40 °C, ,is best as considered from the environmental aspect of view. Refrigerating effect for R1234ze (E) is 13.66% more than R1234yf.
- Major exergy destruction takes place in the condenser, followed by the compressor, expansion valve, evaporator and LVHE; for R22 it is most and least for R1234yf.
- COP increases with increase in the evaporator temperature and decreases with increase in the condenser temperature [11]. The increment in COP for R1234ze (E) is highest with respect to refrigerants R1234yf, R134a, R22. For R1234ze (E) COP is 2.857% higher than R1234yf while including LVHE.

- Exergetic efficiency decreases with increase in the evaporator and for the condenser temperature it is maximum at optimum temperature 241.5 K for R1234ze (E), R1234yf, R134a, for R22 at 246.1 K. Exergetic efficiency for R1234ze (E) is 2.78% higher than R1234yf while including LVHE.
- The actual compressor work is increased while including LVHE, for refrigerants R1234ze(E) where it is 9.47% higher than R1234yf at evaporator temperature of -25 °C and condenser temperature of 40 °C.
- After concluding all the parameters in all respects, R1234ze(E) is considered the best refrigerant.

#### **Future Scope**

Based on the above analysis, the further work can be processed in future.

- To redesign the condenser and compressor as these components are the source for major exergy destruction to improve exergetic efficiency.
- In the future, new alternative refrigerants such as ceramic nano particles, Al<sub>2</sub>O<sub>3</sub>, and CuO based nanorefrigerants could be used to achieve improved outcomes in terms of COP and power consumption.

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# **Supplementary Data**

# EES Coding to Find Out the Thermodynamic Properties of Refrigerants at Different States in VCRS W/O LVHE

R\$ = 'R134a'

Te = convertemp(C,K, -25[C])

Tc = convertemp(C,K, 40[C])

"state 1 compressor inlet/ evaporator exit"

T[1] = Tex[1] = 1[-] h[1] = enthalpy(R\$, T = Te, x = x[1]) s[1] = entropy(R\$, T = T[1], x = x[1]) P[1] = p\_sat(R\$, T = Te)

```
" state 2".
h[2] = h[1] + W c.
s[2] = entropy(R\$, h = h[2], P = P[3]).
T[2] = temperature(R\$, h = h[2], P = P[3]).
P[2] = p \text{ sat}(R\$, T = Tc).
"state 3 isentropic compressor exit/condenser inlet"
s[1] = s[3]
T[3] = temperature(R\$, h = h[3], P = P[3])
P[3] = P[2]
h[3] = enthalpy(R\$, P = P[3], s = s[3])
"state 4".
T[4] = Tc
P[4] = P[3]
x[4] = 1[-]
h[4] = enthalpy(R\$, P = P[3], x = x[4])
s[4] = entropy(R\$, T = T[4], x = x[4])
"state 5 condenser exit/ TV inlet"
x[5] = 0[-]
h[5] = enthalpy(R\$, T = Tc, x = x[5])
s[5] = entropy(R\$, h = h[5], P = P[5])
T[5] = Tc
P[5] = P[4]
"state 6, evaporator inlet/TV exit"
P[6] = P[1]
s[6] = entropy(R\$, h = h[6], P = P[6])
T[6] = temperature(R\$, h = h[6], P = P[6])
h[5] = h[6]
// energy balance
W_c = (h[3]-h[1])/eta_c
eta c = 0.85
```

 $Q_e = h[1] - h[6]$ O dot  $e = m dot^*O e$ Q dot\_e = 3.5167 [KW] W dot  $c = m dot^*W c$ Q c = h[2]-h[5]  $Q \text{ dot } c = m \text{ dot}^*Q c$ COP = Q dot e/W dot c// Exergy Destruction in each components T[0] = convertemp(C,K, 25[C])P[0] = 101.325 [KPA] h[0] = enthalpy(R\$, P = P[0], T = T[0])s[0] = entropy(R\$, T = T[0], P = P[0])Ex me =  $(1 - 0.9 \times 0.84) \times W$  dot c  $Ex_dot_1 = m_dot^*((h[1]-h[0]) - T[0]^*(s[1]-s[0]))$ Ex dot\_2 = m\_dot\*( ( h[2]-h[0]) -T[0]\*( s[2]-s[0]))  $Ex_dot_5 = m_dot^*((h[5]-h[0]) - T[0]^*(s[5]-s[0]))$  $Ex_dot_6 = m_dot^*((h[6]-h[0]) - T[0]^*(s[6]-s[0]))$ eta el = 0.90eta mech = 0.84W dot el = W dot c/(eta mech\*eta el)ED dot  $eva = (Ex dot 6) - (Ex dot 1) + Q dot e^{*(1-T[0]/Te)})$  $ED_dot_comp = (Ex_dot_1) - (Ex_dot_2) + W_dot_el$ ED dot cond = (Ex dot 2) - (Ex dot 5)  $ED_dot_TV = (Ex_dot_5) - (Ex_dot_6)$  $ED_dot_Total = ED_dot_eva + ED_dot_comp + ED_dot_cond + ED_dot_TV$ eta exergetic =  $((Q_dot_e^*((T[0]/Te)-1))/W_dot_c)^*100$ eta\_exergetic1 = (( W\_dot\_c- ED\_dot\_Total)/W\_dot\_c)\*100  $eta\_exergetic2 = ((Q\_dot\_e^*((T[0]/Te)-1))/W\_dot\_e])^*100$ 

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# Parametric Study on Maximum Efficiency of Dielectric Elastomer Generator for Micropower Generation



Rudraksh Sharma, Snehal Prajapati, Kajal Meena, Hrishank Soni, and Deepak Kumar

# 1 Introduction

Dielectric elastomers (DE) are innovative and non-conducting soft electroactive polymers with cross-linked molecular chain networks that exhibit high elastic energy density, high efficiency, and large deformation [1, 2]. Researchers have recently investigated methods to convert mechanical energy, such as wind, waves, and human motion, into electrical energy [3, 4]. For portable electronic devices and distributed sensor networks that demand a small amount of power, micropower generation (MPG) has attracted much interest.

The process of extracting energy from external sources and utilizing that energy in the execution of small portable electronic devices is known as energy harvesting [5]. The devices used are known as energy harvesters. A dielectric elastomer generator is the most significant energy harvester which works on the same conversation phenomenon. EAP (electroactive polymer) can be utilized in DE generators to accomplish this conversation due to their high versatility and simplicity. A thin elastomer layer is sandwiched between the electrode layers in a DE generator, which is a type of EAP. The basic principle of micropower generation is based on converting mechanical energy into electrical energy stored in a capacitor as output [6, 7]. Assume that a DE generator is subjected to mechanical deformation. As a result, the effective area increases, and the thickness is reduced. This increases capacitance, and the deformed DE generator is charged from an electrical power source. Subsequently, the mechanical force responsible for deformation is removed, and the value of capacitance of the DE generator decreases, causing the enhancement of electrical potential between the electrode layers. As a result, charges with escalated electrical potential can be utilized

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**Fig. 1** Working principle of a DE generator: In step 1, prestretch is applied to the DE membrane. In step 2, charges are induced on its surface. Step 3 is the energy harvesting stage in which the load is removed from the DE membrane. In step 4, charges are removed from the surface, and the DE generator returns to its original state

for power generation, as shown in Fig. 1. This study was stimulated by the feasibility of DE generators that can be taken on for MPG from human body motions. In order to respond to human body motions, a DE generator must be flexible (particularly articulation-type motions). Furthermore, DE generators are well-known to possess a high work-power density.

DEG can perform work in different circumstances in various transduction approaches of converting mechanical energy into electrical energy [8, 9]. The dielectric elastomer, an electroactive polymer, is beneficial for a micropower generation due to its high energy density, fast response, lightweight, and large deformation. Pelrine [5] first harnessed the DEG. It is a capacitor that converts energy through mechanical deformation. Its high energy density is more effective than piezoelectric and electromagnetic generators. Furthermore, DEG can be favorable in different conditions, confined from small-scale motion, such as human motion to large scale such as wave energy [10]. Researchers [11, 12] have tried rectifying energy density and electrochemical conversation efficiency in previous years. Two significant measures describe DEG's output performance in a single cycle: energy density and electromechanical conversion efficiency.

Various materials have been tested in the current years; three have come into the picture: Rubber, Silicon elastomer, and acrylic. The properties of DE materials are responsible for defining the output performance of DEG. The effectiveness of DEG depends on the elastic modulus and elongation at the break of the DE material. Breaking down electric strength and relative dielectric constant also plays a crucial role in altering DEG's maximum operating voltage and energy density. In this paper, the primary focus is on transforming the values of these parameters and studying their effect on the efficiency of DE generator.

# 2 Formulation of Efficiency

To derive the expression of efficiency, let us consider *n* layers of the circular lamina, each having radius 'R', being used as a DE generator on which deforming force is assumed to be uniformly distributed over a small circular region of radius  $R_w$  at the center. The undeformed and deformed thicknesses of the membrane are ' $h_o$ ' and 'h', respectively. The initial state of the DEG is taken as the deformed state, and the final state is when the applied load is removed (since this is the energy harvesting step of DEG). Figure 2 shows the notations used for further formulation.

#### 2.1 Actual Expression

The DE generator is charged from the electrical power source with a total charge  $Q_{in}$ , which produces the total electrical energy:



$$J_{E,deformed} = \frac{Q_{in}^2}{2C_d},\tag{1}$$

**Fig. 2** Configuration of DE membrane used and various parameters of a single layer of DEG in an undeformed and deformed state. **a** The DE membrane is circular in shape with an outer radius '*R*' and undeformed thickness ' $h_o$ '. The load is uniformly distributed over a small circular portion of the membrane having radius  $R_w$ . **b** The side view of the deformed DE membrane showing deformation ' $\delta$ ' and deformed thickness '*h*' (h <  $h_o$ )

where  $C_d is$  the capacitance of the DE generator in the deformed state. By removing the force, the DE generator recovers its original shape, and the electrical potential energy increases to

$$J_{E,undeformed} = \frac{Q_{in}^2}{2C_o}.$$
 (2)

Because  $C_d \ge C_o$ , where  $C_o$  is the capacitance of the DE generator in the undeformed state. Hence, the energy generated can be calculated as follows:

$$\Delta J_E = \frac{Q_{in}^2}{2} \left[ \frac{1}{C_o} - \frac{1}{C_d} \right] \tag{3}$$

The increase in the electric potential results from the mechanical energy stored in the form of elastic deformation as follows:

$$J_M = \frac{1}{2} K_{eff} \delta^2, \tag{4}$$

where  $K_{eff}$  represents an effective stiffness, i.e., the constant of proportionality between resisting force and deformation for a system having linear elasticity.

Considering *n* layers of dielectric elastomers stacked one upon the other and assuming the volume of each layer to remain constant, we can write  $nA_oh_o = nAh$  therefore,  $h = \frac{A_oh_o}{A}$ . Let  $V_{in}$  be the electrical voltage of the power source for the initial charging, the initial charge on DEG could be written as  $Q_{in} = C_d V_{in}$ . Also, the capacitance can be expressed in terms of geometric parameters as

$$C_0 = \frac{\varepsilon n A_0}{h_0} \tag{5}$$

$$C_d = \frac{\varepsilon n A^2}{h_o A_o} = \frac{\varepsilon n}{h_o} \left(\frac{A^2}{A_o}\right) \tag{6}$$

From (3), (5), and (6), we have

$$\Delta J_E = \frac{\varepsilon n V_{in}^2 A_o}{2h_o} \ge \left(\frac{A}{A_o}\right)^2 \left\lceil \left(\frac{A}{A_o}\right)^2 - 1 \right\rceil.$$
(7)

Now, to compute the deformed area, we have the original area of  $DEG = \pi R^2$ , its maximum deformation =  $\delta$  and its deformed area = A given by Parametric Study on Maximum Efficiency of Dielectric Elastomer ...

$$A = \pi \left[ \left\{ \sqrt{\delta^2 + (R - R_w)^2} (R + R_w) \right\} + R_w^2 \right],$$
  
$$A = \pi \left( R^2 - R_w^2 \right) \sqrt{1 + \left( \frac{\delta}{R - R_w} \right)} + \pi R_w^2.$$

Now the area ratio will be:

$$\frac{A}{A_{o}} = \frac{\left\{\pi \left(R - R_{w}^{2}\right)\sqrt{1 + \left(\frac{\delta}{\{R - R_{w}\}}\right)^{2}} + \pi R_{w}^{2}\right\}}{\pi R^{2}}$$
(8)

Also, from (4) and (7), the efficiency can be expressed as follows:

$$\eta = \frac{\Delta J_E}{J_M}$$

$$\eta = \frac{\varepsilon n V_{in}^2 A_o}{h_o K_{eff} \delta^2} \left(\frac{A}{A_o}\right)^2 \left[ \left(\frac{A}{A_o}\right)^2 - 1 \right].$$
(9)

Now, (8) and (9) combined represent the actual expression of efficiency. Since the expression is complicated and physical interpretation is difficult, we need a simplified expression for efficiency.

# 2.2 Approximate Expression

For simplicity, we can assume that the working radius  $(R_w)$  is very small in comparison to the overall radius (R). The area ratio can be expressed as

$$\frac{A}{A_o} = \left(1 - \left(\frac{R_w}{R}\right)^2\right) \sqrt{1 + \left(\frac{\delta}{R - R_w}\right)^2} + \left(\frac{R_w}{R}\right)^2,$$

Since  $\frac{R_w}{R} \ll 1$  so,

$$\frac{A}{A_o} = \sqrt{1 + \left(\frac{\delta}{R}\right)^2}.$$
(10)

Using (7) and (10),  $\Delta J_E$  can be written as:

$$\Delta J_E \frac{\varepsilon n V_{in}^2 A_o}{2h_o} \left[ 1 + \left(\frac{\delta}{R}\right)^2 \right] \left(\frac{\delta}{R}\right)^2.$$

So, efficiency could be approximated as:

$$\eta = \frac{\Delta J_E}{J_M}, \eta = \frac{\varepsilon n V_{in}^2 \pi}{h_o K_{eff}} \left[ 1 + \left(\frac{\delta}{R}\right)^2 \right]. \tag{11}$$

# **3** Results and Discussion

This section discusses the variation of efficiency with respect to various parameters. For this purpose, we have two different expressions of efficiency, the exact one is given by (8) and (9), and the approximate expression is given by (11). Although the exact expression gives more accurate values, due to the complexity of the expression and the highly non-linear dependency on different parameters, we can not use it to predict the nature of the curve. Also, the graphs shown in Figs. 3, 4, and 5 show that the nature of variation is more or less the same for both actual and real expressions. Suppose the objective is to find the exact values of efficiency. In that case, the exact expression can be used, but our main concern is knowing how different parameters can be varied to maximize efficiency.

For all the plots, the working radius of DE generator is taken to be 0.12 mm, and the number of layers is taken as 7. The relative electric permittivity of 4.5 is assumed in all the cases, which may vary from material to material. Permittivity is assumed to be totally dependent on the material used and does not vary with change in any other parameter. While studying variation under a particular parameter, all



Fig. 3 Plots showing the variation of efficiency with deformation and charging voltage. The plot obtained using an approximate equation is shown in red color while the plot obtained using an actual equation is shown in blue color. **a** The variation of efficiency (in %) with respect to deformation (delta) of the dielectric membrane in meters. **b** The efficiency increases quadratically with charging voltage (in volts)



**Fig. 4** Plots showing the variation of efficiency with effective stiffness and outer radius of DEG. The plot obtained using an approximate equation is shown in red color while the plot obtained using an actual equation is shown in blue color. **a** Efficiency decreases with an increase in effective stiffness **b** Efficiency firstly decreases drastically and then gradually, as seen from its variation with the outer radius of DEG in meters



other parameters are kept constant. Hence, while plotting the graphs, parameters like deformation, charging voltage, effective stiffness, radius of DEG, effective radius, and initial thickness are fixed at 0.05 m, 1 kV, 340 N/m, 125, 9, and 0.12 mm, respectively, whenever they are not varied.

In Fig. 3a, efficiency variation against deformation of the dielectric membrane is plotted. The derived approximate equation shows the relationship between efficiency and deformation of the parabolic type. This indicates that to increase the efficiency, we would have to increase the deformation. This could be interpreted as: when the mechanical deformation is large, the effective area increases, corresponding to a rise in its capacitance value. Thus, the resultant elevated electrical potential contributes to higher efficiency. However, due to some limitations imposed by the physical strength of the material, it could only be enhanced up to a certain point.

The efficiency also increases with the square of the voltage applied as per the expression (11). This is evident because the electrical energy is proportional to the square of the voltage applied. It implied that increasing the voltage will increase the efficiency, but every dielectric loses its dielectric properties after a certain breakdown voltage. This will cause wrinkling and even damage to the DE generator, and the phenomenon is commonly known as static instability. Due to this constraint, the voltage is generally kept far less than the breakdown voltage. Figure 3b shows the variation of efficiency with voltage.

The variation of efficiency with respect to the effective stiffness of the material is illustrated in Fig. 4a. For a system having linear elasticity, the resisting forces are proportional to the deformation caused, and the constant of proportionality is effective stiffness. The derived approximate equation shows that the efficiency is inversely proportional to the stiffness of the material. A greater stiffness would simply mean that more mechanical work would be required to get the deformation. At the same time, the electrical energy produced as an output will not increase since it depends on instantaneous capacitance value, not on stiffness. This will cause a reduction in efficiency. Therefore, a less value of effective stiffness would be desirable. This parameter, however, depends on both material and geometrical properties. Hence, while decreasing its value, it should be ensured that no other parameter is changed so that it adversely affects the efficiency.

The relation between efficiency and radius could be approximated as a hyperbolic function. Therefore, efficiency decreases with an increase in radius up to a certain value and becomes almost constant (Fig. 4b). For micropower generation, we use small devices. Hence, the radius value would not be substantial, so a significant decrease in efficiency will be observed with an increase in radius. However, a larger radius allows more considerable deformation, increasing the efficiency and power generated. Moreover, the radius selection also depends upon the particular application for which it is used. A simple way of increasing efficiency without hampering the power requirement would be to use multiple small DE generators in place of a single larger one.

The thickness of DE membrane also significantly affects the generator's efficiency. Figure 5 shows the inversely proportional variation in nature as justified by Eq. (11). A greater thickness means a lesser value of capacitance and, subsequently a lesser value of electrical energy generated from particular mechanical energy. This causes a decrease in efficiency. The use of thinner DE membranes is recommended to obtain greater efficiency values. However, a thin membrane would be weak and unable to sustain large deformations. However, we can replace one thick layer of DE material with a stack of multiple thin layers. Increasing the number of layers also increases efficiency, as seen from the approximate expression.

Other than these parameters, the efficiency of a DE generator also depends upon the permittivity of the material used. As more excellent permittivity value will lead to greater capacitance value and hence greater electrical energy output at the same mechanical input, it will always increase the efficiency. The approximate expression also shows a directly proportional relationship between the two. Certain chemical processes, like the introduction of filler particles, could be used to improve the permittivity of the material [13]. The variation of efficiency with working radius is minimal and is neglected in the current work.

### 4 Conclusion

In this paper, a parametric study to maximize the efficiency of DEG for MPG has been done after reviewing recent DEG evolution and different aspects related to DEG material, deformation modes of DEG, and prototypes in the field of collecting mechanical energy. Recent research on encouraging features of DEG has provided a complete understanding of its characteristics. These characteristics are flexibility, lightweight durability, and the great potential to store energy. Current findings suggest techniques to increase the efficiency of DEG.

The output performance of a DEG is a function of the thickness and the effective stiffness of the DE generator, the dielectric constant, the relative deformation, and the charging voltage. The results clearly show that an acquiescent DEG improves the efficiency which is appropriate for human motions with less resistance from the DEG. To fabricate more efficient DEG, we may redesign it with smaller effective stiffness, larger relative permittivity, and greater charging voltage, as explained. Also, we may reduce its radius and thickness to a limit to make it more efficient. All these changes are limited by some physical or design constraints.

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# Recent Advances in Nanoformulation-Based Intranasal Delivery of Bioactive Compounds and Biologics for Neurodegenerative Disorders (NDDs)



Manisha Singh and Divya Jindal

# **1** Introduction

Since ancient times, Indian Ayurvedic and yogic medicinal traditions have used the intranasal drug delivery (INDD) system to administer a variety of medicinal chemicals. These methods are referred to as "Nasya Karma" or "Nasya Rasayana" [1, 2]. For its unique ability to deliver drugs directly to the brain while bypassing the blood-brain barrier, it is one of the highly praised and practiced processes seen in concurrent Ayurvedic clinical settings [3]. It is among the most specific and highly regarded approach to drug administration being used in Ayurveda since antiquity and is one of the important components of five bio-purificatory procedural practices of Ayurveda (Panchakarma) [4]. In classical ayurvedic literature, there is a methodical description of its standard operative procedures (SOP) along with its dosages, indications, contraindications, and pre-requisition to deliver the therapeutic compounds directly to the CNS [5]. Though the methodology is well documented and is indicated for many specific CNS disorders as a viable therapeutic approach in our ancient literature, it's been researched in the pharmacology or western medicinal system only for the last two to three decades [6]. The pharmaceutical and pharmacological research done so far in this area has provided enough evidence to establish the authenticity and higher viability of this route of drug administration. This method is preferred for extract-loaded nanomedicinal structures, protein, and peptide class medications since it bypasses the first pass effects of the liver and avoids gastrointestinal enzyme breakdown [7]. Additionally, it has been noted that the pharmaceutical sector has been encountering significant difficulties with phytotherapeutics over the past few decades

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since the process of developing drugs for neurodegenerative disorders has tended to become incredibly expensive, hazardous, and incredibly ineffective [8]. Additionally, the blood–brain barrier (BBB) and blood-cerebrospinal fluid barrier (BCSFB), which restrict access to CNS disorders, are the major obstacles to phytotherapeutics intended for CNS disorders (stroke, brain tumor, head injury, neurodegenerative disorders, etc.) [9]. To treat CNS diseases, the Ayurvedic medical system traditionally focuses on two concepts: product efficacy and cutting-edge administration techniques for herbs or their preparations (or both) [10]. Through the development of nanostructured phytotherapeutic carrier systems, such as liposomes, micro/nanoemulsions, and polymeric/metallic nanoparticles (NPs), this two-way method provides a platform to take advantage of the advantages of intra-nasal drug administration [11]. There are many advantages to intranasal administration for CNS medication delivery, and interest in this non-invasive mode of administration has grown. Rapid delivery, circumvention of the BBB, and direct CNS targeting minimize systemic exposure and adverse effects [11].

Furthermore, Natural Products (NPs) are extensively used as one of the effective and efficacious modes of therapy against CNS disorders, and they also exhibit a vital role in traditional medicinal practices [12]. Hence, NPs have been explored for the treatment of CNS disorders, which has led to the discovery of many potential drugs in the modern-day medicinal system as well [13]. Organic phytochemicals and unprocessed plant extracts have been thoroughly investigated for their potential to reduce inflammation, prevent and treat oxidative stress-related damage, and modulate a variety of signal transduction pathways via indirect and direct effects on enzymes like kinases, regulatory proteins, and receptors [14, 15]. Natural chemicals are desirable candidates for the therapy of these disorders when several pathophysiological pathways are affected, and NDDs are one of such categories, where many targets have to be worked upon. This is due to the multi-targeting qualities of natural chemicals [16]. Additionally, it has been hypothesized that chromatin remodeling and epigenetic changes may be a mechanism by which many polyphenols exhibit some of their advantageous biological effects [17]. They are good candidates for the treatment of multifactorial disorders due to the wide range of their pharmacological or biological effects. Among the large groups of phytochemicals, phenolic compounds such as flavonoids, rosmarinic acid, ferulic, caffeic, chlorogenic, vanillic, hydroxyl benzoic acid, protocatechuic acid, Quercetin, Kaempferol, and Isorhamnetin, extracted from various medicinal plants, were identified to contribute for scavenging out the hazardous free radicals through their strong and effective anti-oxidant activities [18]. Oxidative stress is reported to be a major cause of NDD, causing inhibitory actions in signaling pathways and gene expression regulation [19]. The intranasal delivery of various phytocompounds is shown in Fig. 1, discussing the pathway of formulation delivery via the olfactory nerve.

Schematic representation adapted from M. Singh et al., D. Joy et al., N. Limpeanchob et al., V.K. Kashyap et al., T.N. Chinembiri et al., N. Sugimoto et al., C. Vergallo et al., and A. Mishra et al. [2, 20–27]



Fig. 1 Schematic representation of various phytocompounds exhibiting neuroprotective activity against NDDs and delivered through intranasal route

# 2 Phytocompounds Used for CNS Delivery

For the treatment of AD, scientists have investigated a variety of natural products (extracts as well as purified compounds), including crude extracts of *Curcuma longa* [29], *Salvia officinalis* [30], and *Melissa officinalis* [31] as well as pure compounds like—Bilobalide [32], Quercetin [2], (-)-Epigallocatechin-3-gallate (EGCG) [33], and Stilbenes [34]. Due to their relative higher patient compliance and fewer side effects, phytopharmaceuticals are greatly preferred to chemically produced medications [35]. However, many phytoconstituents are susceptible to structural and chemical degradation [36], which reduces their biological effectiveness. Although it has been found that most natural remedies have a greater therapeutic potential for treating CNS disorders than synthetic or modern drug therapies, they also exhibit some significant, unavoidable physiological limitations, such as the BBB and BCSFB. These phenomena prevent drugs from reaching the disease's intended point of onset and prevent the passive diffusion of many chemicals in the central nervous system [37].

Nevertheless, their (phytocompounds) physicochemical property does not always show compound stability as they're very prone to degradation [38] and/or are metabolized to inactive derivatives in circulation [39, 40]. Indeed, many times they undergo extensive methylation, glucuronidation, and sulfation, which lead to various side effects and lesser therapeutic efficiency of these compounds [41]. In addition, many compounds like Resveratrol (RSV) and Curcumin (CUR) had shown reduced bioavailability because of their rapid metabolic degradation and elimination [42].

Following their visits to India in the twelfth and thirteenth centuries, Arab traders and Marco Polo brought curcumin and other spices to Western nations. In many areas of southern and eastern Asia, where it is regarded as a "blood purifier," turmeric is still frequently used as an alternative medicine to treat conditions like dyspepsia, liver diseases, arthritis, urinary disorders, jaundice, eye infections, and skin diseases like acne and pemphigus [43, 44]. Caffeine and other adenosine A2A receptor antagonists may help to prevent or delay the start of AD, as per human epidemiological studies. Around 200 mg of caffeine every day from a long time dramatically reduced the likelihood of getting Alzheimer's disease, according to a case–control study comprising 50-year-old people with probable diagnoses of the condition and sexmatched controls [45]. Green tea catechins, which were previously believed to just act as antioxidants in regards to protection from AD and PD, are now understood to activate a variety of neuroprotective cellular pathways. These include iron chelating ability, free radical scavenging, signaling pathway activation, and mitochondrial function modulation to prevent excessive free radical formation [46–48].

A Novel Drug Delivery System (NDDS) is a drug administration approach, to enhance the therapeutic efficacy, safety, and degradation of drug molecules by various newer techniques, formulation improvisations, targeted approaches, etc., making the delivery of drugs better than the conventional forms [49]. The therapeutic action of drugs is directly related to an optimal concentration range, within which the greatest benefits can be derived and concentrations of the bioavailability of drugs, below or above, this range may turn out to be either with no therapeutic benefit or being more toxic. These potential medications must be administered using unique techniques that have the potential to significantly affect their efficacy in order to reach their significant therapeutic index. Innovative concepts on controlling and regulating the pharmacodynamics, pharmacokinetics, toxicity, immunogenicity, and efficiency of therapeutics are extensively researched. The success or failure of drug delivery depends on its formulation variant and mode of administration. Possible drug release mechanics from the site of action include desorption of adsorbed drugs from the matrix or carrier surface, diffusion of drug molecules via carrier system, and carrier matrix erosion along with a joint erosion/diffusion procedure. Also, amongst the main goals in designing and fabricating new drug delivery systems for CNS, controlled or sustained delivery of the medicinal agent is important. This site-specific or targeted delivery together improves the drug's effectiveness and decreases the possibility of undesirable toxic side effects of the drugs thus, promoting the therapeutic index of the drug [50].

Polymeric NPs (Chitosan based, polycaprolactone), metallic NPs (gold, silver), and colloidal drug delivery systems like microemulsions, nanoemulsions/
nanosuspensions, or nano-coacervates are one of the most promising and efficient systems to attain this goal [51]. With ever-increasing research in the domain of pharmaceutical sciences, various other new forms and modified variants of drug carrier systems are introduced on a faster scale but out of them all, colloidal drug delivery systems have exhibited better performances. They have proved to overcome various physiological barriers (efficient intracellular reuptake, bypassing BBB and BCSFB, evading endosomal stoppage along with reticuloendothelial clearance) in the brain [52].

Then there is the latest edition to this system where Dr. Daniel P. Wermeling has filed for a US patent for intranasal delivery of tricyclic cannabinoids, a psychoactive drug usually known to treat many other problems like pain, glaucoma, and nausea, to alleviate various mental disorders, as a sedative, and as an anti-emetic [53].

A substantial amount of research performed in the last several decades has provided some evidence that cannabinoid preparations may be useful in treating a variety of conditions including multiple sclerosis and pain [54]. In his research study, he proposed alternative, more feasible methods of administration due to the low oral bioavailability of cannabinoids and he reported that intranasal administration was the most suitable one. The different studies of phototherapeutic nanoformulation have been mentioned in Table 1.

#### **3** Delivery of Peptides and Protein Through INDDR

Due to their physiochemical instabilities and hepatic metabolism, proteins and peptide-based medicines are commonly supplied parenterally; however, IN administration appears to be a promising approach [73]. Multiple studies on both humans and animals have shown that many protein-based substances, such as insulin, MSH/ ACTH, neurotrophic factors, and corticotropin-releasing hormone, are successfully transported to the brain by IN (CRH) [74]. In the same way, mice with middle cerebral artery occlusion were given insulin-like growth factor (GF-1) to test its therapeutic potential for stroke (MCAO). IGF-1 injections reduced the volume of strokes while simultaneously enhancing neurological function. The BBB severely hinders the therapeutic delivery of peptides and proteins to the brain; yet, intranasal administration typically provides a painless way to circumvent the BBB [75].

Intranasal administration frequently offers a painless method to get around the BBB. Intranasal administration has the advantage of restricting access to peripheral organs and tissues, thereby minimizing the systemic adverse effects. Additionally, it gives medications time to work that would otherwise swiftly degrade in circulation. When given substrates like cyclodextrins, intra-nasal injection provides the capacity to focus proteins and peptides to particular brain areas. After being supplied intra-venously, peptides and proteins may enter the brain directly or indirectly via coming into touch with the cribriform plate. Potentially, chemicals can enter the brain through the lymphatic or circulatory systems before going directly into the brain. However,

S.No	Neurological disorders	Nanoformulation	Observations	References
1	AD	$\alpha$ -bisabolol entrapped in cholesterol	NPS significantly boosts Bcl-2 protein expression, diminishes gamma-secretase, cholinesterase, and significantly reduces free radical generation	[55]
2	AD	Quercetin entrapped in Cetyl palmitate miglyol-812	In comparison to free drug, it penetrates the BBB more deeply and is safe to hCMEC/D3 cells. NPS also stops the synthesis of $A\beta$ peptide fibrils	[56]
3	AD	Curcumin entrapped in caprylic and capric triglycerides, sorbitan monostearate	In the AD mouse model, curcumin-NPs guard against the behavioral and neurochemical changes brought on by Aβ42	[57]
4	AD	$\alpha$ -bisabolol entrapped in cholesterol	Prevents the $A\beta$ aggregation and shields Neuro-2a cells from $A\beta$ neurotoxocity	[55]
5	AD	Curcumin entrapped in PLGA	The PLGA NPs with curcumin embedded in them disintegrated amyloid clumps, showed an anti-oxidative property, and were non-cytotoxic	[56]
6	AD	Quercetin entrapped in DSPE-PEG2000-MAL	After 4 h, RVG29-NPs had 1.5 folds permeability across the BBB in comparison to non-functionalized NPs	[58]

 Table 1
 Summary of different nanoformulations for neurological disorders and their observation

(continued)

Table 1	(continued)			
S.No	Neurological disorders	Nanoformulation	Observations	References
7	AD	Epigallocatechin-3-gallate entrapped in PEG/PLGA	Synaptophysin (SYP) expression determined the number of synapses, and GCG and AA NPs reduced neuroinflammation, amyloid beta ( $A\beta$ ) plaque load, and cortical levels of soluble and insoluble $A\beta$ peptides	[59]
8	PD	Ginkgolide B entrapped in poly(ethylene glycol)-co-poly(ε-caprolactone)	NPs made it easier for GB to release slowly into the blood, which enhanced its capacity to build up in the brain and treat PD	[60]
9	PD	Acteoside entrapped in chitosan poly ethylene glycol-poly lactic acid	Prevents the dopaminergic (DA) neuron loss in the substantia nigra and striatum of ill mice	[61]
10	PD	Apomorphine (AMP) entrapped in Monomethoxy polyethene glycol	The NPs' incorporation of AMP prevents oxidation. AMP is transported across the BBB via the intranasal delivery of the AMP-loaded NPs	[62]
11	AD	Coenzyme Q10 6-coumarin with Trimethylated chitosan-conjugated PLGA NPs	↓ Senile plaques ↓ Memory impairment, ↑ bioavailability	[63]
12	AD	HupA in lactoferrin-conjugated N-trimethylated chitosan NPs (Lf-TMC NPs)	Sustained release, increased bioavailability and targeting ability	[64]
13	AD	Berberine in MWCNTs coated with phospholipid and polysorbate	Memory deterioration was temporarily suspended, and AChEI activity was reduced	[65]

 Table 1 (continued)

(continued)

S.No	Neurological disorders	Nanoformulation	Observations	References
14	AD	Hesperetin in Nanocrystal	Improve identification of memory consolidation and increased activity of antioxidant enzymes	[66]
15	AD	Vitamin E in PEG-based nanospheres	Improved and increased antioxidant activity of vitamin E	[67]
16	PD	Retinoic acid (RA) in PNPs	Neuroprotective effect on DA neurons	[68]
17	AD	Chrysin in SLNs	Increased oral bioavailability, free radical scavenging activity, and decreased neuronal damage	[69]
18	AD	Sialic acid and peptide-B6 in Selenium NPs	Disaggregated the $A\beta$ fibrils and inhibited the $A\beta$ aggregation	[70]
19	AD	Cysteine in Selenium NPs	$\downarrow$ ROS prevented A $\beta$ aggregation	[71]
20	AD	NattokINse in enzyme (NK) PNPs	Downregulate amyloid aggregation	[72]

Table 1 (continued)

for chemicals to reach the brain, they must pass through the BBB after entering the bloodstream [76].

# 4 Delivery of Stem Cells Through INDDR

Intraneuronal transport, which frequently takes a longer time, uses axonal transport. Because peptides are prone to breakdown via intraneuronal transport, it is almost likely that intranasal peptides enter via intercellular clefts in the olfactory epithelium before diffusing into the brain. This is also in line with the speed at which most peptides enter various regions of the brain. Simple diffusion via the cerebrospinal fluid or the interstitial fluid of the brain parenchyma might result in extraneuronal transport for CSF [77].

Danielyan L et al. group looked into stem cell delivery and proposed that the stem cells traveled along the olfactory pathway before arriving at the olfactory bulb and other parts of the brain. Additionally, they looked into the challenges of stem cell transplant surgery for PD and whether the safe nasal delivery of stem cells could replace surgery [78]. Recently, the possibility of treating intracerebral glioma

with neural stem/progenitor cell intraneural injection (IN) has grown. NSPC that was supplied by IN rapidly moved to malignant glioma via the olfactory pathway, according to reports. They may contain an enzyme that, when administered intracerebrally, converts the prodrug 5-fluorouracil into the active drug fluorouracil during operation. Phase I clinical tests on people are now being conducted with genetically modified NSPC [79].

Neuroinflammation is a major factor in the development and transformation of neurological diseases, especially in PD and AD. However, pharmaceutical therapy alone cannot produce the best outcomes for neuroinflammation in neurological disorders. Thankfully, an increasing body of research has demonstrated that stem cells infused into the brain can regulate the lesion's microenvironment and alter inflammatory mediators to minimize neurological condition symptoms [80].

Loss of dopaminergic neurons in the substantia nigra and the development of Lewy bodies are the pathological characteristics of Parkinson's disease. The majority of current PD therapies involve medication therapy and supplemental surgery, which attenuates motor fluctuation symptoms [81]. Other therapeutic modalities being investigated for PD have produced encouraging results, including gene therapy, immunological and inflammatory therapy using antibodies, and stem cell therapy [82]. The substantia nigra of PD patients retains its dopaminergic neurons thanks to stem cell transplantation. The primary transplantation technique involves the invasive stereotactic injection of the cells into the brain parenchyma. As a result, noninvasive IN has received a lot of interest. In a rat model with unilateral substantia nigra injury brought on by 6-OHDA, Danielyan et al. made the initial effort to treat Parkinson's disease (PD) with intranasal MSCs in 2011 [83]. MSCs remained in the brain parenchyma for at least 4.5 months, where they flourished and proliferated. Intranasal transplantation of MSCs significantly reduced tyrosine hydroxylase (TH) levels in the damaged substantia nigra and striatum in addition to the motor symptoms in model rats [83]. Then, intranasal injections of BM-MSCs, NSCs, DPSCs, and endometrial MSCs were given to treat PD model animals. Each of them has some therapeutic and healing effects [84–87]. However, there are still many questions that need to be answered, including how different forms of intranasally injected stem cells enter the body, what influences them, and what consequences they have. The IN of stem cells may potentially have an anti-inflammatory effect, according to certain studies. For instance, Danielyan et al. [78] reported a noninvasive IN of MSCs to the brains of unilaterally 6-hydroxydopamine (6-OHDA)-lesioned rats. After 40-110 days of stem cell infusion, interleukin (IL)-1, IL-2, IL-6, IL-12, tumor necrosis factor, interferon, and granulocyte-macrophage colony-stimulating factor concentrations in the lesioned side were lowered by MSCs to those observed in the unharmed hemisphere. McDonald et al. in 2019 [88] discovered that in a rat model of neonatal hypoxic-ischemic brain injury, IN of a therapeutically significant dosage of human umbilical cord-derived MSCs exhibited neuroprotective benefits by restoring neuronal cell counts and lowering brain inflammation.

Another prominent illness is AD, the most common neurodegenerative disorder. Amyloid plaques formed of amyloid-(A) and neurofibrillary tangles composed of hyperphosphorylated tau are the pathological hallmarks of AD. Neurodegeneration and reduced synaptic plasticity have been observed in AD patients' brains. Exogenous stem cells play an essential role in the regeneration and repair of damaged brain circuits [89, 90]. In 2014, Danielyan L's research group administered an intranasal infusion of BM-MSCs to treat AD transgenic APP/PS1 mice. The hippocampus and occipital cortex around the A $\beta$  deposition were shown to contain stem cells 7 days after IN. Furthermore, the transplanted cells could have phagocytic and scavenging effects on A $\beta$  if it was positive for A $\beta$ . Intranasal administration of serum-free control stem cells generated from human exfoliated deciduous teeth enhanced the cognitive function of AD model mice, according to research by Mita et al. in 2015. (SHED-CM) [91]. Intravenously injected MSC exosomes [93] decrease A $\beta$  while lowering inflammation in AD mice.

#### 5 Therapeutic Limitations of INDDS for CNS Application

The intranasal pathway for therapeutic compounds' delivery is appealing as it provides rapid and precise direct entry to the brain and also exhibits many benefits, including BBB avoidance, patient compliant, non-invasive, and provides very conducive access [11]. It has a more rapid onset of action, higher therapeutic targeting ability, larger surface area for drug absorption, avoiding hepatic first-pass metabolism, and having negligible systemic adverse effects. However, there remains a considerable distance for its clinical application as it still has efficacy limitation due to its insufficient drug penetrability through the nasal mucous membrane, enzymatic degradability of the therapeutic in the nasal cavity and high rate of mucociliary clearance (MCC) [94]. To improve drug penetrability and uptake, varied targeted delivery systems like —emulsion-based colloidal system (Nano/Microemulsions) with mucoadhesive properties and permeation enhancer's approaches-were utilized [95]. It has been demonstrated that using an appropriate mucoadhesive system (adhesive polymers, gelatins, hydrogel, Gums, etc.) increases the residence time while decreasing the MCC [96]. Likewise, some safeguards, such as enhanced encapsulation efficiency of drug/extract/compound inside a nanocarrier system, are needed to avert enzymatic degradation of the drug same and reduce the nasal irritation caused due to higher doses/frequency of administration [97].

#### 6 Future Perspective of INDDS in CNS Disorders

One of the major challenges continues to remain the efficient drug delivery for neurological diseases, and though nanotechnology advancement has offered enticing solutions to this challenge up to some extent. Efficient drug delivery for neurological diseases remains a significant obstacle, despite some progress offered by advancements in nanotechnology. Various nanocarrier systems, including polymeric nanoparticles, solid lipid nanoparticles, liposomes, nanogels, and nanoemulsions, have greatly supported the delivery of therapeutics into the brain [98]. Moreover, since there are still some outstanding problems existing with intranasal delivery, this responsive drug delivery method towards the brain is a prospective research area. Also, strategies to overcome the concern of heavier molecular weight, polar compounds (Proteins, Peptides, Biologics, Antibodies etc.) encapsulation, permeability, MCC, etc. [73] needs to be addressed to further improve NP-based drug delivery carrier systems through INDD route. Besides that, sufficient preclinical and clinical investigations are required to increase the evidence-based claim in intranasal delivery systems. Also, more research is necessary to better comprehend the precise mechanism of drug movement through the intranasal route to the various cortical regions of brain. At last, the use of nanocarrier system is going to increase through this route so the toxicity analysis of such nanocarriers must be thoroughly examined.

#### 7 Conclusion

The question of drug delivery and accessing the brain has always been a persistent challenge when developing treatments for central nervous system disorders. The drugs developed for the CNS thus far have demonstrated lower efficacy and face significant hurdles in permeating the blood-brain barrier, as well as experiencing reduced first-pass effect or enzymatic degradation. In the pursuit of effective drug delivery to the brain, intranasal drug delivery systems (INDDS) have emerged as a promising and preferred alternative to other delivery routes. Researchers are currently employing innovative approaches such as ligand targeting, nanoparticlebased systems, nano-coacervates, and nanoconjugated systems to develop a viable INDDS. While most studies are still in the early stages of preclinical or early clinical research, there is a limited number of studies that have progressed to human clinical trials. The results of these trials have demonstrated the relative success of INDDS in accessing the central nervous system, establishing it as a potential future method for brain drug delivery. Our review explores various perspectives related to INDDS in the treatment of CNS disorders, providing a comprehensive overview of this emerging technique. Several biologics and compounds are currently under investigation for intranasal delivery and are expected to yield positive outcomes in the near future.

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# Simulation of Fixed-Bed Adsorption for Biogas Upgrading



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# 1 Introduction

Great efforts have been devoted to developing clean energy sources of energy that can contribute to keeping global warming below 2 °C in the incoming 30 years. Global warming is mainly caused by the emission of anthropogenic greenhouse gas such as methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>), being CH<sub>4</sub> almost 28 times more damaging than CO<sub>2</sub> [4]. Biogas is a sustainable and renewable source of energy mainly composed of CH<sub>4</sub> and CO<sub>2</sub> and low levels of N<sub>2</sub> [2, 8]. In this way, producing biogas and upgrading it to biomethane is an alternative solution to prevent greenhouse gas emissions at the same time it can be supplied as a renewable source of biofuel. Furthermore, biogas can be a decentralized alternative to produce clean energy everywhere, as it is easily produced from the methanation of biomass and organic wastes from sewage sludge anaerobic digestion, commercial composting, landfills, biomass gasification (thermos-chemical production process), animal farm manure anaerobic

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co-digestion with energy crops, agro-food industry digestion facilities [2], among others.

The presence of CO<sub>2</sub> (up to 40 vol. %) and N<sub>2</sub> (up to 15 vol.%) in the biogas composition (landfill gas), reduces its calorific value and causes corrosion of engines and pipelines, limiting its use and transportation via natural gas pipelines [2]. Accordingly, biogas needs to be upgraded (by removing CO<sub>2</sub> and N<sub>2</sub>) to obtain biomethane that can be either injected into natural gas grids or directly used as a vehicle/domestic fuel. However, to use biomethane as a vehicle fuel or to inject it into natural gas pipelines, standard requirements must be followed depending on country rules. For example, the methane content in Switzerland must be  $\geq$ 96 vol%, and only  $\geq$ 86 vol% in France. In these two countries, the CO<sub>2</sub> content is also different, being  $\leq$ 4 (Switzerland) and  $\leq$ 2.5 vol% (France) [2].

To meet the standard requirements for biogas upgrading the main separation techniques reported in the literature can be water or organic solvent scrubbing, chemical absorption, adsorption, cryogenic separation, membrane technology, biological upgrading, and in-situ upgrading methods [2, 5, 6]. Among them, adsorption processes such as Pressure/Vacuum or Temperature Swing Adsorption (PSA/VSA or TSA) have been employed, being very competitive with low energy consumption. At the same time, a variety of solid adsorbents are already available or will be developed in the future to increase the performance of the adsorption processes [6, 8, 16]. Moreover, several operating parameters namely pressure, flow rates, temperatures, different cycle steps (e.g. pressurization, feed-high pressure, blowdown/depressurization, equalization, backfill, low-pressure purge, etc.), and their tuning should be optimized to provide efficient performance in the biogas upgrading. Thus, mathematical modeling is a fundamental tool for the design of adsorption processes allowing us to evaluate the effect of several operating parameters to find the best-operating conditions, besides significantly reducing the number of experiments required.

In this work, an adsorption simulation package to study the separation of the main components of biogas  $(CO_2/CH_4/N_2)$  in a fixed bed was developed and validated by predicting experimental single and ternary breakthrough curves on binder-free zeolite 4A and KY. Overall, the simulator proved to be very efficient to predict the fixed-bed experimental data adsorption dynamics, and it has now been used in the simulation and design of more complex systems like PSA/VSA to TSA processes for biogas upgrading at the industrial level with proper boundary conditions.

#### 2 Materials and Methods

#### 2.1 Materials

In this work, two types of benchmark zeolites were studied, namely, potassium exchanged (95%) type Y (BFKY) and sodium type A (BF4A). These zeolites were synthesized and transformed into beads through the binder-free method [10, 11] by Chemiewerk Bas Köstritz GmbH (Germany). The adsorbent bead's particle diameter ranges from 1.6 to 2.5 mm. He (99.9998%),  $CO_2$  (99.998%),  $CH_4$  (99.95%), and  $N_2$  (99.999%) were supplied by Air Liquide.

#### 2.2 Experimental Procedure

A homemade fixed-bed adsorption apparatus has been used to collect the breakthrough curves of  $CO_2$ ,  $CH_4$ , and  $N_2$  and their binary/ternary mixtures which were used to validate the adsorption mathematical model simulation package. This apparatus has been used in our previous work [15], where detailed information on its layout can be found. In the adsorption studies, a stainless steel adsorption column (0.0286 m i.d. and 0.0646 m length) has been used. For the experiments, the column was filled with 23.8 g of BF4A and 26.2 g of BFKY, which leads to a bulk density of 590 and 649 kg m<sup>-3</sup>, respectively.

# 2.3 Mathematical Model

The adsorption mathematical model and respective boundary conditions for fixedbed adsorption are shown in Table 1 and were derived according to the following assumptions: (i) the gas is considered to follow the ideal gas law; (ii) an axially dispersed plug flow model is used to represent the bulk fluid flow through the bed; (iii) constant bulk density in the bed; (iv) the pressure drop is negligible; (v) the radial gradients of concentration, temperature, and pressure are negligible; and (vi) the adsorption equilibrium is described by the extended dual-site Langmuir isotherm model (DSL). Moreover, it was considered a column of length *L*, void fraction  $\varepsilon_b$ (=0.4), packed with a solid adsorbent through which an ideal biogas stream (mainly CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub>) flows at a molar flow rate *F*, where *C* is the total gas concentration of the species in the mixture,  $y_i$  represent the molar fraction of adsorbable species *i* in the fluid, and  $\overline{q}i$  the average adsorbed concentration of adsorbable species *i* in the adsorbent solid phase.

Model	Equations	
Ideal gas	$C = \frac{P}{RT}$	(1)
Overall mass balance	$\frac{\partial F}{\partial z} + \varepsilon_b \frac{\partial C}{\partial t} + \rho_p (1 - \varepsilon_b) \sum_{i=1}^n \frac{\partial \overline{q}_i}{\partial t} = 0$	(2)
Component mass balance	$\left  -\varepsilon_b D_{ax} \frac{\partial}{\partial z} \left( C \frac{\partial y_i}{\partial z} \right) + \frac{\partial (F y_i)}{\partial z} + \varepsilon_b \frac{\partial (C y_i)}{\partial t} + \right.$	(3)
	$\rho_p(1-\varepsilon_b)\frac{\partial \overline{q_i}}{\partial t} = 0$	
Mass transfer rate	$\frac{\partial \overline{q}_i}{\partial t} = K_{LDF} (q^* - \overline{q}_i)$	(4)
Linear Driving Force (LDF)	$\frac{1}{K_{LDF}} = \frac{R_p}{3k_f} + \frac{R_p^2}{15\epsilon_p D_p} + \frac{r_c^2}{15KD_c}$	(5)
Gas-phase energy balance	$\begin{aligned} -K_{ax}\frac{\partial^2 T}{\partial z^2} + Fc_{pg}\frac{\partial T}{\partial z} + C\varepsilon_b C_{pg}\frac{\partial T}{\partial t} + \\ (1 - \varepsilon_b)a_p h_p (T - T_s) + a_c h_w (T - T_w) = 0 \end{aligned}$	(6)
Solid-phase energy balance	$C_{ps} \frac{\partial T_s}{\partial t} =$	(7)
	$a_p h_p (T - T_s) + \rho_p \sum_{i=1}^n (-\Delta H_{st,i}) \frac{\partial q_i}{\partial t}$	
Isotherm model (DSL)	$q_i = \frac{q_{m1}b_{1i}p_i}{1 + \sum_{j=1}^{n} b_{1j}p_j} + \frac{q_{m2}b_{2i}p_i}{1 + \sum_{j=1}^{n} b_{2j}p_j}$	(8)
Boundary conditions	$Fy_{if} = Fy_i - \varepsilon_b D_{ax} C \frac{\partial y_i}{\partial z}$	(9)
	$z = 0 \begin{cases} Fc_{pg}T_f = Fc_{pg}T - K_{ax}\frac{\partial I}{\partial z} \\ F = F_f \end{cases}$	
	$z = L \begin{cases} \frac{\partial y_i}{\partial z} = 0\\ \frac{\partial T}{\partial z} = 0 \end{cases}$	

Table 1 Fixed-bed adsorption mathematical model equations

# 2.4 Numerical Model

For the solution of the model, the method of the lines was applied to reduce the set of coupled partial and algebraic differential equations into a system of ordinary and algebraic differential equations [9]. The spatial coordinate was discretized by the orthogonal collocation method [14]. In the orthogonal collocation method, the collocation points which represent each spatial coordinate or node in the numerical grid are determined by using Jacobi polynomials,  $P_{N^{(\alpha,\beta)}}(x)$ , with  $\alpha = 0$ ,  $\beta = 0$ , where *N* is the number of collocation points. The approximation of the first and second derivatives was made by collocation matrices routines  $A_{i,j}$  and  $B_{i,j}$ , respectively. Therefore, the reduced system of ordinary differential equations was solved using the integrator ode15s available in the MATLAB library [12], and the algebraic differential equations were solved by Gauss elimination described elsewhere [14]. The simulator shows satisfactory accuracy and stability by using 25 spatial collocation points.

#### **3** Results and Discussion

#### 3.1 Equilibrium of Adsorption

The adsorption equilibrium data of  $CO_2$ ,  $CH_4$ , and  $N_2$  in BF4A and BFKY were collected at 313 K and partial pressures up to 3.5 bar by fixed-bed breakthrough experiments described in a previous work [1, 15]. Figure 1 shows the isotherms collected for  $CO_2$ ,  $CH_4$ , and  $N_2$  together with the standard Langmuir (for  $CH_4$  and  $N_2$ ) and dual-site Langmuir (DSL for  $CO_2$ ) isotherm models fittings (lines), for BF4A (open symbols) and BFKY (closed symbols) at 313 K.

From Fig. 1, it is possible to see that, as the pressure increases, the amount adsorbed of all components increases, which means that the equilibrium data is thermodynamic consistent. At 3.5 bar, the adsorbed equilibrium amount for CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> in BFKY is around 6.42, 1.45, and 0.67 mol kg<sup>-1</sup>, respectively, against 4.48, 1.34, and 0.81 mol kg<sup>-1</sup> in BF4A. Regarding the affinity of adsorption for each component, CO<sub>2</sub> has a much higher affinity than CH<sub>4</sub> and N<sub>2</sub> in both adsorbents. This can be explained due to its large linear quadrupole moment, which leads to a strong interaction with the intracrystalline charge density framework. An important note is that the CO<sub>2</sub> adsorption equilibrium amount is 45% higher on BFKY than BF4A, which can be explained by the higher electric field in the zeolite faujasite type Y framework induced by an increasing number of charged sites present at the surface as compared to the type A framework [3]. However, the CH<sub>4</sub> and N<sub>2</sub> equilibrium of adsorption on both BF4A and BFKY do not present significant differences at the temperature and pressure studied.

Table 2 summarizes the DSL and standard (one-site) Langmuir isotherm parameters obtained from the fitting of the adsorption equilibrium data of  $CO_2$ ,  $CH_4$ , and  $N_2$ in the BF4A and BFKY. Figure 1 clearly shows that the DSL and Langmuir models



Material	Species	$q_m (\mathrm{mol}\cdot\mathrm{kg}^{-1})$		$b (bar^{-1})^{a}$		$(\Delta H_i)$ (kJ·mol <sup>-1</sup> )	
		$q_{m1}$	$q_{m2}$	$b_1$	$b_2$	$(\Delta H_i)_1$	$(\Delta H_i)_2$
BF4A	CO <sub>2</sub>	1.97	2.68	2.44	88.3	-35.6	-38.7
	CH <sub>4</sub>	3.39	-	0.19	-	-18.0	-
	N <sub>2</sub>	3.47	-	0.09	-	-16.2	-
BFKY	CO <sub>2</sub>	3.35	3.25	6.27	16.2	-45.0	-37.4
	CH <sub>4</sub>	4.81	-	0.12	-	-16.9	-
	N <sub>2</sub>	2.98	-	0.08	-	-18.7	-

Table 2 Dual-site and standard Langmuir model parameters for sorption of CO<sub>2</sub>, CH4, and N<sub>2</sub> on BF4A and BFKY

<sup>a</sup>The reference temperature used is 313.15 K

describe the equilibrium data with good accuracy. The extended DSL (Eqs. 2–8) model was used to predict the multicomponent data in the simulations.

The selectivity of CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub> on BF4A in a typical biogas composition from landfill gas (CO<sub>2</sub>/CH<sub>4</sub>/N<sub>2</sub>:33/52/15 vol.% at 1 bar and 313 K) is equal to 38 and 37, respectively. In the case of BFKY, the selectivity increases to 68 and 66 for CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub>, respectively. These results point out that the BF4A and BFKY can be used to efficiently separate CO<sub>2</sub> from CO<sub>2</sub>/CH<sub>4</sub>/N<sub>2</sub>. These values were calculated by using the extended DSL model and validated experimentally.

It is worth mentioning that raw biogas contains other contaminants such as  $H_2O$ ,  $H_2S$ ,  $O_2$ , ammonia, and siloxanes whose concentration depends on the source of biogas production [2, 13]. These contaminants can affect significantly the adsorption and separation of  $CH_4/CO_2/N_2$ . For example, water can strongly adsorb on both zeolites studied in this work which could reduce their adsorption capacity towards  $CO_2$  leading to a decrease in the overall performance. To use zeolites for biogas upgrading, pretreatment beds (guard beds), for example, for drying the gas stream before feeding the main adsorption column, are necessary to protect it from these contaminants. However, we focus here only on the study of the adsorption dynamics of an ideal mixture of  $CH_4/CO_2/N_2$  free of contaminants. For more information about the effect of these contaminants and how they can be removed, detailed information can be found in the work of [2].

#### 3.2 Modeling the Breakthrough Data of $CH_4/CO_2/N_2$

Mathematical modeling of fixed-bed adsorption breakthrough data is a valuable tool to collect adsorption equilibrium data, as well as find the kinetics sorption. The fitting of the experimental breakthrough curves makes it also possible to calculate all model parameters, and thereafter predict the adsorption process performance in a more complex cyclic system, such as: pressure/vacuum swing adsorption; necessary to assure continuous operation in biogas upgrading or any other gas separation process

by adsorption. In this section, the mathematical model developed will be validated and used to predict the dynamics of fixed-bed adsorption by matching the history profiles of the breakthrough curves. As an example, two simulations of a ternary mixture of  $CH_4/CO_2/N_2$  at a certain feed biogas concentration (Table 3) were selected and depicted in Figs. 2 and 3. The experimental conditions and mathematical model parameters are summarized in Table 3.

The relative importance of the individual transport mechanisms such as the axial dispersion coefficient  $(D_{ax})$  and mass transfer resistance  $(K_{LDF})$  was evaluated by performing simulations, where these two parameters were varied to see their effects on the history profile of the breakthrough curves. The  $K_{LDF}$  is the linear driving force coefficient that represents the mass transfer resistance regarding the transport of the solute between the bulk fluid gas phase and the solid phase, and the axial dispersion coefficient  $(D_{ax})$  is a resistance arising from fluid mixing and molecular diffusivity in the bulk fluid gas phase.

Figure 2 shows the parametric study performed to evaluate the effect of  $D_{ax}$  and  $K_{LDF}$  in the profile of the breakthrough curves. Figure 2a, c shows that by increasing or decreasing two times the  $K_{LDF}$  and kept  $D_{ax}$  constant, the history profiles of the breakthrough curves are unchanged. On contrary, Fig. 2b, d show that by changing the same values the  $D_{ax}$  and kept  $K_{LDF}$  constant the breakthrough curves are affected. Thus, from this parametric study, we can conclude that experimental breakthrough curves are dependent on the  $D_{ax}$  value. These results agree with the method of moments [7] explored in our previous work [15], where it was shown that axial dispersion mechanisms ( $D_{ax}$ ) are prevailing over the mass transfer resistances ( $K_{LDF}$ ), in the experimental system studied being the numerical model a valuable tool to evaluate such effects.

Figure 3 shows the experimental (symbols) and simulation (lines) ternary breakthrough curve of a mixture  $CO_2/CH_4/N_2$  (20/20/20 vol% balanced with He) in the zeolites (a) BF4A and (b) BFKY. As shown in Fig. 3a-b,  $CO_2$  is the most retained component due to its high interaction with both zeolite frameworks. In the case of CH<sub>4</sub> and N<sub>2</sub>, they break through the column practically at the beginning of the experiments. Thus, we can conclude that both zeolites are excellent adsorbents to separate  $CO_2$  from a mixture of  $CO_2/CH_4/N_2$ . In general, the numerical simulations represented by the lines in Figs. 2 and 3 describe very well the dynamics of the fixedbed adsorption system for pure and mixture adsorption. Moreover, the methodology shown here with the validation of the mathematical through laboratory experimentation is the first step and the basis for the rapid scale-up of column testing for the design of cyclic adsorption processes such as PSA/VSA or TSA at an industrial scale regarding biogas upgrading applications.

Table 3	Experim	ental condit	tions and ma	athematical mode	d parameter	S				
Run	T (K)	P (bar)	Specie	F (mLn/min)	$K_{LDF}$ (1/s)	$D_{ax} \ ({ m m}^2/{ m s})$	$K_{ax}$ (W/m/K)	C <sub>Pg</sub> (J/mol/K)	$h_p$ (W/m/K)	$h_w$ (W/m/K)
1	313	1	CO <sub>2</sub>	28.6	98	$1.94 \times 10^{-4}$	0.25	29.0	190	27
			He	42.4		$1.94 \times 10^{-4}$				
5	313		CO2	12.8	15.5	$4.17 imes10^{-5}$	0.13	30.4	37	30
			N <sub>2</sub>	72.2	16.7	$4.17 \times 10^{-5}$				
en	313	5	CO <sub>2</sub>	117	13	$1.50  imes 10^{-5}$	0.20	18.4	50	137
			CH <sub>4</sub>	110	5.3	$1.72 \times 10^{-5}$				
			N <sub>2</sub>	121	12.7	$1.70 \times 10^{-5}$				
			Не	351	1	$3.62 \times 10^{-5}$				
4	313	1	CO <sub>2</sub>	17.3	29.4	$3.09 \times 10^{-5}$	0.17	29.0	63.4	10.0
			CH <sub>4</sub>	17.4	42.8	$3.54 \times 10^{-5}$				
			$N_2$	17.5	42.8	$3.45 \times 10^{-5}$				
			He	33.7	1	$7.10 \times 10^{-5}$				

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Fig. 2 Effect of changing overall mass transfer coefficient  $K_{LDF}$  (a and c) and axial dispersion Dax (b and d) on the simulated breakthrough curves of CO<sub>2</sub> at 313 K



Fig. 3 Ternary breakthrough curves of  $CO_2/CH_4/N_2$  on **a** BF4A and **b** BFKY. Experimental = symbols; Simulation = lines

# 4 Conclusions

In this work, an adsorption package simulator to study the separation of the main components of biogas ( $CO_2/CH_4/N_2$ ) in a fixed bed was developed and validated by fitting experimental single and ternary breakthrough curves on binder-free zeolite 4A and KY. Both zeolites show a significant  $CO_2$  adsorption capacity with also excellent selectivity over  $CH_4$  and  $N_2$ . BFKY adsorbs almost 45% more  $CO_2$  than BF4A, which is related to the higher electric field presented in the faujasite framework. The mathematical model was validated by predicting the experimental data, at the same time, it gives insights into the prevailing mass transport mechanisms in the fixed bed, being clear that the axial dispersion is the dominant one affecting the history profile of the single and multicomponent breakthrough curves. Overall, the adsorption simulator predicts very well the experimental data shown in this work and, therefore, can be a valuable tool for designing pilot-scale columns and also the development of cyclic adsorption processes, such as PSA, VPSA, and TSA for biogas upgrading.

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# **Biological Synthesis of Nanoparticles and Their Applications in Bioremediation: A Mini-Review**



Mohan Jujaru and Amit Jain

# 1 Introduction

One of the fields that have witnessed remarkable growth in recent years is nanotechnology. The word "nano" is derived from the Greek "Nanos," meaning "dwarf," which cites things of one-billionth  $(10^{-9} \text{ m})$  in size. Nanoparticles have numerous applications in catalysis, electronics, coating, drug delivery, cosmetics, and biotechnology. Most applications depend on nanomaterial size, shape, and functionality [46]. The size and shape of nanoparticles conventionally rely on the method of synthesis and the substrates utilized. Nanoparticle synthesis predominantly uses chemical processes and displays toxic by-products [10]. Most of the available techniques generate dangerous waste by-products and produce unsteady nanoparticles. Therefore, non-toxic, clean, and environmentally friendly procedures are required to advance the comprehensive synthesis of nanoparticles for industrial and medical applications. Thereby, the synthesis of nanoparticles requires a purification step to eliminate any hazardous reactants from their synthesis [18]. One such approach is the biological synthesis of nanoparticles. The biological synthesis route utilizes bacteria, fungi, and yeast to produce nanoparticles such as silver, gold, and iron [15]. Nanoparticles synthesized from the enzymatic processes surpass the nanoparticles formed by chemical methods in many ways. But, one major drawback of microbial synthesis includes lofty time duration in generation and optimal production. Considering the need for a greener synthesis of nanoparticles and overcoming the drawbacks of biological synthesis, the biosurfactant-mediated process becomes an alternative for the synthesis of nanoparticles [5].

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Biosurfactants are majorly produced by microbes and can be synthesized using industrial waste, dairy waste, food waste, tannery waste, and agricultural waste. They have the main advantage of being environmentally friendly, biodegradability, and lower toxicity. Because of these characteristics, biosurfactants can be used in emulsification and separation processes [13]. Besides, they have unique qualities like selectivity and specificity at high temperatures, p<sup>H</sup>, and salinity. Based on their chemical composition and microbial origin, microbes like bacteria, fungi, and yeast produce different biosurfactants. Some of the significant classes of biosurfactants are glycolipids, lipopeptides, fatty acids, and phospholipids [50]. Over the last few years, biosurfactants are emerging as 'green products' with increasing consumer demand and friendly attributes. The biosurfactant market size outstripped \$1.35 Billion in 2019 and was gauged to grow at over 5.5% compound annual growth rate (CAGR) between 2020 and 2026. The world market is expected to reach \$52.4 billion by 2025, and it is estimated that the demand for biosurfactants will escalate at a rate of 35% per year [43]. Despite various remarkable advantages of biosurfactants, there are a few limitations, one of which is the pathogenicity of bacteria [7]. Biosurfactant production using non-pathogenic strains demands additional attention and investigation. Some benefits of non-pathogenic strains include benign biosurfactants suitable for all factory applications and better implicit surface-active properties than synthetic and pathogenic ones. However, many non-pathogenic strains have recently been documented for optimal biosurfactant production. Still, more research has to be done in this area, aiming mainly at enhanced biosurfactant production by these strains. Besides, optimizing biosurfactant production and finding new recombinant strains using mutagenesis would strengthen its production [48].

The nanoparticles produced by microbial and a biosurfactant-mediated process can be used as co-promotor and adsorbing agents in pollutant removal, bioremediation, removal of organic contaminants, microbial enhanced oil recovery (MEOR), and heavy metal removal [33]. In this review, we focus on nanoparticle synthesis using biological and biosurfactant-mediated synthesis and the application of nanoparticles in bioremediation.

#### 2 Biosurfactant Production

Microorganisms utilize mainly carbon sources for their growth. It is found that a combination of carbon sources with insoluble substrates fastens the intracellular diffusion and production of various substances like biomolecules. Biosurfactants are surface-active amphiphilic agents containing both hydrophobic and hydrophilic groups. These compounds also exhibit (antimicrobial and antifungal) properties other than lowering the surface tension and are, named according to their use, such as soaps, detergents, wetting agents, dispersants, emulsifiers, and foaming agents. The microbial surface-active compounds can be classified by their chemical structure as low molecular weight and high molecular weight molecules and by their microbial

origin as bacterial or fungal biosurfactants. A few examples of biosurfactants are glycolipids, rhamnolipids, and sophorolipids [25].

On the other hand, chemical surfactants have dominated the global markets for a long time. Surfactant products have been extensively developed for large-scale industrial and domestic applications such as biodegradation, MEOR (microbial enhanced oil recovery), etc. These compounds are readily available at a low cost and are also very efficient for applications [24]. However, there are certain disadvantages of chemical surfactants. The presence of definite functional groups in chemical surfactants has proved to be non-biodegradable and toxic to the environment. Therefore, to overcome the problems mentioned above, one possible solution is to replace some of the chemical surfactants with surfactants of biological origin, i.e., synthesized by microorganisms. There are only a few manufacturers (BASF Cognis, Evonik, Akzo Nobel, etc.) of biosurfactants around the globe [35].

Biosurfactants have various advantages over chemical surfactants, such as low toxicity, biodegradability, higher foaming, and broad selectivity. Regardless of these applications, biosurfactant production is limited because of high downstream processing costs. Biosurfactant production takes place when microbes are made to feed on a suitable substrate, followed by recovery of the biosurfactant from the system with the help of appropriate downstream processing techniques. The low-cost and waste substrates reported in the literature for the cost-effective production of biosurfactants are vegetable oil and oil wastes, agro-industrial wastes, and dairy and distillery wastes. Another parameter on which the cost of biosurfactant production adversely depends is the downstream processing technique that is used to recover the product successfully [12, 13].

Biosurfactant production can occur in a batch, continuous, and fed-batch process with industrial, dairy, food, or other carbon sources as substrates in MSM (minimal salt media/mineral salt media) by adding micro/macronutrients. For the analysis of biosurfactants, some of the screening methods are the blood agar hemolysis method, CTAB agar plate method, drop collapse test, oil displacement method, penetration assay, emulsification activity test, and emulsification index test. By change in producer strain and culture conditions, the emulsifying activity and composition are get influenced. Besides, the quantity of biosurfactant produced and the polymer chain is affected by C:N ratio, temperature, p<sup>H</sup>, aeration rates, and nutrition. Economical biosurfactant production can be accomplished using growth enhancers, nanoparticles, immobilized organisms, and a biofilm reactor [41].

The biosurfactants are majorly produced by *Pseudomonas aeruginosa, Alcaligenes faecalis, Serratia marcescens, Cronobacter sakazakii,* and *E.Coli,* which are pathogenic strains. These strains cause numerous infectious diseases. Predominantly, biosurfactants produced from strains of *Pseudomonas aeruginosa* cannot be regarded as secure raw materials in manufacturing pharmaceuticals and food products. Because of the safety and health issues associated with these strains, new non-pathogenic biosurfactant producers are gaining more attention. The dominance of using non-pathogenic organisms may include the possibility of biosurfactants with less or no toxic effects on living cells. For example, non-pathogenic strains such as *Burkholderia thailandensis* utilized cooking oil as a substrate to produce rhamnolipids. *B. thailandensis* was reported to produce up to 2.2 g/L of di-rhamnolipid Rha-Rha-C14-C14 [20]. Hence, more research needs to be focused on new bacterial strains, which produce eco-friendly biosurfactants.

# **3** Biological Synthesis of Metal Nanoparticles

Microbial production of nanoparticles is a good technique that imparts a non-toxic, safe, and eco-friendly approach in producing latent nanoparticles. The nanoparticles synthesized from microbes have physicochemical and optoelectronic properties, which exhibit their effectiveness in several industries [15]. Biologically synthesized nanoparticles are superior to chemical methods because of the removal of hazardous toxic wastes and expensive chemicals. When the microorganisms such as bacteria, fungi, and yeast interact with the metal ions, they convert the metals into possible elemental forms through processes like cellular enzymatic activities. Extracellular and intracellular processes synthesize microbial nanoparticles, and the synthesis mechanism differs when metals come in contact with different microorganisms. The production routes are predominantly mediated by biomolecules, proteins, and other enzymes, which reduce metal compounds to their molecular level. In extracellular synthesis, ion assembly takes place in the cell to produce nanoparticles with the help of specific biomolecules [56].

# 3.1 Intracellular Synthesis Mechanism

Predominantly, ionic charges are settled on the microorganism cell wall, which are carried over by ionic mobility and are backed by various enzymes and proteins. Due to the active sites on the cellular wall and negatively charged ions from the carboxy-late groups in several polypeptides, the metal ions exhibit more affinity towards it. Through microbial gripping, these metal ions were trapped electrostatically inside the cell wall, and there is a risk to these microbes. Subsequently, the trapped ions undergo enzymatic reduction and transform into their basic form via NADH (Nicotinamide adenine dinucleotide) conditional reductase activity. Then they are confined in the cell tissue and finally converted into nanoparticles [39]. Later, the nanoparticles are concentrated on the cell surface. Dissimilar macromolecules such as amino acids and proteins help to sustain these nanoparticles [17]. The mechanism of intracellular routes of nanoparticles has mentioned below in Fig. 1.



Fig. 1 Microbial Intracellular routes of nanoparticles

# 3.2 Extracellular Synthesis Mechanism

It can take place by.

- (a) Biomass-cell surface and enzyme,
- (b) Microbe supernatant, and
- (c) Cell-free extract
- (a) In biomass-cell surface and enzyme, enzyme activities such as NADH-dependent hydrogenase, nitrate reductase, acetate permease, iron reductase, cysteine desulfhydrase, superoxide dismutase, phenol oxidase have been reported for different metal nanoparticle syntheses. These enzyme activities control the electron transfer from NADH (nicotinamide adenine dinucleotide). Subsequently, after capturing electrons, the metal ions are confined to a basic form and succeed in the development of nanoparticles. The reductase enzymes have been constrained in periplasmic regions and on the membrane. The reduction can be confirmed by protein examination and identification. When the concerned enzyme comes into contact with NADH, electron transfer occurs, and the nanoparticles are formed [1].
- (b) Firstly, microbial supernatants (proteins, biomolecules, organic molecules) are produced from microorganisms grown under optimal conditions. These supernatants come in contact with metal compounds to produce nanoparticles. The bioreduction takes place with the help of biomolecules in the supernatant. These biomolecules act as reducing and stabilizing agents in the synthesis of nanoparticles [40].
- (c) One more enzyme, called hydrogenase, is involved in the metal reduction in periplasmic and cytoplasmic regions. A cell-free extract made from the microbial media is produced and uses the biomolecules, amino acids, and proteins in the metal reduction of nanoparticles [3].

All three routes of extracellular synthesis have been explained thoroughly with the help of Fig. 2.



**Extracellular Synthesis** 

Fig. 2 Extracellular routes of nanoparticles

# 3.3 Parameters that Affect the Synthesis Process

**p<sup>H</sup>:** For the required texture and optimum size of nanoparticles, an optimum  $p^{H}$  setup is necessary. Prakash et al. [31] explained that immense nanoparticles could be formed when there is a drop in  $p^{H}$ . In another report, silver nanoparticles are synthesized by varying the  $p^{H}$ . At  $p^{H} = 7$ , nanoparticles with high symmetrical and uniform distribution were observed [35].

**Temperature:** The microbial pathway is accomplished at a temperature of less than 100 °C [49].

**Pressure:** Nanoparticles morphology is greatly affected by the applied pressure on solution media [47].

**Time:** It plays a vital role in synthesizing nanoparticles, which affects their quality. The formation of nanoparticles, i.e., Shrunk or expanded form, is highly dependent on time. For instance, variations in size can be seen from 40 to 90 nm as temperature conditions are regulated when the synthesis time is varied [16].

**Environmental factors:** Clusters are formed using the compounds in the surroundings as their substrates. The physical properties of nanoparticles are changed due to environmental conditions [19].

# 3.4 Nanoparticles Synthesized Using a Biological Process

Vetchinkina et al. [54] produced spherical silver nanoparticles by an *Azospirillum brasilense* strain. After 12 h of incubation, the observed size was 10–50 nm. The fabricated silver nanoparticle's shape and size were diverse and represented by regular and irregular spheres. In a similar way, endophytic fungi, notably Penicillium sp.

isolated from Curcuma longa, have been used to create silver nanoparticles. The average size of the synthesized nanoparticles was 25 nm. These had spherical shapes and antibacterial properties [42]. *Streptacidiphilus griseoplanus* species produced silver nanoparticles with an average size of 22 nm after 96–98 h of incubation [55]. [53] synthesized silicon nanoparticles using biological synthesis and sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>), which led to nanoparticles. [37] reported nanoparticles with effective catalytic activity sizes ranging from 20 to 30 nm and quasi-spherical shaped. Stable Fe<sub>3</sub>O<sub>4</sub> nanoparticles of 60–80 nm size were synthesized by an extracellular mechanism, which was explained by Ghani et al. [14]. Fatemi et al. [11] reported stable spherical-shaped Fe<sub>3</sub>O<sub>4</sub> nanoparticles produced from *B*. cereus *HMH1* strain, with an average size of 23 nm. A gram-negative bacterium named *Pseudomonas denitrificans* used the denitrification process to release NADH-dependent enzymes, i.e., nitrate reductase. This process led to the size of 15–20 nm at a p<sup>H</sup> 3 and an optimum temperature of 37° [39].

#### 4 Biosurfactant-Mediated Nanoparticle Synthesis

Two major problems associated with the biological synthesis of nanoparticles are (a) microbes produce nanoparticles at a slower rate than with reducing agents, and (b) biological synthesis has a more prolonged reduction time and complex downstream process. Because of rising interest in synthesizing biologically mediated nanoparticles, biosurfactants are gaining importance because they can be used as reducing agents, capping agents for metallic nanoparticles, and stabilizers. Accordingly, they can be used as a greener alternative for nanoparticle synthesis [36].

Typically, nanoparticle production is attained by three methods: (a) physical, (b) chemical, and (c) biological. Traditionally, nanoparticles are synthesized by two approaches, viz., top-down and bottom-up. The physical methods for synthesis include high-energy ball milling, inert gas condensation (IGC), physical vapor deposition (PVD), laser pyrolysis, electrospraying, and melt mixing. The chemical methods include sol–gel, microemulsion, hydrothermal, polyol, chemical vapor deposition, and wet-chemical methods. The physical and chemical processes are condescending for attaining stable nanostructures of uniform size but not for long durations. By keeping in mind these limitations, eco-friendly methods come into the picture, which are clean, non-toxic, and cheap [46]. The microemulsion method is considered the most promising because it is thermodynamically stable and optically transparent. This method stabilizes isotropic dispersions of aqueous and hydrocarbon liquids by an interfacial film of surfactant molecules. Since it is an isotropic mixture that consists of three components:

- (a) Polar phase (usually water)—about 45% component,
- (b) Nonpolar phase (usually oil)—about 45% component, and

#### (c) Surfactant—about 10%

The amphiphilic surfactant molecules (non-ionic, anionic, cationic, and zwitter ion) act as an emulsifier and stabilize the microemulsion droplets. The microemulsion system consists of droplets of three types: water-in-oil (w/o), oil-in-water (o/w), and bi-continuous microemulsions based on the category of biosurfactant spent. Of all these three, the water in oil reverse micellar system has gained importance for the synthesis of nanoparticles. The microemulsion method relays on: how much water is available in the system, the amount of biosurfactant, the presence of cosurfactants, and the concentration of reagents [21]. This approach has produced core nanoparticles such as metals, semiconductors, and shell composites. In order to obtain spherical nanoparticles, water-in-oil emulsion systems are well-known mediated processes. In this microemulsion technique, the chemical surfactant can be replaced by a biosurfactant, which acts as a reducing agent. Biosurfactant has a high affinity for metallic nanoparticles, which makes them form a micelle-like aggregate on the surface of nanoparticles and thus promote stabilization [51].

In this method, each droplet behaves as a micro-reactor in the microemulsion system and has water-soluble biomolecules. By increasing the concentration of biosurfactant, there is a decrease in particle size, which causes a reduction in droplet size. This behavior makes nanoparticles stable and uniform for more extended periods. The biosurfactant functions to get adsorbed onto nanoparticles, preventing aggregation and stabilizing the nanoparticles. The type of biosurfactant and coating on the adsorbed layer influences the mechanism of biosurfactant adsorption [5]. The water-to-surfactant molar ratio ( $\omega$ ) dissolved in the microemulsion helps control nanoparticle size and morphology. Biosurfactant gets adsorbed on the particle surface, preventing the particles from forming aggregates. Controllable parameters in this technique are the water-to-surfactant molar ratio, the type of continuous oil phase, the reducing agent and its concentration, and the type and concentration of biosurfactant [45].

Ohadi et al. [27] produced lipopeptide biosurfactant using Acinetobacter junii B6 strain and synthesized gold nanoparticles, using biosurfactant as a reducing agent. FTIR analysis revealed lipopeptides could attract nanoparticles through the electrostatic attraction of negatively charged COO-groups. These lipopeptides can change the surface properties of nanoparticles and can stabilize them. Singh et al. [44] formulated cadmium sulfide quantum dots of 2.5-4 nm by utilizing waste tea leaves as a source of biosurfactants. FTIR confirmed phytochemicals such as minerals, amino acids, polyphenols, and vitamins in the synthesis and stabilization of quantum dots. Similarly, Bezza et al. [2] produced silver nanoparticles using a lipopeptide biosurfactant by chemical reduction. Adsorbed lipopeptides provide colloidal stability to the nanoparticles during synthesis and sustain from electrostatic stabilization. Prakash [29] synthesized nickel oxide nanorods using the water-in-oil emulsion technique. The nanorods were found to be approximately 22 nm in diameter and 150-250 nm in length. He used biosurfactant dispersed in *n*-heptane hydrocarbon phase. Reddy et al. [34] used anionic biosurfactant surfactin for the synthesis of gold nanoparticles. Lipopeptide surfactin is used to stabilize the gold nanoparticles in aqueous

solution. At room temperature and pH 7, nanoparticles with uniform shape and size of 528–566 nm were obtained. The structural changes in surfactin which stabilized gold nanoparticles mainly caused by differing proton concentrations.

# **5** Applications of Nanoparticles

Compared with traditional physicochemical methods for the remediation of contaminants, bioremediation is gaining importance because of its eco-friendly nature and economic attributes. For assistance, nanoparticles can be used directly to remove organic contaminants through adsorption or chemical modification. It can be used as a promotor in microbial remediation of contaminants by enhancing microbial growth, immobilizing the remediating agents, or inducing the production of remediating microbial enzymes. Besides, nanoparticles induce enhanced production of biosurfactants in microorganisms and also contribute to improved solubility of hydrophobic hydrocarbons, thereby creating a conducive environment for microbial degradation of these compounds in the background [23].

Recent research findings established the reaction of biosurfactants on hydrocarbon biodegradation by enhancing microbial availability to insoluble substrates and thus improving their biodegradation. Biosurfactants can increase bioremediation by two mechanisms. Firstly, by increasing the substrate bioavailability for microorganisms, the other involves interaction with the cell surface. Polycyclic aromatic hydrocarbons (PAHs) are dangerous toxic contaminants and are considered significant pollutants because most of them are carcinogenic and mutagenic. Parthipan et al. [30] degraded mixed poly aromatic hydrocarbons by biosurfactant produced from Bacillus subtilis A1. The biodegradation was increased by adding the iron nanoparticles resulting in 85% degradation efficiency. Silva et al. [41] simulated a bioremediation process in sea and samples. In two cases, oil degradation rates were higher than 90% because of the presence of biosurfactants. El-Sheshtawy et al. [9] degraded divergent polyaromatics with the help of biosurfactants. The biodegradation percentage of polyaromatics increased with the help of two distinct types of nanoparticles (zinc and iron). The biosurfactant was produced using *Pseudomonas xanthomarina KMM* 1447 and Pseudomonas stutzeri ATCC 17,588 strains. Ojha et al. [28] explained the yeast-mediated bioremediation and optimization of the whole process using the response surface methodology. Mu et al. [26] used *Bacillus cereus* strain, a poly aromatic hydrocarbons degrading bacteria. The strain used aromatic compounds as substrates and removed the oil contamination with the help of graphene oxide quantum dots.

Dyes are typically referred to as organic pollutants, which cause water and soil pollution and are hazardous to live entities. Wastewater coming from industries under uncontrolled conditions accompanies substantial environmental distress. Dyes possess a color that impedes the penetration of light in water [8]. So, dye wastewater must be treated before it is discharged. However, there is a mechanism for organic pollutant removal, in which the wastes are converted from one form

to another again and again with the help of microbes. This process is considered bioaugmentation, and the microbes act as bioremediators. In the textile industries, malachite green dye is a primary dye used to impart color to cotton, wool, jute, and leather. Hence, the removal of organic contamination is necessary for environmental safety. To achieve that, Sharma et al. [38] explained the decolorization of malachite green dye  $[C_{23}H_{25}CIN_2]$  using iron nanoparticles that are synthesized using an extracellular polymeric substance (EPS) which exhibited biosurfactant activity. The EPS was produced by the bacterium *Alcaligenes sp.* Hazra et al. [52] synthesized zinc sulfide nanoparticles using a biosurfactant from the *Pseudomonas* aeruginosa BS01 strain. Biosurfactant-capped zinc sulfide nanoparticles showed efficiency in textile dye degradation. Kumar et al. [22] demonstrated the methylene blue dye removal using magnesium oxide nanoparticles prepared using clove, i.e., Syzygium aromaticum extract. 90% removal was achieved using magnesium oxide nanoparticles. Bhosale et al. [4] synthesized iron nanoparticles using glycolipid biosurfactant. Rhamnolipid was produced by *Pseudomonas aeruginosa* ATCC 9027 for dye removal from wastewater.

On the other hand, bioremediation and electrokinetic remediation combination can remediate organic contaminants in soil when combined with biosurfactants, nanoparticles, and oxidizing chemicals. Electrokinetics can be combined with in situ chemical oxidation, bioremediation, and phytoremediation, to have a combined effect on the removal of organic contaminants in soil [6]. Prakash et al. [32] analyzed the effect of bioremediation and electrokinetic remediation with the help of *Bacillus* subtilis *AS2*, *Bacillus licheniformis AS3*, and *Bacillus velezensis AS4* strains. Biodegradation of crude oil was found to be 88, 92, and 97% for strains AS2, AS3, and AS4, with the optimum temperature of 37 °C and p<sup>H</sup> 7. Using biosurfactants in electrokinetic remediation enhanced the biodegradation rate up to 92%.

# 6 Conclusion

Many microbial surfactants have been extensively investigated in the last decade, and their potential in the bioremediation field has been highlighted. However, commercialization is still an issue of concern because of primary treatments (filtration, extraction, drying, ball milling) for low-cost substrate, down-streaming process, and purification of biosurfactants. The industrial production of nanoparticles with the help of biosurfactant-mediated synthesis is still in the early stages and needs to be improved a lot. Innovative research needs to be done to minimize production costs and optimize the production process. Biomolecules are becoming leading eco-friendly products with increasing demand because of their potential in bioremediation, heavy metal removal, wastewater treatment, and dye removal. To conclude, there is a promising future for the microbial synthesis of metal nanoparticles and applications compared to chemically synthesized nanoparticles.

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# Palladium@Copper Tungstate: A Non-corrosive and Methanol Tolerant Electro-Catalyst Towards Oxygen Reduction Reaction



Rahul Rajan, Anagha Yatheendran, and N. Sandhyarani

# 1 Introduction

The development of an efficient cathode catalyst is one of the significant challenges in the production of a commercial fuel cell. Oxygen Reduction Reaction (ORR) is the cathode reaction in the fuel cells. Due to its quiescent kinetics, ORR is considered the rate-determining step in the overall response of a fuel cell [18]. Platinum supported over high surface area carbon (Pt/C) is the commercially used electrocatalyst for ORR. Depending on Pt, rare and precious metal as cathode catalyst adds to the cost of developing a commercial fuel cell. Extensive research has been going on to improve the catalytic activity of Pt. The use of support materials, primarily carbonbased nanomaterials like carbon black and carbon nanotube, has been reported to enhance the electro-catalytic activity by improving the stabilization and dispersion of catalysts [15]. Enhanced ORR performance has also been reported for several Pt-based alloys [12] and Pt-M binary catalysts [2, 25]. Pt single-atom catalysts were also developed to ensure maximum utilization of the catalyst, thereby reducing the loading and cost [29].

Methanol tolerance of ORR catalysts is one of the pivotal factors affecting the efficiency of direct methanol fuel cells. Pt/C is highly prone to methanol oxidation reaction, decreasing the ORR performance as both oxygen and methanol compete for the active sites of the catalyst [6]. Thus, developing a low-cost, methanol-tolerant electrocatalyst for ORR is an area of prime interest. Among the materials that have been identified as promising replacements for Pt/C, transition metal oxides (TMO) and mixed transition metal oxides (MTMO) are attracting great interest. TMOs are low-cost materials present in abundance on the earth's surface. Moreover, the ability

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of TMOs to mix well into materials and the presence of multiple oxidation states make the usage of TMOs for catalytic activities highly advantageous. The catalytic activity of TMOs could be tuned to improve the performance by altering the morphology and composition through doping [23, 27]. TMOs generally have inherited lower conductivity, which limits their ORR applications. Developments in this context have been reported by improving extrinsic and intrinsic conductivity. Improvement in extrinsic conductivity of catalysts was achieved with proper support materials, while intrinsic conductivity was improved through doping, altering the structure and morphology of the catalyst [3, 8, 22]. Copper-based catalyst has also shown excellent ORR performance in alkaline medium. Several works have reported developing durable and highly selective copper oxide-based catalysts for ORR [17, 26]. Mixed transition metal oxides of several elements like Co, Cu, Mn, Ni, Fe, and Ag have also been reported [11, 13, 14, 21].

Herein, we report Pd@CuWO<sub>4</sub> as a promising electrocatalyst for ORR with excellent methanol tolerance and corrosion resistance. Enhanced ORR activity for the catalyst was achieved through the combination of highly ORR-active palladium with stable and methanol-tolerant CuWO<sub>4</sub>. The proper introduction of the support CuWO<sub>4</sub> resulted in enhanced methanol tolerance of Pd nanoparticles. Cerium was also used as a dopant; however, Pd is more effective in increasing the ORR activity. CuWO<sub>4</sub> was synthesized via a novel facile co-precipitation synthesis followed by calcination. Pd@CuWO<sub>4</sub> was synthesized via ex-situ treatment of palladium, and its catalytic activity towards oxygen reduction reaction was investigated. Pd incorporation significantly improved the ORR activity as compared to pristine CuWO<sub>4</sub>. Pd@CuWO<sub>4</sub> displayed higher durability and superior selectivity towards ORR in the presence of methanol than commercial Pt/C catalysts. High methanol tolerance and excellent stability make Pd@CuWO<sub>4</sub> a promising catalyst for DMFC applications.

## 2 Experimental Methods

## **3** Materials Used

Cupric nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O) and sodium tungstate dihydrate (Na<sub>2</sub>WO<sub>4</sub>.2H<sub>2</sub>O) were purchased from Qualigen Fine Chemicals and Sigma Aldrich, respectively. Palladium chloride (PdCl<sub>2</sub>) and sodium hydroxide were purchased from Spectrochem and Merck Life Science, respectively. Premium-grade ethanol (100%) was purchased from Hayman. Perchloric Acid (70%) used for electrochemical cleaning was purchased from Qualigen Fine Chemicals. All experiments were done using ultrapure water obtained using an ultra-filtration system (ELGA-PureLab Quest) with a measured resistivity above 18 M $\Omega$  cm. All chemicals purchased were used as such without any further cleaning procedures.

## 4 Synthesis

Synthesis of CuWO<sub>4</sub>: 25 mL 0.1 M Cu  $(NO_3)_2$  3H<sub>2</sub>O and 25 mL 0.2 M Na<sub>2</sub>WO<sub>4</sub>.2H<sub>2</sub>O solutions were prepared separately, and copper nitrate solution was added dropwise to sodium tungstate solution under vigorous stirring. A bluish-green suspension was obtained, and the mixture was stirred for 12 h. The precipitate was centrifuged, washed several times with DI water and ethanol, dried overnight at a temperature of 70 °C, and calcined at 500 °C for 5 h.

**Ex-situ synthesis of Pd@ CuWO**<sub>4</sub>: Pd was incorporated on CuWO<sub>4</sub> via a facile *ex-situ* method. Two sets of samples were synthesized with 1:1 and 1:2 ratios of PdCl<sub>2</sub> and CuWO<sub>4</sub>. To prepare a 1:1 sample, 40 mg of CuWO<sub>4</sub> was added to a 1 wt % solution of PdCl<sub>2</sub> (~40 mg) in ethanol. The mixture was stirred for 5 h. The obtained residue was washed, centrifuged several times with water, and dried at 120 °C. Similarly, a 1:2 sample was synthesized with 80 mg CuWO<sub>4</sub>.

In-situ synthesis of Pd incorporated CuWO<sub>4</sub>: Solution of 0.604 g Cu  $(NO_3)_2.3H_2O$  in 15 mL DI water and 30 mg PdCl<sub>2</sub> in 10 mL DI water were prepared separately. Palladium chloride solution was added dropwise to 25 mL 0.2 M Na<sub>2</sub>WO<sub>4</sub> 2H<sub>2</sub>O solution, followed by copper nitrate solution under vigorous stirring. The mixture was stirred for 12 h. The precipitate was centrifuged and washed several times with DI water and ethanol, then dried overnight at a temperature of 70 °C and calcined at 500 °C for 5 h.

### **5** Instrumentation

SEM images were analyzed with the Carl Zeiss Sigma model (RA-ZEI-001) operating at a maximum accelerating voltage of 15 kV. Elemental analysis of respective samples was performed using an Energy Dispersive X-ray spectrometer coupled with the SEM instrument. Raman spectra were recorded using Horiba LabRAM HR Evolution Confocal Raman Spectrometer (532 nm). Fourier Transform Infrared Spectroscopy (FTIR) was performed using a Perkin-Elmer Frontier FTIR spectrometer. The crystal structure was analyzed using a PANalytical X'Pert<sup>3</sup> diffractometer using a Cu K $\alpha$  radiation source.

### **6** Electrochemical Measurements

All electrochemical measurements were performed using an electrochemical workstation Multi Autolab M204 connected with a rotating disc electrode (RDE) system from Metrohm AG (Switzerland, Herisau). A standard three-electrode set-up was used for all electrochemical measurements with a silver-silver chloride (Ag/AgCl) electrode with 3 M KCl and Pt coiled wire as a reference and counter electrodes, respectively. Potentials were converted to RHE using the equation,  $E_{RHE} = E_{Ag/AgCl} + E_{Ag/AgCl}^0 + 0.059 pH$  where,  $E_{Ag/AgCl}^0 = 0.210V$ . A catalyst-coated glassy carbon rotating disc electrode (RDE) or rotating ring disc electrode (RRDE) was used as the working electrode. A catalyst ink having catalyst to DI water in a 1:1 ratio was prepared, and 10 µL of the ink was drop cast onto the GC electrode and dried at room temperature. A glassy carbon electrode with a polycrystalline Pt ring was employed for RRDE measurements. All electrochemical measurements were carried out in 0.1 M NaOH electrolyte solution. Before ORR measurements, the electrolyte was purged with high-quality O<sub>2</sub> (99.6%) for 1800s to ensure oxygen saturation.

#### 7 Results and Discussion

The morphology of the material was analyzed using FE- SEM. Figure 1a shows the SEM image of pristine CuWO<sub>4</sub>. SEM micrographs portray nanoparticles with an average size of 141 nm and non-uniform size distribution in the short range. Figure 1b shows the morphology of Pd@CuWO<sub>4</sub>. FE-SEM images show that Pd nanoparticles are embedded over CuWO<sub>4</sub>. The average size of these nanoparticles was measured as ~61.7 nm. Further examination of the surface composition of synthesized samples was performed with EDS analysis. Figure 1c confirms the presence of Cu, W, O, and Pd in Pd@CuWO<sub>4</sub>. Atomic concentrations of each element were tabulated and shown in the inset of EDS spectra. The elemental distribution of the sample was analyzed with the help of EDS mapping, and Fig. 1d portraits of the portion of the SEM image used for EDS mapping. Figure 1e-h shows the elemental mapping corresponding to Cu, O, Pd, and W. The uniform distribution of constituent elements Cu, W, and O suggests the formation of CuWO<sub>4</sub>. DLS measurements were performed to analyze the particle size distribution, shown in Fig. 1i, j for CuWO<sub>4</sub> and Pd@CuWO<sub>4</sub>, respectively. It indicates the polydisperse nature of the materials. CuWO<sub>4</sub> demonstrated a size range from 200 to 500 nm with an average size of 350 nm. Pd@CuWO<sub>4</sub> exhibited a size distribution between 90 and 330 nm with an average size of 200 nm. The higher size in DLS compared to SEM is due to the hydrodynamic radius measured in DLS.

The crystal structure of materials was examined using X-ray diffraction. Figure 2a shows XRD of pristine copper tungstate, Pd@CuWO<sub>4</sub>, and JCPDS data of CuWO<sub>4</sub>, Pd nanoparticle, and PdO. The diffraction pattern of both pristine CuWO<sub>4</sub> and Pd@CuWO<sub>4</sub> shows the characteristic peaks of triclinic CuWO<sub>4</sub> and matches with characteristic peaks of (010), (100), (-110), (011), (0-11), (020), (-101), (-111), (1-11), (1-11), (021) (0-21), (002), (120), (-130), (1-31) crystallographic planes (JCPDS no 01-088-0269) [9, 28]. The diffraction pattern also shows the characteristic peak of cubic palladium, and peaks at 40.4°, 46.8°, and 67.95° correspond to (111), (200), and (220) crystallographic planes of Pd nanoparticles (JCPDS no 03-065-2867) [24]. The intensity of peaks at corresponding regions enhanced after



**Fig. 1** FE-SEM images of **a** CuWO<sub>4</sub> and **b** Pd@CuWO<sub>4</sub>, **c** EDS spectrum of Pd@CuWO<sub>4</sub>, **d** the area of SEM image where elemental mapping was done, **e**–**h** elemental mapping of corresponding elements Cu, O, Pd, and W, respectively, **i** DLS of CuWO<sub>4</sub>, **j** DLS of Pd@CuWO<sub>4</sub>

the incorporation of Pd in  $CuWO_4$ , and it is indicated in the figure. A small extent of the formation of PdO was also visible from XRD (JCPDS no 01-088-2434) [5, 19].

FT-IR spectra of Pd@CuWO<sub>4</sub> and pristine CuWO<sub>4</sub> are shown in Fig. 2b. The broad peak at 3386  $\text{cm}^{-1}$  is attributed to the stretching vibrations of the O–H bond due to surface-adsorbed water molecules. The peak at 1638 cm<sup>-1</sup> is due to bending vibrations of W–O–H bonds [13]. The peaks at around 907 and 707  $cm^{-1}$  could be assigned to the symmetric stretching vibrations and antisymmetric stretching vibrations in the distorted octahedral  $[WO_6]$  clusters. The peak at 534 cm<sup>-1</sup> is attributed to the stretching and bending vibration of W-O bonds. A peak around 592 cm<sup>-1</sup> is due to the stretching of longer W– $O_3$  bonds. The peak at around 463 cm<sup>-1</sup> can be assigned to the stretching vibrations of Cu–O bonds [16, 20]. Raman spectra of the materials are illustrated in Fig. 2c. Fourteen active modes of CuWO<sub>4</sub> were identified from the spectra, which are located at 117, 142, 169, 181, 210, 272, 303, 338, 394, 471, 536, 731, 765, and 896 cm<sup>-1</sup>. Active modes of CuWO<sub>4</sub> spectra can be categorized into internal and external modes of WO<sub>6</sub> octahedra. Within the WO<sub>6</sub> octahedra, internal modes represent the vibrations of O atoms against W, and exterior modes represent the movement of WO<sub>6</sub> octahedra as rigid units against Cu [28]. Among the internal modes, peaks at 394, 536, 731, and 766 cm<sup>-1</sup> are antisymmetric vibrations of W–O bonds. Active modes in the region 360-129 cm<sup>-1</sup> are attributed to the external modes. These external modes include bending, translational, or rotational modes. A strong peak at 896 cm<sup>-1</sup> corresponds to symmetric stretching of W-O bonds [28]. The peak at 624  $\text{cm}^{-1}$  could be due to the Pd–O vibrations [7, 10] or Cu-O vibrations.



Fig. 2 a XRD pattern, b FT-IR spectra, and c Raman spectra of CuWO4 and Pd@CuWO4

**Electrochemical analysis** ORR performance analysis of samples was first examined using cyclic voltammetry (CV) measurements performed at a potential 0.1-1.1 V versus RHE at a scan rate of  $10 \text{ mVs}^{-1}$ . Figure 3a shows the cyclic voltammogram of Pd@CuWO<sub>4</sub> and pristine CuWO<sub>4</sub> in N<sub>2</sub>-saturated and O<sub>2</sub>-saturated atmospheres. A prominent peak of oxygen reduction reaction was observed at 0.63 V in the O<sub>2</sub>-rich condition for Pd@CuWO<sub>4</sub>, while it was absent in the N<sub>2</sub>-rich condition. Similarly, for pristine CuWO<sub>4</sub>, the peak was observed at 0.66 V in O<sub>2</sub>-rich conditions. These peaks due to oxygen reduction indicate the prominent electro-catalytic activity of CuWO<sub>4</sub> and Pd@CuWO<sub>4</sub>.

To further understand the ORR activity of the catalyst, linear sweep voltammetry (LSV) measurements were performed using a rotating disc electrode in 0.1 M NaOH. Figure 3b shows the LSV plots of CuWO<sub>4</sub> at different RPMs from zero to 2600. LSV of pristine Pd@CuWO<sub>4</sub> shown in Fig. 3c exhibited an onset potential ( $E^{\circ}$ ) and halfwave potential ( $E_{1/2}$ ) of 0.73 and 0.62 V, respectively. Pristine CuWO<sub>4</sub> synthesized in this work showed superior performance than the molten salts derived CuWO<sub>4</sub> nanoparticles [1]. Pd anchored CuWO<sub>4</sub> with different concentrations (1:1 and 1:2), and synthesis methods such as in-situ and ex-situ were synthesized to compare the ORR performance. A comparison of the electrochemical performance of samples having different Pd and CuWO<sub>4</sub> loadings and different synthesis procedures is shown in Fig. 3d. From the different modes of synthesis and compositions, it was identified that Pd@CuWO<sub>4</sub> synthesized through the ex-situ method with a 1:1



**Fig. 3** a Cyclic voltammogram of pristine CuWO<sub>4</sub> and Pd@CuWO<sub>4</sub> in O<sub>2</sub> and N<sub>2</sub> purged 0.1 M NaOH; linear sweep voltammogram of **b** pristine CuWO<sub>4</sub>, **c** ex-situ Pd@CuWO<sub>4</sub>, **d** Comparison of activities of pristine CuWO<sub>4</sub>, ex-situ derived Pd@CuWO<sub>4</sub>(1:1), (1:2) and in-situ derived Pd-incorporated CuWO<sub>4</sub> and ORR performance in 0.1 M H<sub>2</sub>SO<sub>4</sub> (inset), **e** HER before and after 25 CV cycles, and **f** comparison of OER performance of Pd@CuWO<sub>4</sub> and IrO<sub>2</sub>

 $PdCl_2$  to copper tungstate ratio results in better ORR performance. The ORR performance was analyzed in the acidic medium of 0.1 M  $H_2SO_{4,}$  and the respective data obtained are shown in the inset of Fig. 3d. The current density was very low, indicating that the catalyst is only suitable for ORR in an alkaline medium. The suitability of the catalyst for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) performance was also evaluated for Pd@CuWO\_4. The corresponding HER

and OER performances are shown in Fig. 3e, f. For the HER and OER measurements,  $0.5 \text{ M H}_2\text{SO}_4$  and 0.1 M KOH were used as the electrolyte medium. The catalyst was active toward HER however exhibited poor stability. After 25 continuous CV cycles, the catalyst showed a reduction in performance, and the lower stability suggests it is unsuitable for HER in an acidic medium. The OER performance was analyzed with the LSV technique in 0.1 M KOH saturated with N<sub>2</sub>. While comparing the performance with standard IrO<sub>2</sub>, the catalyst exhibited a lower current density and higher onset potential. Thus, the catalyst is promising for only ORR applications.

A comparison of ORR activities of pristine CuWO<sub>4</sub> and Pd@CuWO<sub>4</sub> is shown in Fig. 4a, and a comparison with state-of-the-art Pt/C is shown in the inset of Fig. 4a. Compared with pristine CuWO<sub>4</sub>, ex-situ derived Pd@CuWO<sub>4</sub> with PdCl<sub>2</sub> and CuWO<sub>4</sub> in a 1:1 ratio showed higher current density and more positive  $E_{1/2}$ . Figure 4b indicates the Tafel slope of  $Pd@CuWO_4$  and pristine CuWO<sub>4</sub>. Pristine CuWO<sub>4</sub> possesses a higher slope of -71.7 mV/dec as compared to -68.8 mV/dec of Pd@CuWO<sub>4</sub> which points to faster kinetics in the latter due to Pd incorporation. Upon comparison of the performance of the electrocatalysts with benchmark Pt/C, the standard catalyst possesses higher current density and more positive  $E_{1/2}$  and onset potentials. However, Pt/C is not tolerant towards methanol and prone to corrosion, while the Pd@CuWO<sub>4</sub> showed excellent methanol tolerance and durability. Methanol tolerance is one of the prime challenges in developing ORR catalysts. In DMFCs, there is a probability for methanol (fuel) to move from anode to cathode and hence compete for catalytic sites at the cathode. This methanol crossover would reduce the overall performance of fuel cells. Despite having prominent ORR activity, the major drawback of commercial Pt/C is its low methanol tolerance. Hence, investigating methanol tolerance is of prime importance while developing ORR catalysts.

Methanol tolerance of  $Pd@CuWO_4$  and Pt/C were examined using LSV at 1600 rpm, and results are illustrated in Fig. 4c, d. After adding 1 M methanol,  $Pd@CuWO_4$  showed commendable methanol tolerance with no shift in onset potential and a slight change in current density. While in the case of Pt/C addition of 1 M methanol resulted in a prominent methanol oxidation peak, indicating reduced ORR activity. Pt/C also depicted a negative shift in both onset potential and halfwave potential in the presence of methanol. Thus,  $Pd@CuWO_4$  derived through *ex-situ* synthesis has proved to be a highly methanol-tolerant ORR catalyst compared to Pt/C.

Another decisive factor in the efficient performance of a fuel cell catalyst is its electro-catalytic stability. An accelerated durability test (ADT) involving 2500 CV cycles in the potential range of 0.1 to 1 V vs. RHE was performed to analyze the durability of Pd@CuWO<sub>4</sub>. Figure 5a, b, c display the linear sweep voltammograms of pristine CuWO<sub>4</sub>, Pd@CuWO<sub>4</sub>, and Pt/C at 1600 RPM before and after 2500 continuous CV scans in 0.1 M NaOH. After 2500 cycles, LSV curves of Pd@CuWO<sub>4</sub> showed a minimal reduction of 0.121 mA/cm<sup>2</sup> in current density and a 6 mV shift in  $E_{1/2}$ . Pristine CuWO<sub>4</sub> was also depicting high stability in the ADT. The commercial catalyst Pt/C, on the other hand, showed a reduction of current density by 0.77 mA/cm<sup>2</sup> along with a negative shift of 31 mV in  $E_{1/2}$ . The enhanced methanol tolerance and durability of Pd@CuWO<sub>4</sub> depict it as a suitable catalyst for DMFC applications.



**Fig. 4** a Comparison of activities of pristine CuWO<sub>4</sub>, Pd@CuWO<sub>4</sub>, and Pt/C and **b** Tafel plot of pristine CuWO<sub>4</sub> and Pd@CuWO<sub>4</sub>; Linear Sweep voltammograms of **c** Pd@CuWO<sub>4</sub> and **d** Pt/C before and after addition of 1 M methanol at 1600 RPM

Electrochemical impedance spectroscopy (EIS) was carried out on both pristine CuWO<sub>4</sub> and Pd@CuWO<sub>4</sub> to understand the electron transfer rate in the material and its effect on ORR kinetics. EIS was performed at onset potential in 0.1 M NaOH solution at zero RPM for both pristine CuWO<sub>4</sub> and Pd@CuWO<sub>4</sub> in the frequency range of 25-0.1 Hz. Figure 5d depicts Nyquist plots for both materials, which were of a semi-circle shape. The diameter of this semi-circle is an indication of the charge transfer resistance between electrode and electrolyte interfaces. Pd@CuWO<sub>4</sub> has a smaller semi-circle indicating the low charge transfer resistance, which was also evident in ORR performance as it showed higher current density. The Randles circuit used for fitting the EIS curve is R(QR)(QR) and is shown as an inset in the figure. The Randle circuit consists of  $R_S$  in combination with two QR elements such as  $Q_1$ ,  $R_{1,}$  and  $Q_{2}$ ,  $R_{2}$ . In which  $R_{S}$  represents solution resistance, initial  $(R_{1}, Q_{1})$  elements represent the charge-transfer process through the electrode-electrolyte interface, and the second  $(R_2, Q_2)$  can be attributed to the mass transport process.  $R_1$  and  $R_2$ represent the charge transfer resistances, and Q1 and Q2 represent constant phase elements (CPE).

For a better understanding of the ORR catalytic pathway, RRDE measurements were carried out at 1600 RPM in  $O_2$ -saturated 0.1 M NaOH for CuWO<sub>4</sub> and



**Fig. 5** Linear sweep voltammograms of **a** pristine CuWO<sub>4</sub>, **b** Pd@CuWO<sub>4</sub>, and **c** Pt/C before and after 2500 continuous CV cycles@1600 RPM in 0.1 M NaOH and **d** Nyquist plots of CuWO<sub>4</sub> and Pd@CuWO<sub>4</sub> in 0.1 M NaOH

Pd@CuWO<sub>4</sub>. The disc and ring currents of CuWO<sub>4</sub> and Pd@CuWO<sub>4</sub> are illustrated in Fig. 6a, b, respectively. The ring current for Pd@CuWO<sub>4</sub> was lower, resulting in lower peroxide yields than CuWO<sub>4</sub>.

The number of electrons involved in the catalytic reduction of oxygen can be calculated from RRDE measurements using the following equation

number of electrons(n) = 4 \* 
$$I_D / \left( I_D + \frac{I_R}{N} \right)$$
 (1)

where  $I_D$ ,  $I_{R_1}$  and N correspond to the disc current, ring current, and electron collection efficiency of the Pt ring, respectively (N = 0.32). Figure 6c shows the number of electrons calculated at different potentials, and its values are 3.65 and 3.5 for Pd@CuWO<sub>4</sub> and pristine CuWO<sub>4</sub>, which is closer to the ideal four-electron transfer.

The percentage yield of H<sub>2</sub>O<sub>2</sub> was calculated using the equation

% of H<sub>2</sub>O<sub>2</sub> = 200 \* 
$$\frac{I_R}{N} / \left( I_D + \frac{I_R}{N} \right)$$
 (2)



**Fig. 6** RRDE voltammograms of pristine  $CuWO_4$  and  $Pd@CuWO_4$  in  $O_2$  saturated 0.1 M NaOH **a** disc current, **b** ring current, **c** number of electrons transferred involved during catalysis, and **d** percentage hydrogen peroxide yield

Figure 6d illustrates the calculated values of percentage peroxide yield for pristine CuWO<sub>4</sub> and Pd@CuWO<sub>4</sub>. An apparent reduction in peroxide yield from 26.3% to 17.36% after Pd introduction indicates an improved ORR performance of the catalyst. Even in the presence of  $H_2O_2$ , the catalyst exhibited excellent durability after continuous CV cycles of 2500, indicating that  $H_2O_2$  is not corroding the catalyst.

In this work,  $Pd@CuWO_4$  showed a 4e<sup>-</sup> pathway during the catalytic reaction, which could be attributed to the interactions between palladium nanoparticles and mixed transition metal oxide (CuWO<sub>4</sub>). It is reported in the literature that Pd nanoparticles on the surface will improve the intrinsic conductivity of base materials favoring faster electron transfer and reduced polarization of electrodes during the catalytic ORR [4]. The presence of Pd nanoparticles increases the electron transfer efficiency during the catalytic reaction, thereby improving the charge transfer kinetics evident from the EIS studies. Thus, the enhanced catalytic performance of Pd@CuWO<sub>4</sub> as compared to pristine CuWO<sub>4</sub> could be attributed to the strong interaction between mixed transition metal oxide and metal nanoparticles improving charge transfer efficiency.

# 8 Conclusion

In summary, we have synthesized and tested the CuWO<sub>4</sub> catalyst via a simple coprecipitation synthesis followed by ex-situ introduction of Pd nanoparticle for an efficient and stable ORR. The enhanced ORR activity of Pd@CuWO<sub>4</sub> could be attributed to the synergistic effect between metal nanoparticles and mixed transition metal oxides, improving the intrinsic conductivity and charge transfer kinetics. Pd@CuWO<sub>4</sub>, as an electrocatalyst, depicted higher methanol tolerance and superior stability in comparison with commercial state-of-the-art Pt/C, thus making it a promising cost-effective electrocatalyst for DMFC applications.

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# Synthesis of Graphene-Type Materials from Agricultural Residues



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## 1 Introduction

Graphene oxide (GO), composed of single atomic layered sp<sup>2</sup> carbon with functional oxygen groups, has attracted major attention due to its potential applications in various fields like electronics [1, 2], catalysis [3, 4], sensors [5], storage for energy and conversion [6, 7] and biology [4], etc. In the early stage of history, GO used to be prepared by single and multilayered graphene films through reduction process. Further studies revealed the substantial structure imperfection of graphene oxide, due to the defects in initial graphite and incompletion of the reducing process.

Many researchers have succeeded in synthesizing GO from commercially available graphite powder through Hummer's method and Modified Hummer's method [8, 9]. However, the production of the graphite powder in the industry is made through a series of steps on the raw materials such as petroleum coke, pitch coke, carbon black, etc. by powder preparation, shape forming, baking, and graphitization. After grounding the raw materials to different screen sizes, they are shaped with binders through techniques such as isostatic pressing, die molding, etc. The baking and graphitization steps require high temperatures of 1000–1200 °C and 2500–3000 °C, respectively [10, 11]. This makes the overall process energy intensive, thus increasing the price of graphite, as high as 194 INR per g, as quoted by Sigma Aldrich, India [12]. Synthesizing GO from agricultural residues could be an alternative cost-effective method and at the same time solving the problem of environmental deterioration caused by burning of agricultural waste [13]. Biomass typically consists of carbon content between 45 and 50%. The sequestration of carbon from other chemical elements is accomplished by thermochemical treatments, such

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as pyrolysis, hydrothermal carbonization (HTC), or a combination of both processes [14, 15]. The first attempt to synthesize GO from rice straw-derived graphite using conventional Hummer's method was reported by Goswami in [16]. Supriyanto et al. in [17], reported the conversion of graphite obtained from different Indonesian biomass such as coconut shell, rice husk, and bagasse. Hummer's method is applied to convert graphite to GO [17]. Conventional Hummer's method needs an excessive quantity of chemicals such as NaNO<sub>3</sub>, KMnO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub>, thus increasing the cost and contributing to environmental deterioration due to the release of NO<sub>x</sub> gases.

Other than this few papers on several works have reported on the application of transition metal (Ni, Co, and Fe) nitrates for the preparation of graphite from agricultural residues. In this method, the biomass goes through an intermediate metal carbide formation step at a moderate temperature (500–1400 °C). Hence, it could be considered as a cost-effective method [10, 16, 18, 19]. On the other hand, the use of ferrocene for conversion of agricultural residues to graphene-like material at 300 °C has been reported. Biomass is mixed with ferrocene and directly placed in a muffle furnace at 300 °C under atmospheric conditions. Ferrocene exceeds its boiling point at 250 °C, which allows it to interact with the carbon matrix of biomass and induce transformations via secondary reactions. Ferrocene transforms carbon matrix by donating an electron. This produces ferrocenium ions, which take part in both hole and electron catalysis. The combination of these reactions leads to the formation of graphene-like structures [20, 21].

Herein, we report the synthesis of graphite powder from sugarcane bagasse, wheat straw by ferrocene and catalytic graphitization using nickel nitrate and iron nitrate catalyst and then using improved Hummer's method to convert graphite powder to GO [8, 22]. The use of improved Hummer's method not only gets us rid of the excessive amount of chemicals being used, thus increasing the cost, but also ensures the eco-friendly production of GO.

#### 2 Experiment and Methods

## 2.1 Materials and Reagents

*Biomass (Sugarcane Bagasse)* was obtained from local shops. *Nickel nitrate* hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O) (99.99%, Qualikems Fine Chem. Pvt. Ltd, Vadodara, India, CAS No. 13138–45-9 13,478-00-7). *Ferrocene* (98% Sigma Aldrich, CAS No 102-54-5) *Iron nitrate* nonahydrate (98%, Avra, CAS No 7782-61-8). HCl (37%, Merck & Co, CAS No 7647-01-0). Isopropanol (99.8%, Merck & Co, CAS No 67-63-0). Potassium permanganate (99%, Finar, CAS No 7722-64-7). H<sub>2</sub>SO<sub>4</sub> (98%, Finar, CAS No 7664-93-9). Hydrogen Peroxide (30%, Merck & Co, CAS No. 7722-84-1).

## 2.2 Preparation of Graphite

Wheat straw (WS) was rinsed with water to remove dust and impurities and left to dry at room temperature for 72 h. The dried residue was then ball-milled to a size below 150  $\mu$ m. Then the ground WS is mixed with ferrocene manually in two different ratios 5:1 and 5:2. Other than simple manual mixing, wet impregnation with toluene was carried out. Here ferrocene was first dissolved in toluene to which WS is mixed. The sample is then placed in a vacuum oven at 60 °C for 1 h and dried completely afterwards in a hot air oven.

All the samples (manually mixed and wet impregnated) are then carbonized in a horizontal tube furnace at 300 °C for certain hold times. The experiment trials, sample names, and corresponding experiment conditions for ferrocene method on wheat straw are displayed in Table 1.

In the second method, iron nitrate (IN) and nickel nitrate (NN) salts were used for catalytic graphitization of wheat straw (WS) and sugarcane bagasse (SCB). Solutions of 2 M Fe (NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O and 2 M Ni (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O in isopropanol were prepared to which 10 g of biomass is added. The samples were then impregnated in a vacuum oven at 60 °C for 2 h. The impregnated samples were dried overnight in a hot air oven at 80 °C. The dried samples were pyrolyzed in a muffle furnace under N<sub>2</sub> flow of 20 ml/min, heated to a temperature of 900 °C and 1200 °C. The maximum temperature was held for 2 h. The samples were then allowed to cool and bring down to room temperature and washed with 1 M HCl (37%) under stirring for 2 h, to remove the residual metal. This was followed by washing with distilled water until the pH become neutral. The samples were then dried in a hot air oven at 80 °C for 2 h to obtain a black powder (graphite) [11, 13]. The experiment trials for catalytic graphitization are displayed in Table 2.

Trials	Sample name	Impregnation ratio (Wheat Straw: Ferrocene (mg))	Impregnation method	Carbonization temperature (°C)/Hold time (min)
T-1	FM-1	500:100	Manual mixing	300/10
T-2	FM-2	500:200	Manual mixing	300/10
T-3	FM-3	500:100	Manual mixing	300/15
T-4	FM-4	500:200	Manual mixing	300/15
T-5	FM-5	500:200	Wet impregnation	300/15

 $\label{eq:table_$ 

Trial	Sample name	Agricultural residue (AR)	Catalyst	Impregnation ratio (AR: catalyst (gm))	Graphitization temperature (°C)/Hold time (hr)
T-1	CG-1	Sugarcane bagasse	Iron nitrate	10:32	900/2
T-2	CG-2	Sugarcane bagasse	Nickel nitrate	10:23	900/2
T-3	CG-3	Wheat straw	Iron nitrate	10:32	900/2
T-4	CG-4	Wheat straw	Nickel nitrate	10:23	900/2
T-5	CG-5	Sugarcane bagasse	Iron nitrate	10:32	1200/2
T-6	CG-6	Sugarcane bagasse	Nickel nitrate	10:23	1200/2
T-7	CG-7	Wheat straw	Iron nitrate	10:32	1200/2
T-8	CG-8	Wheat straw	Nickel nitrate	10:23	1200/2

 Table 2
 Trials, sample names, and corresponding experiment conditions for catalytic graphitization using wet impregnation method

# 2.3 Preparation of GO

The following paragraph describes, in detail, the preparation method for graphene oxide from graphite obtained from biomass. GO powder was prepared using improved Hummer's method as discussed by Chen et al. [8, 22, 23]. 1 g of prepared graphite powder was taken in a 500 mL beaker and 23 mL H<sub>2</sub>SO<sub>4</sub> (98%) was added slowly and stirred for 3 h at room temperature. The beaker was put in an ice bath and 3 g KMnO<sub>4</sub> powder was added slowly under continuous stirring. Then the beaker was removed, placed on a hot plate at 40 °C and continued stirring for 15 h. After 15 h, 30 mL water was added to this and the resultant solution (dark brown) was heated to 95°C while stirring was continued for 15 min more. To this, 100 mL water was added followed by slow drop-wise addition of H<sub>2</sub>O<sub>2</sub> (30%), till the color of the solution changed from dark brown to yellow. The suspended powder was separated by centrifuging at 4000 RPM for 10 min and washed thoroughly with 5% HCl followed by deionized (DI) water till the pH of the effluent became neutral. The resulting slurry was air-dried to obtain brownish graphite oxide powder, which contains some unreacted graphite. This powder is diluted (1 mg/mL) in distilled water to make graphite oxide dispersion. This dispersion was stirred overnight followed by ultrasonication about 1 h for exfoliation to GO, while unreacted graphite powder settled down at the bottom of the beaker. The GO suspension was separated from graphite and centrifuged at 6000 rotations per minute (RPM) for 15 min. The concentrated slurry was freeze-dried for 24 h to obtain GO powder.

### 2.4 Characterizations

Powder X-ray diffraction (Rigaku miniflex II, Cu-K $\alpha$  ( $\lambda = 1.54$  Å); 30 kV and 15 mA) technique is used for identifying phase composition of graphite and GO. Samples are scanned 2 theta (2 $\Theta$ ) range of 5–15° for GO and 15–35° for graphite at a rate 0.5°/min.

FTIR (Perkin Elmer Frontier<sup>TM</sup>) data are procured by using KBr pellet procedure within the wavenumber range of 4000–1000 cm<sup>-1</sup> and the data averaged over 10 scans.

Raman spectroscopy (Horiba LabRam HR spectrometer, Model 171) data are acquired by using 532 nm Argon laser with scanning range 1200-1800 cm<sup>-1</sup>.

Powder morphology and elemental analysis were performed using a FESEM (Nova Nano FE-SEM 450 (FEI), Oxford Instruments, UK) coupled with an X-ray energy dispersive spectrometer (EDX). Prior to the analysis, samples were sputter coated with platinum grid.

TEM investigation was performed in a transmission electron microscope JEOL JEM-2100F model furnished with an EDS from JEOL. Pictures of GO were procured utilizing 200 kV accelerating voltage. Samples were analyzed by placing a droplet of diluted GO suspension onto the TEM framework.

# **3** Results

## 3.1 XRD

X-ray diffraction spectrum of graphite (PDF#1100003) and GO [24] is shown in Fig. 1a, b, respectively. Here, we chose to explain FM-1 and FM-2 samples out of five trial samples (Table 1), from the ferrocene method, will understand the effect of composition along with reaction conditions. CG-3 and CG-5 samples chosen out of eight trail samples (Table 2) from the catalytic graphitization method.

In Fig. 1a, iron nitrate-impregnated samples are shown a strong graphitic peak at  $26^{\circ}$  and a weak graphitic peak (or amorphous carbon) at  $22^{\circ}$ . But, nickel nitrate samples are shown reverse trend, which indicates the improper graphitization [25]. Negligible peak shift was noticed for FM-1 and FM-4 samples; however, CG-3 and CG-5 samples noticed peak shift slightly lower 2-theta position compared with FM-1 and FM-4 samples. Graphene oxide is prepared by using improved Hummer's method. Graphite peak could not be detected for the samples prepared using sugarcane bagasse (SCB) by ferrocene method, and this could be due to poor carbonization. But graphite peak was well detected in samples prepared wheat straw. GO peak could not detected for all samples prepared by ferrocene method, this could be graphite prepared at low temperature (300 °C). But, GO noticed 2-theta position around  $11^{\circ}$  for all samples prepared by catalytic graphitization method. This peak corresponds to (001) plane of GO. The interlayer spacing (d), calculated from



Fig. 1 XRD spectra for (a) Graphite and (b) Graphene oxide

*Bragg's law*  $(d = \lambda / 2 \sin \theta)$ , for graphite and GO powders was found to be 12.73 and 52.01 nm, respectively.

#### 3.2 FTIR

FTIR spectra show the presence of serval bands in graphite (Fig. 2(a)) and graphene oxide (Fig. 2(b)). The graphite samples reveal the peaks at 3605, 3384, 1079, and 1602 cm<sup>-1</sup> indicating the presence of carboxyl(–COOH), hydroxyl(–OH), alkoxy(–C–O) oxygen functional groups and (C = C) stretching of aromatic rings of graphite, respectively. In addition to these four bands, the GO samples show one peak at around 1730 cm<sup>-1</sup> corresponds to epoxy(–C = O) group. This confirmed the addition of oxygen functional groups upon oxidation of graphene oxide to GO [26, 27].



Fig. 2 FTIR spectra for (a) Graphite and (b) Graphene oxide

#### 3.3 Raman

The Raman spectroscopy results for ferrocene samples (Trial 1–5) are given in Fig. 3a. The plots are in correspondence with Trials 1–5. Trials 1 and 3 show two peaks around 1580 and 1290  $\text{cm}^{-1}$ , which corresponds to the G-band and D-band.

The G band indicates the presence of graphitic structure and D band indicates the defects present in carbon lattice. The G-band at  $1580 \text{ cm}^{-1}$  for graphite occurs due to in-plane vibrations of graphite lattice [27]. Trial 1, 2, 3, 4 all showed G band peaks but it was most intense in Trial 1. Trial 5, i.e., wet impregnated sample showed none of the peaks though. Raman spectra of graphite and GO as obtained and after deconvolution are shown in Fig. 3b, c.

The peaks at around 1353, 1586, and 1592 cm<sup>-1</sup> correspond to D-band and G-band in graphite and GO [28]. The G-band at 1586 cm<sup>-1</sup> for graphite and at 1592 cm<sup>-1</sup> for GO occurs due to in-plane vibrations of graphite lattice [9, 29]. Deconvolution of the Raman spectra was implemented for correcting the baseline and obtaining accurate values for  $I_D/I_G$ . The analysis was performed in terms of the intensity ratio  $I_D/I_G$  calculation and Raman shift measurement. A higher Raman shift from 1586 to 1592 cm<sup>-1</sup> for GO indicates an efficient oxidation of graphite. An increase in the intensity ratio from 0.256 to 0.827 in case of GO could be attributed to the increased defects in between the layers of graphite, owing to the introduction of oxygen and sulfur functional groups [29, 30].



Fig. 3 Raman Spectroscopy results (a) *Ferrocene* method; Catalytic graphitization method of graphite powder (b) CG-3; CG-5; and (c) Deconvoluted RAMAN Spectra of graphite powder

## 3.4 FESEM with EDX

Figure 4a, b, c depict the FESEM image with EDX spectrum for sugarcane bagasse, graphite, and GO, respectively. The EDX analysis shows an increase in oxygen and Sulphur content upon oxidation to GO. A closely associated structure appears on the GO for different mass fractions, which demonstrates that the exfoliated GO flakes can be seen in Fig. 4c.

## 3.5 TEM

Figure 4d shows the TEM image with EDX spectrum for GO obtained from bagasse. The image depicts a transparent sheet with a thickness of nanometer range. The folds in the image can be attributed to the overlapping of multiple sheets; however, the



**Fig. 4** FESEM image and EDX Spectra of (a) *Sugarcane Bagasse* (b) Graphite (c) GO (d) TEM image + EDX Spectra of GO

transparency of the region confirms that GO exists in a single or a very few layers [31, 32].

Single and double lamellar layer structure GO sheets were observed in the TEM image, while the size of the lamellar structure was about 1  $\mu$ m, and slight wrinkles were observed [31]. Furthermore, owing to the oxidation of graphite oxide during ultra-sonication, oxygen-containing functional groups were introduced into the surface of GO, and the orderly structure of the layers might be broken, which

would weaken the intra-molecular interactions and enhance the dispersion stability [32].

## 4 Discussion

## 4.1 Structural Characterization of Graphene Oxide

J. Chen et al. demonstrated the preparation of GO through improved hummers method, and, in this work, all the XRD profiles are exhibiting a sharp peak around 26° (JCPDS #1100003), which corresponds to the lattice plane (002) of graphite [23]. R. Tamilselvi et al., illustrated the ferrocene method using biomass mixed with ferrocene catalyst in muffle furnace at 300 °C [21, 33]. In this work, the sample prepared from ferrocene-derived graphite (FM-1) gave no peak thus indicating it could not be oxidized to graphene oxide. But through catalytic graphitization, a sharp peak around 11.4° was observed for the graphite sample prepared from CG-3 and broad peak at 10.6° was observed for the graphite sample prepared from CG-5 which is in better agreement with the J. Chen et al., improved Hummers method results, and S. Ding et al. work on preparation and adsorption property of graphene oxide [8, 22]. B. Kartick et al. discussed the interlayer spacing (d) increase happened because of the addition of oxygen functional groups and water molecules in between the graphite layers, and E. Mahmoudi et al. found that was connected to the graphite's interlayer spacing would vanish as a result of the lattice distortion that happened during the oxidation phase. The interplanar distance of graphene oxide is also increased, i.e., the miller indices (001) for GO and results were found to be similar with literatures [29, 30]. The presentation of C = C groups showed in FTIR analysis that even graphite had been oxidized into GO, which is in compact with J. Song et al. synthesis of GO. The main structure of layer graphite was still retained. The results of XRD and FTIR synthesis both further demonstrated the successful synthesis of GO powder [31].

## 4.2 Raman Analysis of Graphite and Graphene Oxide

G. Wu et al. explained that the two main bands in the graphite spectrum are known as the G-band at ~1582 cm<sup>-1</sup> and the 2D-band at ~2685 cm<sup>-1</sup>. A third band known as the D-band at ~1350 cm<sup>-1</sup> is also worth some discussion, although it is usually very weak in graphite. Now we will take a closer look at each of these bands. The D-band is connected to the motion of the carbon sp<sup>2</sup> atom pairs stretching their bonds in plane, which is attributed to the defects and disorders in the hexagonal graphitic layers. The G-band is concerned with the breathing modes of rings [32].

## 4.3 Morphological Characterization of GO

N. M. S. Hidayah et al. depicted the SEM images of graphene oxide, on the surface, the flakes can be observed to be wrinkled and stratified. Flakes indicate that the graphene layers were totally oxidized to GO, since their presence indicates this. In like manner, GO is observed to have a layered structure with bent corners, in contrast to graphite, which has a flaky structure and can be seen in Fig. 4c [26, 28].

Also, TEM image confirms the wrinkled sheet structure of GO, which possesses a lower energy state than an elastic structure, indicating the structural stability of GO [32]. In addition, the transparency indicates that the exfoliated GO exists in a single layer or a few layers, which is visible in Fig. 4d.

### 5 Conclusions

A typical graphite synthesis process from agricultural residue requires biomass to be treated with transition metal salts and carbonization temperatures in the range of 800–1200 °C. This process also requires an inert atmosphere, which further adds to the cost. The ferrocene method process seems to produce graphite at much lower temperature and without requiring any inert atmosphere. Various impregnation ratios and hold times were tried in the experiment. But all the samples showed similar graphitic peak in XRD at 26°. Thus, the impregnation ratio and hold time do not seem to be affecting the end product. The method of mixing (manual or wet impregnation) also does not affect the result of the process. Thus, it seems better to use 5:1 impregnation ratio of wheat straw to ferrocene and use manual mixing to keep the process simpler and cheaper. But the graphite obtained could not be oxidized to graphene oxide via improved Hummer's method.

Meanwhile, in the catalytic graphitization process, iron nitrate came out to be the superior catalyst compared to nickel nitrate at carbonization temperatures of 900, 1200 °C. The graphite obtained from CG-3 and CG-5 was successfully oxidized to graphene oxide via improved Hummer's method. Thus, an eco-friendly route of conversion of agricultural residue to a valuable nanomaterial is established.

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# Effect of Viscoelasticity on the Solidification and Melting of a Phase Change Material



Deepak Talan, Shyam Sunder Yadav, and Arkaprovo Ghosal

# **1** Introduction

The liquid–solid phase change process is ubiquitous in nature (formation of snow and ice, solidification of lava) as well as in industries (casting and welding of metals, preparation of dairy products by freezing). The solidification and melting of viscoelastic materials is particularly important for a number of industrial applications, namely, injection molding of polymers in plastic industries, Cao et al. [1], Liu et al. [2]; during polymer melt spinning of fibers, Ghosal et al. [3]; during the preparation of various items in food industries, Fischer and Windhab [3] etc. In this manuscript, we numerically investigate the effect of viscoelasticity on the solidification of a fluid inside a square shaped cavity. In the following, we briefly summarize the important previous works on the numerical simulation of the liquid–solid phase change process and on the simulation of viscoelastic flows.

The very first works on the liquid–solid phase change process are based on the enthalpy porosity method, a few important works on the technique are by Voller et al. [4], Brent et al. [5], Voller et al. [6], Swaminathan and Voller [7], etc. In this approach, the enthalpy of the fluid is divided into sensible part and latent part. The sensible part of enthalpy is solved in terms of temperature of the fluid subjected to the boundary conditions while the latent part is modeled as a source term. The liquid fraction and temperature of the fluid are updated in an iterative manner during each time step of the simulation process. The momentum conservation equation is solved

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in the whole domain with the fluid velocities enforced to very small values in the solid region with the help of Karman-Kozney relation [8, 9]. A comprehensive benchmark on these so-called fixed grid-based techniques has been published recently by König-Haagen et al. [10]. The enthalpy porosity method is now a classical technique, but work is still going on in this area due to the renewed interest in phase change materials for renewable energy storage. Adaptive re-meshing-based techniques are being developed for simulating the liquid–solid phase process [11].

The numerical simulation of viscoelastic flows has its own challenges, the solution process diverges for higher values of elasticity of the fluid. The phenomenon is so severe that it has been given the name of 'High Weissenberg number problem'. The log conformation approach by Fattal and Kupferman [12] seems to successfully tackle this problem. Fattal and Kupferman [13] used this approach to study time-dependent viscoelastic flows at high Weissenberg numbers. Figueiredo et al. [14] used a log conformation approach-based numerical formulation for investigating viscoelastic two-phase flows. Comminal et al. [15] used a stream-function and vorticity-based formulation along with the log conformation approach for simulating viscoelastic flows at high Weissenberg numbers. Recently, López-Herrera et al. [16] implemented the log conformation approach in the open-source simulation software called Basilisk flow solver [17]. The formulation has been tested on different viscoelastic single-and two-phase flows.

From this brief literature survey, we conclude that the enthalpy-porosity method and the log conformation approach are potent techniques, which can be used to accurately simulate the liquid–solid phase change process of viscoelastic fluids. In the current work, we simulate the phase change process of a viscoelastic fluid in a square-shaped cavity with the help of these techniques. As a reference, we consider the experimental and simulation-based works on the freezing and melting of water inside a square cavity by Kowalewski and Rebow [18, 19]. This paper is organized as follows: in Sect. 2, we present the equations governing the flow and phase change process of a viscoelastic fluid along with the numerical formulation; in Sect. 3, we present and discuss the various results obtained by us; finally, in Sect. 4, we conclude the current work.

## **2** Governing Equations and Numerical Formulation

The equations governing the non-isothermal flow of an incompressible, viscoelastic fluid with phase change are as follows:

$$\begin{aligned} \frac{\partial \vec{u_i}}{\partial x_i} &= 0\\ \frac{\partial \vec{u_i}}{\partial t} &+ \frac{\partial \left(\vec{u_j} \cdot \vec{u_i}\right)}{\partial x_i} = \frac{-1}{\rho} \frac{\partial p}{\partial x_i} + \frac{-1}{\rho} \frac{\partial}{\partial x_i} \left(\mu_s \frac{\partial u_i}{\partial x_j} + \mu_s \frac{\partial u_j}{\partial x_i}\right) + \frac{1}{\rho} F_i + \frac{1}{\rho} \nabla \cdot \tau_{p'} \\ \frac{\partial \rho c_p T}{\partial t} &+ \frac{\partial \left(\vec{u_j} \cdot \rho c_p T\right)}{\partial x_j} = \frac{\partial}{\partial x_j} \left(k \frac{\partial T}{\partial x_j}\right) - \frac{\partial \rho L f_l}{\partial t} - \frac{\partial \left(\vec{u_j} \cdot \rho L f_l\right)}{\partial x_j}. \end{aligned}$$

In the above equations,  $\rho$  is the density,  $\mu_s$  is the solvent viscosity,  $c_p$  is the specific heat, k is the thermal conductivity, L is the latent heat,  $u_i$  is a velocity component, p is pressure, T is temperature,  $f_l$  is the liquid fraction, and finally,  $\tau_p$  denotes the viscoelastic stresses in the uid.  $F_i$  represents the volumetric forces acting on the fluid, namely, the buoyant forces due to density difference which causes natural convection in the liquid phase and the drag force acting on the liquid due to porous media flow in the solid phase.

The buoyancy forces causing natural convection are modeled with the help of Boussinesq approximation giving

$$F_B = -\rho g \beta (T - T_{ref})$$

where  $\beta$  is the coefficient of volume expansion, and  $T_{ref}$  is the reference temperature. The flow in the solid region is handled with help of Karman Kozney relation giving the volumetric force on the fluid as follows

$$F_D = -C \frac{(1-\epsilon)^2}{\epsilon^3} \vec{u}_i = A \vec{u}_i$$

where *C* is a constant and  $\in$  is the local porosity. A large value is taken for the constant *C* such that it drives the fluid velocities to very small values in the region. The stresses  $\tau_p$  are calculated with the help of conformation tensor c,  $\tau_p = \frac{\mu_p}{\mu_R}(c-I)$ , the evolution equation for *c* based on the Oldroyd-B model is given by

$$\frac{\partial c}{\partial t} + \vec{v} \cdot \nabla c - c \cdot \nabla \vec{v} - \nabla \vec{v}^T \cdot c = -\frac{c - I}{\lambda_R}$$

In the above equations,  $\mu_p$  is the polymer viscosity and  $\lambda_R$  is the relaxation time of the fluid. Directly solving the above evolution equation for *c* is prone to the High Weissenberg number problem causing divergence at higher value of relaxation time  $\lambda_R$ . In the log conformation approach, the logarithm of the conformation tensor,  $\psi = logc$ , is evolved in time using the following equation.

$$\frac{\partial \Psi}{\partial t} + u \cdot \nabla \Psi = \Omega \cdot \Psi - \Psi \cdot \Omega + 2B + \frac{I - e^{-\Psi}}{\lambda_R}.$$

In the above equation,  $\Omega$  and *B* are obtained from the following decomposition of the transpose of the velocity gradient.

$$\nabla \vec{v}^T = \Omega + B + Nc^{-1}.$$

The governing equations, Eqs. 1–3, are solved with the help of finite volume method on Quadtree grids using the open source flow solver Basilisk [17]. The numerical formulation is second-order accurate in both space as well time. The convective terms in the different equations are discretized using second-order accurate scheme by Bell et al. [20]. The pressure velocity coupling for incompressible flows is discretized using the projection method, Popinet [21]. The log conformation approach by Fattal and Kupferman [13] is used for solving Eq. 7. Further details on the formulation can be seen in López-Herrera et al. [16]. The properties used for the fluid during the simulations are given in Table 1. The properties of the Newtonian fluid test case are taken from the test case studies in Kowalewski and Rebow [18, 19].

The computational domain for the problem is a square cavity as shown in Fig. 1 with side length equal to 0.0445 m. A temperature value of 283.15 K is enforced on the left wall of the domain while a value of 263.15 K is applied on the right wall.

The top and bottom wall of the domain are assumed insulated so zero heat flux condition is applied on these walls. The melting temperature of the fluid is assumed as 273.15 while the solidus and liquidus temperatures are respectively taken as 273.0 and 273.3 K. The higher temperature on the left wall drives the natural convection

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Phase	Density ρ	Viscoelasticity $\mu_s$	Viscoelasticity μp	Weissenberg numbers	Specific heat <i>cp</i>	Latent heat L	Thermal conductivity k
Liquid	999.8	0.001	0.001	1	4184.0	335e3	0.561
Solid	917.0	-	-	-	2093.0	335e3	2.22

 Table 1
 Physical properties of the phases used in the current work





0.0445 m

flow of the liquid while the lower temperature on the right wall promotes the solidification. A balance between these opposing effects is expected under steady-state conditions. The no-slip condition is applied on all the walls of the domain. Following assumptions are taken while solving for the phase change process in this paper: (i) The melting and solidification process is simulated in a two-dimensional domain, (ii) The thermal radiation effects are neglected, (iii) Laminar and incompressible flow is assumed, (iv) The viscous dissipation due to fluid viscosity is neglected, (v) The Boussinesq approximation is valid, (vi) The fluid thermophysical properties are assumed constant.

In the following section, we discuss the various results obtained by using the numerical formulation described above.

#### **3** Results and Discussion

In this section, we discuss the simulation-based results on the distribution of various physical quantities inside the domain at time t = 160.5 s after the start of simulation. It may be noted here that these results do not represent the steady state distribution of various quantities.

Figure 2 shows the temperature distribution inside the cavity at time t = 160.5 s. As can be noted from the figure, the hot fluid rises up along the left wall and then turns right at the top wall causing high temperature in the regions. The lower temperature at the right wall causes a drop in the temperature in part of the domain, thus causing solidification.

The resulting velocity distribution is shown in Fig. 3 where a maximum velocity of 2.5 mm/s is reached in the domain near the left wall. The right black portion is the solidified material where the velocity value is very small ( $\sim 10^{-17}$  m/s). The colder



Fig. 2 Contours of temperature (Kelvin) inside the domain at time t =160.5 s for the viscoelastic case fluid in contact with the solidified material slides down the domain resulting in a natural convection pattern.

The solidification profile is better shown in Fig. 4 where the liquid fraction is plotted. The solidified material near the right wall has a liquid fraction value of zero. The liquid–solid interface at the bottom of the domain is a little diffused due to the fact that the temperature lies between solidus and liquidus temperatures in that portion of the cavity.

Figures 5 and 7, respectively, show the distribution of viscoelastic stresses  $\tau_{p,xx}$ ,  $\tau_{p,xy}$ , and  $\tau_{p,yy}$  in the domain. In these figures, the contours are plotted on a logarithmic scale. It may be noted that higher values of viscoelastic stresses appear near the hot wall and the liquid–solid interface.

Among these stresses, the component  $\tau_{p,yy}$  has the highest magnitude of 0.02 N/m<sup>2</sup> near the hot wall, which is due to the stretching produced by the hot, rising fluid along the vertical direction. Also, worth noting is the fact that the central portion





Fig. 4 Contours of liquid fraction inside the domain at time t = 160.5 s for the viscoelastic case



of the cavity is almost free of the viscoelastic stresses. This is due to the very small velocity in this region as can be seen in Fig. 3.

The liquid–solid interface position for the viscoelastic and Newtonian cases is shown in Fig. 8. It can be noted from the figure that a larger portion of the viscoelastic fluid has solidified compared to the Newtonian one at a time instant of 160.5 s. The reason for the faster solidification of the viscoelastic fluid can be attributed to the smaller velocity created in the viscoelastic fluid due to polymer viscosity and stresses. A viscoelastic fluid has extra viscosity due to the polymer part which imparts extra resistance to fluid flow for the same driving potential, that is, the temperature difference between the walls. The polymer elasticity affects the transient process dynamics on the time scales of the order of the relaxation time of the fluid. Even under steady flow conditions, part of the driving potential (the temperature difference) is utilized in creating elastic stresses in the fluid as it circulates inside the cavity. The net result is that the hot fluid from the hot wall is circulated at a lower rate, which







causes faster solidification due to low temperature of the right, cold wall. The velocity distribution for the Newtonian fluid is shown in Fig. 9.

Figure 9 shows the velocity distribution for the Newtonian fluid having same thermophysical properties as the viscoelastic one. It can be observed from the figure that a maximum velocity of 3.6 mm/s appears near the hot wall for the Newtonian fluid. This higher value of velocity is due to the fact that polymer viscosity and viscoelastic stresses are absent for this Newtonian fluid case causing higher velocity for the same driving temperature difference between the walls. These higher velocities carry hot fluid from the left wall to the liquid–solid interface causing a slower solidification. In the next section, we conclude the current work.

**Fig. 7** Contours of  $\tau_{p,yy}$ 

time t = 160.5 s for the viscoelastic case

 $(N/m^2)$  inside the domain at



Fig. 9 Contours of velocity (m/s) inside the domain at time t = 160.5 s for the Newtonian case

# 4 Conclusions

To summarize the current work, we performed numerical simulations of the natural convection-driven solidification process of a viscoelastic fluid inside a square cavity using the enthalpy porosity approach. We considered two different cases of the solidification process, one of which assumed viscoelastic fluid behavior while the other assumed Newtonian behavior. We observe that the viscoelastic properties, namely, polymer viscosity and the elastic stresses, promote solidification inside the cavity. Compared to the Newtonian case, the viscoelastic fluid solidifies at a faster rate for a given temperature difference between the hot and cold walls. This can be partly attributed to the increased viscosity of the viscoelastic fluid due to the polymer part and partly due to the elastic stresses in the fluid. We also observed that the viscoelastic stresses are dominant near the hot wall and the solid-liquid interface. Among the stress components,  $\tau_{p,yy}$  has the largest magnitude due to the stretching in the fluid produced by the hot rising fluid at the left cavity wall and the cold falling fluid on the solid-liquid interface. The central portion of the cavity far from the boundaries is free of viscoelastic stresses due to the very small fluid velocity present in that region. Further work is underway on the effect of variable thermophysical properties of the fluid on the solidification pattern.

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# The Role of Nanomaterials in Radioactive Waste Reduction and Decontamination: A Concise Review



Yadaiah Salwadi and Sathish Kumar Kurapati

### **1** Introduction

Radioactive elements show some unique properties, such as the emission of highenergy particles like neutrons, alpha rays, X-rays, and gamma rays. As a result, radioactive materials are used in several potential applications, such as nuclear power [33, 56, 85, 110], agricultural products [1], industry [93], nuclear warheads [2, 71], and research [24, 29, 61, 80]. Hence, the usage of radioactive materials is rapidly increasing, and consequently, the radioactive waste is also growing. The disposal, transport, and experimentation of radioactive waste contaminate water bodies, soil, and air [37, 79]. The mining for useful radioactive nuclides and other non-radioactive metals is also one of the significant sources of radioactive contamination [50, 65, 81]. Accidents in nuclear power plants also significantly contribute to radioactive pollution [106]. The levels of radioactive pollution in the environment are hazardous for humanity and other living creatures, including wildlife [39, 59, 97]. The radioactive nuclides enter the food cycle, accumulate in the tissues of organisms, and develop chronic health issues. Besides preventing radioactive pollution, it is also essential to remove radioactive pollution to decontaminate the polluted natural resources. Several methods and materials are applied to decontaminate radioactive polluted natural resources.

Nanomaterials are one of the essential classes of materials of the twenty-first century. Nanomaterials show few unique properties in contrast to corresponding

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bulk materials, such as surface area, electronic properties, absorption and emission of UV–Vis radiation, higher mechanical strength, conductivity, and a variety of morphologies [6, 67, 69, 94]. As a result, nanomaterials have many applications in the fields of energy production and storage [10, 19, 89], heterogeneous catalysis [26, 83, 105], electrocatalytic water splitting [101, 103, 109], medicine [11, 22, 30, 64], construction [45, 86], and electronics [40, 42, 95]. One of the important properties of nanomaterials is porosity and layered nature. The nanomaterials with such unique features expose nanosized pores and cavities. Hence, layered or porous nanomaterials are excellent adsorbents toward atoms, ions, molecules, and tiny nanoparticles [72, 87]. The polar hydroxide groups on layered nanomaterials further enhance their adsorbent capabilities [47]. Nanomaterials are explored as adsorbents for carbon dioxide and methane capture [4], metal ion removal from aqueous solutions [47, 72, 87], and other organic pollutants from water [8]. From the above observations, nanomaterials can be the most excellent tool for environmental chemists to decontaminate pollutants, including radioactive contaminants.

In this light, a variety of nanomaterials are tested to remove radioactive nuclides from the natural/artificial contaminated samples. Hence, in this review, we summarize different categories of nanomaterials that have been used for radioactive decontamination. More emphasis will be given to the highly effective and recent case studies.

#### 2 Nanomaterials for Removal of Radioactive Waste

A variety of nanomaterials were used to decontaminate radioactive pollutants from natural resources. Carbon-based nanomaterials such as carbon nanotubes (CNTs), graphene, graphene oxide (GO), and reduced graphene oxide (r-GO) have been employed as nano adsorbents. Metal nanoparticles such as Ag nanoparticles and gold nanoparticles were used to remove a variety of radionuclides. Metal-oxides and metal sulfides of many transition metals, naturally occurring zeolite nanomaterials, biologically formed hydroxy appetite and cellulose-based nanomaterials, and metal–organic frameworks (MOFs) are mostly reported for the removal of a variety of radionuclides. Functionalization of these materials with polar functional groups such as -OH, -COOH, and  $-NH_2$  increased their adsorption capabilities towards radioactive metal ions. These polar functional groups enhance the surface polarity of the nanoadsorbents and also offer coordination sites (as the Oxygen and Nitrogen serves as ligating atoms towards metal ions). As a result, the materials strongly binds and stabilizes the radionuclides through polar-polar interactions and coordination bonds and show better adsorption in contrast to non-functionalized materials.

#### 2.1 Carbon-Based Nanoparticles

#### 2.1.1 Carbon Nanotubes

Carbon nanotubes are one of the allotropes of elemental carbon. In general, CNTs are two types: single-walled CNTs and multi-walled CNTs. The CNTs are used as nano-adsorbents to remove radionuclides from contaminants [12]. However, the adsorption mechanism is assumed that the unsaturation sites, hollow space, and interlayered interstitial positions of CNTs will accommodate the metal ions and stabilizes the adduct [77]. Modifying CNTs with polar functional groups such as amines (-NH<sub>2</sub>) and hydroxides (-OH) will further increase their adsorption capacity toward heavy metal ions [44, 76, 88]. The diameter and aggregation capacity of CNTs (SWCNTs & MWCNTs) also play a very important role in pertaining to their adsorption capacities. The SWCNTs possess diameters of 0.3 nm to 3 nm whereas MWCNTs are with diameters up to 100 nm. The aggregation of SWCNTs are more compared to MWCNTs, and as a result, the SWCNTs creates numerous intestitial adsorption sites. However, the flexible SWCNTs offers large and adjustable pores for the adsoption of organic pollutants. The MWCNTs offer suitable interstitial cavities or pores to accommodate inorganic metal ions. The MWCNTs show superior adsorption capacity over activated carbon and graphene for metal ions such as Ni<sup>2+</sup>, Sr<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup> and Cr<sup>2+</sup> [5]. Another important property of CNTs is chirality or helicity. However, the chirality of CNTs is a very essential feature for the adsorption and sensing of optically active organic compounds [31, 46] and biological molecules [63]. Whereas the radionuclides are mostly in their ionic form. It is observed that the monocationic metal ions prefer to bind armchair CNTs over Zig-Zag CNTs while dicationic species bind in the opposite manner [84]. The pH-dependent Adsorption of <sup>243</sup>Am(III) from aqueous solutions is known as the first report where multi-walled carbon nanotubes (MWCNT) are employed as an adsorbent [90]. Later several CNT-based nanomaterials were reported for the sequestration of radionuclides [13].

Uranium is a well-known nuclear fuel for generating nuclear power; consequently, its usage also leads to lots of radioactive waste. MWCNTs are explored as nano adsorbents to remove the U(VI) radionuclides from aqueous solutions in the form of  $UO_2^{2+}$  ions. Chitosan grafting on MWCNTs further enhances the U(VI) removal capacity by a factor of 2.4 and reduces the contact time [17]. The pH of the contaminated solution significantly influences the adsorption of U(VI). The adsorption studies carried out at different pH intervals revealed that the optimum pH for maximum adsorption is found to be pH = 7, and beyond the neutral pH, either acidic or basic, the amount of U(VI) sorption on both MWCNT and chitosan grafted MWCNT (MWCNT–CS) considerably decreases. In the acidic medium, the functional groups on the MWCNT adsorbents will be strongly protonated, making them weak coordinating groups and, consequently weak adsorbents. Whereas in the alkaline pH, the U(VI) ions might form soluble hydroxides, which make themselves unavailable for adsorption by nano adsorbents. However, at neutral pH the U(VI) ions are available in their free form

and the functional groups on the adsorbents can easily deprotonate and shows their maximum adsorption capacity. The carboxylic groups on MWCNT-CS are expected to increase their surface polarity and play a critical mechanistic role in enhancing U(VI) nuclide sorption by MWCT-CS in contrast to non-grafted MWCNT. However, the U(VI) adsorption profiles were monitored by XPS analysis. In another report, pristine MWCNTs were explored to adsorb U(VI) from aqueous solutions at pH = 4 [73]. The MWCNTs are treated with a mineral acid mixture of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (3:1) for 16 h to enhance their adsorption ability towards U(VI). The U(VI) adsorption amounts at pH = 4 are 5 mmol/g and 61 mmol/g for pristine MWCNTs and acid-treated MWCNTs. Chemically decorated SWCNTs with carboxylic acid (SWCNH-COOH) and triethylenetetramine (SWCNH-TETA) functionalities were employed as adsorbents to efficiently remove U(VI) [88]. The maximum U(VI) adsorption on SWCNT-TETA calculated from the Langmuir adsorption isotherm is 333.13 mg/g. The SWCNH-TETA material was also found to show an excellent selectivity towards U(VI) in the presence of several competing ions such as Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Mn<sup>2+</sup>, etc. From the pH optimization curves and adsorption isotherms of SWCNH-COOH and SWCNT-TETA, it is obviously known that SWCNH-TETA is the efficient adsorbent for the U(VI) radionuclides compared to SWCNH-COOH. An NH<sub>2</sub> functionalized magnetic CNT-Fe<sub>2</sub>O<sub>3</sub> composite (NH<sub>2</sub>-PZS/CNT/Fe<sub>2</sub>O<sub>3</sub>) shows excellent adsorption capacity towards U(VI) radionuclide [51]. A phosphazene-based polymer is coated on CNTs with the help of  $Fe_2O_3$ nanoparticles to prepare the aforesaid magnetic composite. The Langmuir adsorption isotherm indicates that 250 mg of U(VI) nuclides were adsorbed on one gram of modified magnetic nano adsorbent. The selectivity of functionalized CNT composite is very high towards U(VI) even in the presence of competing metal ions such as Mg(II), Ni(II), Zn(II), Mg(II), Sr(II), and Na(I) ions. This study studied the effect of pH, initial concentration of U(VI), and temperature on adsorption capacity as usual. The adsorption mechanism and the amount of adsorption were measured using X-ray photoelectron spectroscopy and FTIR spectroscopy.

Thorium is also used as nuclear fuel like Uranium, in nuclear power plants. MWCNTs-based nano adsorbents show an excellent adsorption capacity towards Th(IV) radionuclides for contaminated water [16]. The oxidation of original MWCNTs was carried out by treatment with 3 M HNO<sub>3</sub> for 24 h under ultrasonication. The oxidized MWCNTs adsorb 40  $\mu$ g of Th(VI) per one gram of adsorbent from the aqueous solution with 32.32 µmol/L of concentration. The study of adsorption kinetics reveals that adsorption follows second-order kinetics, and most adsorption is done within the first 15 min. In addition, these adsorbents show decent desorption of Th(IV) nuclides after adjusting the pH of the solution. In another recent report, chemically modified MWCNTs were explored as adsorbents [102]. The chemical modification was carried out by reaction of MWCNTs with KMnO<sub>4</sub> and citric acid. The adsorption capacities of MWCNTs treated with  $KMnO_4$  and citric acid are 105.28 and 50.67 mg  $g^{-1}$ , respectively. Similar to the previous observations, the adsorption capacities of these chemically modified MWCNTs are dependent on the pH of the contaminant solutions. MWCNTs, prepared by the chemical vapor deposition method, show adsorption capacity towards Uranium-238, Thorium-232, and



**Fig. 1** a Schematic illustration for the preparation of SWCNH – COOH and SWCNH – TETA, b Influence of pH on U(VI) removal for SWCNH – COOH and SWCNH – TETA, c Influence of time on the adsorption of U(VI) with SWCNH – COOH and SWCNH – TETA, and d Selective adsorption capacity of coexisting ions on two (pH = 6.0). [88] Copyright 2020. Reproduced with permission from the American Chemical Society

Potassium-40 nuclides from the wastewater [36]. The effect of pH, temperature, the concentration of radioactive metal, and the amount of adsorbent is evident in the adsorption of radionuclides. It is observed that within 15 min of contact time, 98% of metal adsorption was observed at pH = 6, and 10 g/L of MWCNTs were used. The adsorption process was observed to follow pseudo-second-order kinetics. The powder XRD patterns reveal no change in the crystal structure of MWCNTs even after adsorbing radionuclides (Fig. 1).

#### 2.1.2 Graphene Oxide(GO)

Graphene oxide is the oxidation derivative of graphene and contains polar functional groups such as –OH and –COOH. In contrast to graphene, the GO exhibits higher surface polarity, and as a result, GOs exhibit excellent adsorption towards radioactive ions and atoms.

GO prepared by Hummer's method shows excellent adsorption towards high halflife radionuclides such as Am(III), Th(IV), Pu(IV), U(VI), Sr(II), Tc(VII), and Np(V) even from aqueous media with pH = 2 [70]. The binding of radioactive cations to the polar functional groups of GO and consequent aggregation of nano GO sheets remove radioactive cations from aqueous solutions. It is important to note that the ability of GO in the removal of radionuclides is found to be better than traditional adsorbents such as bentonite clays and activated carbon. In another example, the pristine GO is employed to study its adsorbent properties towards Cs(I) radionuclides [41]. The GO adsorbs a maximum of 528 mg Cs/g from solutions having pH = 12. The adsorption capacities of GO at acidic pH (pH = 3) and neutral pH (pH = 7) are 180 and 465 mg Cs/g, respectively.

GO nanoflakes that are modified with amino siloxane oligomer functionalities have shown unprecedented adsorption capabilities for U(VI) and Eu(III) radio cations [107]. The amine groups (-NH<sub>2</sub>) on the surface of modified GO nanoflakes (PAS-GO) are expected to facilitate the maximum adsorption of U(VI) and Eu(III) ions by interacting with the lone pairs of nitrogen. U(VI) and Eu(III) adsorptions on PAS-GO are 310.63 and 243.90 mg/g, respectively. In another report, to increase the surface area of nano GO sheets, polyacrylacetamine groups were introduced on the surface of GO sheets and explored as adsorbents for the decontamination of U(VI), Eu(III), and Co(II) nuclides [78]. At pH = 5, the observed adsorption capacities of modified GO (PAM/GO) for U(VI), Eu(III), and Co(II) ions are 0.698, 1.245, and 1.621 mmol/g, respectively. The study also suggests that the effect of pH and temperature while adsorption is very significant. The change in the enthalpy, entropy and free-energy data indicates a strong complexation of radionuclides with PAM/ GO adsorbent. A GO composite with Bismuth shows excellent adsorption chemistry toward radioactive iodate ions in radioactive wastewater [34]. It is found that when Bi-GO composite interacts with iodate ions, they form BiOI and Bi(IO<sub>3</sub>)<sub>3</sub> species, and the formation of these species is crucial for the adsorption of iodate  $(IO_3^{-})$  ions. The selectivity of Bi-GO material for  $IO_3^-$  ions is very high and removes > 95% of iodates from wastewater, even in the presence of competing Cl<sup>-</sup> ions (KCl) (Fig. 2).

#### 2.1.3 Metal Nanoparticles

Nanoscale zerovalent iron (NZVI) particles are known to have surface oxo-hydroxyl functionalities, which adds an adsorbent property to NZVI particles. NZVI particles are explored as adsorbents for removing U(VI) radionuclides from water with excellent efficiency [49]. It is found that the NZVI particles removed 97% of the U(VI) radionuclides, and the adsorption process follows first-order reaction kinetics. However, U(VI) adsorption was 120 mg per gram of NZVI particles at pH = 5.5. The low activation energy for the adsorption reaction indicates a feasible and faster removal of radioactive ions from the solution. Surface modification of NZVI particles is explored to prevent oxide layer formation and rapid self-aggregation. Montmorillonite-supported NZVI particles show optimum adsorption of 97% of U(VI) at pH = 3.0 [98]. The results obtained during the adsorption studies show the role of montmorillonite in reducing particle aggregation and enhancing the specific surface area of NZVI particles. Diatomite is another important supporting material for the NZVI particles for aggregation prevention and surface area enhancement. The cooperativity between diatomite and NZVI particles further enhances the adsorption



Fig. 2 Grafting of graphene oxide with amino siloxane oligomer functionalities and  $-NH_2$  groups assisted adsorption of Uranium and Europium (schematic representation). Copyright 2017. Reproduced with permission from the American Chemical Society [107]

of toxic  $UO_2^{2+}$  in the form of  $UO_2$  [74]. The surface modification of NZVI particles with -NH<sub>2</sub> functional groups greatly enhances the absorptivity of these NZVI-based materials. The enhanced adsorption is attributed to the electron-donating ability and binding capacity of -NH<sub>2</sub> groups. The -NH<sub>2</sub> groups were successfully introduced onto the surface of NZVI particles by treating with 3-aminopropyl trimethoxysilane and diethylenetriamine followed by 2 pyridine carboxaldehyde to produce NZVI-NH<sub>2</sub> and NZVI-DETA-PY materials to remove radioactive Co(II), <sup>65</sup>Zn(II) and <sup>60</sup>Co(II) from contaminated water with a removal efficiency of 93.6–98.7% [75]. High retention capacity, 30 mg I<sup>-</sup>/g Ag-CAM, indicates the formation of a stronger adsorption adduct. Gold nanoparticles (AU-NPs) also perform excellently as radionuclide adsorbents towards iodine radionuclides [21]. Au-NPs adsorb 99% of <sup>125</sup>I<sup>-</sup> ions from the aqueous solutions in 15 min of contact time. In another example, the Au-NPs coated on CNTs show adsorption of radioactive UO<sub>2</sub><sup>2+</sup> ions from aqueous solutions [62]. Removal of 98% of radioactive  $UO_2^{2+}$  was accomplished by ultrasoundassisted adsorption in 5 min due to cavitation and elevated local temperature caused by microstreaming and microturbulence.

Metal nanoparticle composite materials are another important class of materials. The composites of metal nanoparticles with natural adsorbents such as cellulose, chitosan, and chitin show significant improvement in the adsorption of radionuclides. After modification with cellulose, chitin, and chitosan, the Ti and Ni metal nanoparticles offer excellent adsorption capabilities towards <sup>137</sup>Cs, <sup>60</sup>Co, <sup>85</sup>Sr, <sup>152</sup>Eu, and <sup>154</sup>Eu radionuclides [68]. The synergetic effect of metal nanoparticles and biopolymers (cellulose, chitin, and chitosan) dramatically improves the adsorption

capacities of these hybrid materials. However, The Ti-biopolymer composite shows high adsorption of Sr(II) (11.83 mg Sr(II)/g) in contrast to Ni-biopolymer composite and bare biopolymers.

#### 2.1.4 Metal-Oxide Nanoparticles

TiO<sub>2</sub> nanoparticles are widely used in semiconductor, photocatalysis, environmental, and energy applications [32]. In addition, the  $TiO_2$  nanoparticles are highly explored metal-oxide nanoparticles as nano adsorbents for removing radioactive nuclides from contaminated water. Crystalline TiO<sub>2</sub> nanoparticles prepared from isopropyl alcohol are an excellent adsorbing agent for the mixer of <sup>99</sup>Mo and <sup>99m</sup>Tc radionuclides [27]. The TiO<sub>2</sub> nanomaterial packed in a chromatographic column shows excellent adsorption capacity for <sup>99</sup>Mo (142 mg/g TiO<sub>2</sub>) and separation of <sup>99m</sup>Tc radionuclides in the form of pure  $TcO_4^- (\geq 97\%$  radiochemical purity). The radionuclide purity found for  $^{99m}$ Tc is  $\geq$  99.99%. The TiO<sub>2</sub> and polymer nanocomposite material, derived from  $\gamma$ -rays-initiated polymerization of acrylate and styrene sodium sulfate monomers with TiO<sub>2</sub>, show an excellent adsorption ability towards radioactive Cs(I), Co(II), and Eu(III) nuclides [14]. The high surface area and availability of abundant polar functional groups greatly enhance the adsorption capacity of TiO<sub>2</sub> nanocomposites and show maximum adsorption. The adsorption capacities for Cs(I), Co(II), and Eu(III) are 200, 100.9, and 85.7 g/kg, respectively. The nanomagnetic dual-core-shell adsorbents, prepared by depositing thin films of  $TiO_2$ nanoparticles coated with polydopamine, show significant adsorption toward U(VI) radionuclides [104]. The -OH, -NH<sub>2</sub>, and Ti-O- functional groups of polydopamine coating strongly interact with the U(VI) radionuclides. The removal of U(VI) from water containing 5.89, 11.47, and 30.33 mg/L of U(VI) was found to be 96.45, 94.88, and 89.94%, respectively. In addition, these adsorbents can be easily isolated by applying a magnetic field. The hierarchical nanostructures of sodium titanates, C@Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>·9H<sub>2</sub>O (CSTHNs), fabricated via hydrothermal reaction followed by chemical deposition methods, were explored as radionuclide adsorbents [82]. Very high Brunauer-Emmett-Teller (BET) surface area and large adsorption constant values clearly explain the extraordinary adsorption capacities of CSTHNs material. The maximum adsorption capacities of nano CSTHNs towards  $Cs^+$ ,  $UO_2^{2+}$ , and Eu3<sup>+</sup> species are 5.757 mmol  $g^{-1}$ , 8.151 mmol  $g^{-1}$ , and 4.846 mmol  $g^{-1}$ , respectively. The TiO<sub>2</sub> nanoparticle-based adsorbent materials explored for radioactive waste removals, such as Layered sodium titanate (Ag<sub>2</sub>O-T<sub>3</sub>NT, Ag<sub>2</sub>O-T<sub>3</sub>NF) for the removal  $^{137}$ Cs(I) and  $^{125}I^{-}$  [99], Copper–iron-titanate for the removal of  $^{241}$ Am(III) and <sup>152,154</sup>Eu(III) [60], and Fe3O4@titanate for Ba(II) removal [108], are worth to mention among several.

The aggregates of silver oxide (Ag<sub>2</sub>O) nanoparticles with other high surface area composite nanomaterials show adsorbent properties towards radionuclides. For example, the hierarchical Ag<sub>2</sub>O@Mg(OH)<sub>2</sub> nanocomposites can remove UO<sub>2</sub><sup>2+</sup> and I<sup>-</sup> simultaneously [20]. The Mg(OH)<sub>2</sub> material supports the dispersion of Ag<sub>2</sub>O

nanoparticles, controls the pH of the solution, and widens the pH range for adsorption. As a result, the adsorption equilibria can be achieved in five minutes, removing 96.82% of I<sup>-</sup> and 99.39% of UO<sub>2</sub><sup>2+</sup> species from contaminated water. The Ag<sub>2</sub>O with nano-fibrillated cellulose (Ag<sub>2</sub>O@NFC) can uptake 90% of radioactive I<sup>-</sup> from contaminated water with 500 ppm of I<sup>-</sup>. In another example, nano-polyaniline-coated Ag<sub>2</sub>O nanoparticles are explored to remove <sup>65</sup>Zn(II) and <sup>60</sup>Co(II) from radioactive wastewater [53]. The materials show considerable removal capacities, 139.75 mg/g for Zn(II) and 112.1 mg/g for Co(II), respectively.

Artificial hematite nanoparticles, such as iron oxide nanofibers, are explored to remove radioactive <sup>51</sup>Cr, and <sup>131</sup>I, and 70% removal for <sup>51</sup>Cr and 90% for <sup>131</sup>I<sup>-</sup> were observed [7]. The selectivity towards iodine in the presence of cations such as Mn(II), Co(II), Ni(II), and Zn(II) is an essential feature of these iron oxide nanofibers. On the other hand, they show excellent acidic resistance and can remove <sup>51</sup>Cr, and <sup>131</sup>I even from 1 M HCl solution. Iron oxide nanomaterials are ferromagnetic and can be isolated and recycled by applying a magnetic field. Ferromagnetic Attapulgite–iron oxide nanocomposite is explored to remove Eu(III) from radioactive wastewater [52]. The maximum adsorption was 0.75 mmol/g from the water at pH 5. The efficiency is high compared to other natural materials such as ZSM-5 and bentonite and less than GO. Magnetically separable iron oxide (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles trapped in the polypyrrole matrix (Fe<sub>3</sub>O<sub>4</sub>@PPy) can remove I<sup>-</sup> from an aqueous solution with a maximum uptake capacity of 1627 mg/g at room temperature [35]. Iron oxide and silicate nanocomposite, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, show high selective adsorption for U(VI) radionuclide with an adsorption capacity of 52 mg/g [25].

Along with mechanical, thermal, and chemical stability and resistance to an acidic environment, the high surface area of silicate nanomaterials can be considered adsorbents for removing radionuclides. Amine functionalized mesoporous silica-carbon dots are studied as adsorbents for rapidly removing radioactive U(VI) from contaminated water [92]. As the fluorescence intensity decreases with the adsorption of U(VI), The luminescent property of carbon dots can be used as a tool to monitor in situ U(VI) adsorption. Similar amine-functionalized silica was also reported for U(VI) adsorption with a maximum uptake of 573 mg/g [38]. However, the carbon dot introduction on mesoporous silica enhances the selectivity and rapidity of the adsorption process. Inorganically modified mesoporous silica with copper ferrocyanide nanoparticles show selective adsorption towards radioactive <sup>137</sup>Cs nuclides from saline waters [57]. The adsorption occurs via an ion exchange mechanism, and the selectivity is very high even in competing cations such as K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>, commonly present in natural saline water. In another example, the SBA-15 mesoporous silica functionalized with Schiff-Base shows U(VI) adsorption from the contaminated water samples [23]. The maximum adsorption can be achieved in 15 min at pH 4 and 25 °C. The modified adsorbent shows selective U(VI) adsorption in the presence of other competing ions like Cd<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Cr<sup>3+</sup>, Ba<sup>2+</sup>, Fe<sup>3+</sup>, and Eu<sup>3+</sup>. The selectivity is attributed to the Schiff-Base functionality on the silica nanoparticles and can be used as U(VI) ion separator.

#### 2.1.5 Metal–Organic Frameworks (MOFs)

Metal–organic frameworks (MOFs) are synthetic inorganic–organic hybrid materials. The properties of MOFs, such as porosity, adsorption, and thermal and chemical stability, are very similar to the naturally occurring zeolites. The accessibility to a wide range of functional groups on MOFs can be used to fine-tune the MOF's properties and make them excellent adsorbents for radionuclides.

Rodshaped MOF nanoparticles derived from MOF-5 (derived from Zn and BDC) show <sup>235</sup>U(VI) adsorption from contaminated water [96]. The MOF-based adsorbents are pH-dependent and adsorb 237 mg of U(VI) per gram of MOF nanoparticles at pH 5 and 298 K. The thermal profile of adsorption indicates the process is spontaneous, and the feasibility of adsorption is perhaps due to the presence of C–O and C = O functional groups on the surface of the MOF nanorods. The removal of U(VI) radionuclides was also observed by the nanomaterials derived from luminescent MOF-76 [100], highly porous UI-68 [15], and amidoxime appended UI-66-AO(AO = amidoxime) [18]. Besides the bare MOF nanomaterials, modified MOFs such as carboxylate functionalized MIL-101 MOF were also tested for the adsorption of radioactive U(VI) ions from the water [48]. The adsorption capacity for postsynthetic functionalized MOF nanomaterials is high compared to naked MOF materials. The maximum sorption capacity is 314 mg/g, and the material shows very high selectivity for U(VI) even in the presence of Co(II), Ni(II), Zn(II), and Sr(II) ions. MIL-101 materials decorated with ethylenediamine (MIL-101-ED) and diethylenetriamine (MIL-101-DETA) were shown U(VI) adsorption at about 200 and 350 mg/ g, respectively [9]. The adsorption capacities are much higher than naked MIL-101 (20 mg/g) and amine-decorated MIL-101-NH<sub>2</sub> (90 mg/g). The strong coordination of amine groups, two -NH<sub>2</sub> groups in MIL-101-ED and three -NH<sub>2</sub> groups in MIL-101-DETA, with U(VI) ions is the reason for the enhanced adsorption. A unique and new polycatenated uranium-based MOF can able to remove 71.81-93.50% Cs(I) radioactive cations selectively from the Cs(I) solution of 1 mg/L [91]. The selectivity of this MOF material towards Cs(I) is tremendous and can remove Cs(I) ions from the water containing 5–20 times excess of completely exchangeable  $[(CH_3)_2NH_2]^+$ cations. The MOF nanomaterials show resistance against  $\beta$  and  $\gamma$  radiation and are stable in the pH range of 3–12. The polycatenated structure is attributed to the selective adsorption and stability against radiation and a wide range of pH. In another study by Peng et al., MOF-88, MIL-101, and their sulfate and sulfonic acid derivatives act as traps for the radioactive Ba nuclides [66]. The MOFs with  $-SO_4$  and SO<sub>3</sub>H functionalities show a strong chelating affection towards Ba(II) ions and can remove 90% of Ba in 5 min of contact time. The maximum adsorption capacity is 131.1 mg/g, and the maximum removal of Ba ions is 99% at equilibrium. SZ-4, a MOF derived from ZrOCl<sub>2</sub>, methylenediphosphonicacid, and N, N-dimethylacetamide, can able to adsorb 90 Sr(II) radionuclides and remove 90% of Sr(II) ions from the aqueous solution [28]. The adsorbent is active over a pH range of 2 to 11 and shows excellent selectivity towards <sup>99</sup>Sr(II). X-ray quality single crystals of SZ-4 MOF show a single-crystal to single-crystal transformation after the adsorption of Sr(II) radioactive cations. The uptake capacity of SZ-4 MOF is 121 mg/g at pH 2 (Fig. 3).

Magnetic MOF, Fe<sub>2</sub>O<sub>3</sub>@ZIF-8, selectively adsorb U(VI) and Ln(III) radionuclides from contaminated water [58]. The adsorption capacity (523.5 mg/L) is considerably high compared to many other MOF-based nano adsorbents reported for U(VI) and Ln(III). The synergetic effect of Zn and U(VI) enhances the hydrogen bond strength and contributes to the selective and high amount of adsorption. Another important contributing factor is rapid separation by applying a magnetic field. The UiO-66-based MOFs anchored with –COOH functional groups (UiO-66-COOH and UiO-66-(COOH)<sub>2</sub>) show increased adsorption towards Th(IV) nuclides from weakly acidic solutions. The decoration of –COOH groups on UiO-66 simultaneously decreases surface area and pore volume, perhaps contributing to enhanced adsorption of Th(IV). The maximum uptake capacity of UiO-66-(COOH)<sub>2</sub> is 370 mg/ g, which is higher than the UiO-66 (350 mg/g) at pH 3.



**Fig. 3** Mechanistic representation of 133Ba ion trapping by –SO4 and –SO3H functionalized MOFs. Comparative adsorption of radioactive Ba(II) ions by MOF-808 and sulfate functionalized MOF-808-SO4. Copyright 2016. Reproduced with permission from the American Chemical Society [66]

# 3 Conclusion

Radioactive contamination is alarming pollution as anthropogenic activities are increasing the pollution pathways. In this article, we have reviewed several nano adsorbents explored to remove radioactive pollutants. Carbon nanotubes, graphene oxides, metal nanoparticles, metal-oxide nanoparticles, and metal-organic frameworks and derivatives of mentioned nanomaterials are widely studied as nanoradioadsorbents. However, after reviewing a diverse range of nanomaterials to remove and decontaminate radioactive nuclides, nanomaterials can be considered a potential candidate for the earlier purpose. However, among the variety of nanomaterials discussed above, it isn't easy to find the best nanoadsorbents as the studies are conducted with different contact times, differently concentrated solutions of radionuclides, and other types of radionuclides. If the amount of radionuclide per one gram of adsorbent is considered, the metal-oxide nanomaterials are found to adsorb the maximum amount of radionuclide (1625 mg/g of  $I^-$ ). U(VI) adsorption is studied using all the classes of nanomaterials. For the adsorption of U (VI), again, the metaloxide nanomaterials are found to be the best among the other type of materials (575 mg/g of U(VI). Further, the research has to be focused on the invention of efficient, nontoxic, less expensive, and recyclable nanomaterials for radioactive waste removal. After reviewing many nanomaterials, it is noted that the emerging materials such as aerogels, functionalized synthetic polymers such as PVC, polystyrene, and hydrogels are less explored as adsorbents for the decontamination of radionuclides. Hence, we believe these materials also can be a great tools for the adsorption of not only the radionuclides and also the toxic metal pollutants.

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# Parametric Optimization for Tribological Behavior of MWCNTs/Al6082 Composites Using Taguchi Analysis



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# **1** Introduction

Currently, aluminum (Al) and its alloys are extensively used in the automotive and aerospace industry because of their lightweight, good thermal conductivity, and high resistance against corrosion [1], but the low wear resistance of Al alloys limits their uses in some sectors. Reinforcing aluminum matrix with particulates is one of the encouraging ways to enhance the resistance against wear and reduce the coefficient of friction (COF) during working. An aluminum matrix can be reinforced with several materials such as SiC [2], Al<sub>2</sub>O<sub>3</sub> [3],  $B_4C$  [4], CNTs [5], etc., to enhance their properties (hardness, specific strength, specific modulus, etc.) and resistance against wear. Incorporation of carbon nanotubes (CNTs) in Al matrix is highly preferred owing to their unique properties such as high specific strength, good electrical conductivity, high thermal conductivity, and excellent mechanical characteristics [6]. CNTs reinforced Al matrix composites can be synthesized using powder metallurgy [7], spark plasma sintering [8], and stir casting [9]. Among these methods, stir casting is preferred due to its simplicity and ability to fabricate intricate shapes at low cost [10]. Low wettability of MWCNTs in Al matrix is one of the main concerns, which can be improved using an ultrasonic probe stirrer during fabrication of nanocomposites [11].

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Wear resistance of Al matrix was improved with CNTs, as observed by some researchers. Wear, and COF of MWCNTs/AA7075 was studied by Aranke et al. [12] on pin-on-disk apparatus. Taguchi L9 orthogonal array was applied for optimization, taking sliding speed, applied load, and time as input parameters. Wear rate reduced with MWCNTs due to their self-lubricating nature. Padmavathi et al. [13] investigated the tribological characteristics of Al composites embedded with MWCNTs. They observed that the applied load mainly influenced the wear rate, and beyond the critical load, the wear rate increased abruptly. Wear behavior of MWCNTs/Al composites was noticed by Choi et al. [14]. The addition of CNTs and reduced grain size decreased the wear rate and COF and enhanced the strength of composites. Wear rate and COF were also affected by applied load and increased with the load. Wear resistance of Al reinforced with various amounts of CNTs (0.5, 1.0, 1.5, 2.0 wt.%) was inspected by Manikandan et al. [15] fabricated via powder metallurgy method. Higher wear resistance and lower COF was observed during mild wear condition, while under severe wear condition, high COF and low wear resistance were noticed. Taguchi L27 with ANOVA was used by Devadiga et al. [16] to study wear characteristics of CNTs reinforced Al composite under a dry sliding environment. Content of CNTs was the main affecting parameter with a contribution of 43.71% among all the input variables. Optimum parameters were 0.25 wt.% CNTs, 500 m sliding distance, 10 N applied load, and 200 rpm sliding speed.

Based on the above literature review, it is inferred that inspection of wear performance of CNTs/Al composite is necessary under dry sliding environment. Wear and tear of some components of a vehicle (tires, brakes, etc.) during dry sliding motion causes various adverse impacts on environment and sustainable living. Airborne and nonairborne wear debris are released due to friction, which remains suspended in the air for a long time and contributes to air pollution. This air pollution is a prime cause of many deaths around the world, as projected by the world health organization (WHO). Reduction in wear rate is responsible for fuel-saving leading to less air pollution [17]. It is also noticed that very few researchers have worked on the tribological behavior of CNTs reinforced Al6082 composites. In this study, a modified stir casting method was utilized to fabricate 0.6 wt.% MWCNTs/Al6082 nanocomposite and their wear behavior were examined using a pin-on-disk machine. The aim of the current study is to optimize the input parameters affecting the wear resistance of nanocomposites using Taguchi orthogonal array and ANOVA.

#### **2** Experimentation

## 2.1 Selection of Materials

Medium strength Al alloy (Al6082) was selected as a matrix having chemical composition displayed in Table 1. MWCNTs were procured and selected as reinforcement. Properties of purchased MWCNTs are displayed in Table 2.

Element	Si	Mg	Mn	Fe	Cu	Ti	Zn	Cr	Al
Wt.%	1.05	0.76	0.56	0.26	0.026	0.023	0.018	0.032	Balance

Table 1 Chemical constituents of Al6082

Table 2 Properties of MWCNTs

Property	Purity (%)	Diameter (nm)	Length (µm)	Density (g/cm <sup>3</sup> )
Values	≥98	30–50	10–30	1.74

## 2.2 Synthesis of Nanocomposites

Stir casting technique equipped with an ultrasonic probe agitator (shown in Fig. 1a) was used to develop the 0.6 wt.% MWCNTs reinforced Al6082 composites. In this method, Al6082 ingots were placed in a crucible, and temperature of furnace was shot up to 800 °C to melt them completely. At the same time, MWCNTs and dies were preheated in a muffle furnace (shown in Fig. 1b) at 300 °C for 20 min to get rid of the moisture existing on the surface of MWCNTs. Once the Al ingots were melted, coverall flux was added for the removal of dross, and purging was done using dry nitrogen gas to deoxidize the melt. Mg tablets (2 wt.%) were also added to amplify the interfacial bonding between MWCNTs and Al, resulting in an improvement in wettability. A 3-blade mechanical stirrer was employed to stir the Al melt and form the vortex. Preheated 0.6 wt.% MWCNTs particles were spread on the verge of the vortex for uniform distribution while stirring. This composite melt was then subjected to ultrasonication (20 kHz for 2 min) to break down the clusters of MWCNTs, resulting in an unvaried distribution of MWCNTs in Al matrix [18]. Finally, the composite melt was poured into the predefined dies and solidified to form nanocomposite casting. Figure 2a, b represent nanocomposites after solidification and wear test specimens after machining.

## 2.3 Microstructural and Wear Characteristics

Microstructure of 0.6 wt.% MWCNTs reinforced Al6082 composites were examined using FESEM (Model: ZEISS ULTRA Plus). Polishing and etching (with Keller's reagent) were done on the machined specimen before the microstructural examination. For tribological testing, cylindrical specimens of 30 mm height and 10 mm diameter (ASTM G99 standard) were produced, and the test was performed on a pin-on-disk machine (Fig. 3) under non-lubricated conditions. Input parameters of wear test were optimized using Taguchi L9 orthogonal array and ANOVA. Input parameters were selected as sliding distance (500, 1000, and 1500 m), applied load (60, 80, and 100 N), and sliding speed (1, 2, and 3 m/s), while wear rate (mm<sup>3</sup>/m), was chosen as an output parameter.



Fig. 1 a Stir casting setup equipped with ultrasonic probe agitator, b Muffle furnace



Fig. 2 a Cast nanocomposites, b Wear test specimens after machining

# 2.4 Design of Experiment (DOE)

Experiment was designed and analyzed using Taguchi L9 orthogonal array to enhance the output parameter. ANOVA and signal-to-noise ratio were used for optimization in MINITAB software. Selected process parameters were applied load (L), sliding speed (V), and sliding distance (D), while wear rate (W) was the output parameter. Input parameters and their levels are displayed in Table 3.



Fig. 3 Pin-on-disk setup

Table 3         Levels of process           parameters	Process parameters	Level 1	Level 2	Level 3
1	<i>L</i> (N)	60	80	100
	V (m/s)	1	2	3
	<i>D</i> (m)	500	1000	1500

# **3** Results and Discussion

# 3.1 Microstructure

Figure 4 represents the morphology of 0.6 wt.% MWCNTs reinforced Al6082 composites showing the lamellar eutectic structure of Al. Eutectic Si can be observed in the dendritic regions. For differentiation between MWCNTs and Si, EDS analysis is also added in Fig. 5. Here, peaks of Si and C can be observed distinctly. MWCNTs are spread uniformly throughout the Al matrix. This uniform dispersion of MWCNTs confirms the positive effect of ultrasonic agitation during stir casting.

# 3.2 Wear Test

Based on Taguchi L9 orthogonal array, nine experiments were conducted, and outcomes are provided in Table 4.



Fig. 4 Microstructure of 0.6 wt.% MWCNTs/Al6082 composites



Fig. 5 EDS analysis of 0.6 wt.% MWCNTs/Al6082 composites

Experiment No	<i>L</i> (N)	V (m/s)	<i>D</i> (m)	$W \times 10^{-3} ({\rm mm^{3}/m})$
1	60	1	500	3.5
2	60	2	1000	4.0
3	60	3	1500	5.1
4	80	1	1000	4.4
5	80	2	1500	5.5
6	80	3	500	5.8
7	100	1	1500	6.0
8	100	2	500	6.4
9	100	3	1000	7.0

 Table 4
 Experimental data after machining

Source	DF	Adj SS	Adj MS	F-value	P-value	Contribution (%)
Regression	3	10.5083	3.50278	115.48	0.000	-
L	1	7.7067	7.70667	254.07	0.000	72.29
V	1	2.6667	2.66667	87.91	0.000	25.02
D	1	0.1350	0.13500	4.45	0.089	1.27
Error	5	0.1517	0.03033			1.42
Total	8	10.6600				100

Table 5 ANOVA of W

S = 0.174165, R-sq = 98.58%, R-sq (adj) = 97.72%, R-sq (pred) = 95.08%

## 3.3 Regression Analysis

#### 3.3.1 Analysis of Variance (ANOVA)

Influence of each input parameter on W was investigated using ANOVA, and the results are displayed in Table 5. Observed P-value is lower than 0.05 for L and V; hence wear rate is significantly affected by these parameters. Percentage contribution shows that W is mainly affected by L and then by V and D. The reliability of the model can be confirmed by R-sq value of 98.58%. High R-sq value represents the best fitting to the data.

#### 3.3.2 Main Effect Plots

Residual plots for wear rate are shown in Fig. 6. All results are close to  $45^{\circ}$  line in the normal probability plot concluding that all values are exact and linear. At the same time, experimental values range from -0.2 to 0.2 in the versus order plot concluding the significance of values. Signal to noise (SN) ratio was also evaluated, and responses can be seen in Table 6. The highest value of level was considered for each process parameter for optimization. The optimum value of each parameter is also shown.

Figure 7 shows the response graph with levels of parameters on x-axis and SN ratio on y-axis. It shows that maximum value of mean of SN ratios is obtained at lowest value of L (60 N), lowest value of V (1 m/s) and medium value of D (1000 m). It confirms the values obtained in Table 6.

Potential variation of output parameters with input parameters is given by contour plots, as shown in Fig. 8. In this plot, input parameters are taken on the x-axis while response parameter is taken on the y-axis. A higher wear rate is represented by the dark green zone having a small area. From Fig. 8a, it can be observed that lowest wear rate (desirable) is obtained when value of V is in the range of 1-2 m/s and L is in the range of 60–70 N. Figure 8b shows lowest wear rate when V is in the range of 1-2 m/s and D is in the range of 500–1000 m.



Fig. 6 a Normal probability plot b Versus order plot





Fig. 7 Response graph of control factor and mean of SN ratios



Fig. 8 Contour plot representing a W versus L, V b W versus V, D

Table 7 Predicted and experimental values

Response	Optimum parameters	Predicted value	Experimental value	% Error
<i>W</i> (mm <sup>3</sup> /m)	LIVID2	3.49	3.6	3.15

#### 3.3.3 Validation of Optimum Parameters

Regression analysis provided the relation between output parameter (W) and input parameters (L, V, and D) in the form of linear Eq. 1.

$$W = -0.867 + 0.05667L + 0.6667V + 0.000300D \tag{1}$$

Predicted optimized values of L, V, and D were put in Eq. 1, and the predicted value of W was calculated. For validation, an experiment was also conducted, taking the optimum value of each input parameter, and W was calculated. Table 7 represents all the predicted and experimental results.

# 4 Conclusions

The conclusions drawn from this investigation are:

- 1. Wettability and dispersion of MWCNTs in Al6082 matrix improved with the addition of Mg tablets and use of ultrasonic probe stirrer during synthesis.
- 2. Input parameters (applied load, sliding speed, and sliding distance) were successfully optimized using Taguchi L9 orthogonal array and ANOVA as confirmed by their P-values.
- 3. Wear rate was mainly affected by applied load (*L*) with the contribution of 72.29%, followed by sliding speed (*V*) of 25.02% contribution and sliding distance (*D*) of 1.27% contribution.

- 4. Contour plots show that lower value of wear rate is obtained when values of input parameters are in lower range.
- 5. Optimum value of input parameters for minimum wear rate were: 60 N of applied load, 1 m/s of sliding speed, and 1000 m of sliding distance.

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# Influence of Various Electrolytes on Surface Morphology of AAO–A Brief Review



Yerolla Pavan Kumar, Ajay Kumar Kaviti, and S. Swetha

### **1** Introduction

Aluminium, the third utmost plentiful metal in the environment following oxygen and silicon, has a diversity of features that represent it advantageous for the effortless formation of good, inexpensive, and resistant to corrosion. In day-to-day existence, aluminum can be found in resources as assorted as kitchen supplies, building development materials, or airplane fabricating resources [1].

Nano porous structure of a material is a novel asset of engineering resources possessing extraordinary properties such as functional as well as physical properties. The materials having nano porous structure are in lightweight and having properties such as larger surface area, good absorptivity, and energy managing routine. Nano porous materials are a subcategory of porous materials having greater penetrability up to 0.4 nm and above and having diameters of pores in the range of 1–100 nm. New properties emerge in the materials having nano porous structure. Pores are of two kinds, open and closed pores. Open type pores are uncovered and closed type pores are isolated from outdoors. There are several forms and morphology of pores such as tube-shaped, sphere-shaped and slit forms [2].

Previously, several approaches were established for the production of nanomaterials, such as photo and scanning beam lithography, molding, and imprinting techniques [3, 4]. Since these approaches are expensive, an electrochemical approach called anodization has been introduced and is considered a viable approach for obtaining the anodic aluminum oxide (AAO) film on the top of the aluminum. The

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AAO layer can be in the form of nano porous structure, nanotubes, nanowires [5]. Anodization can be performed using various types of electrolytes. Some of the most frequently used electrolytes are  $H_2SO_4$ ,  $H_2C_2O_4$ ,  $H_3PO_4$ , NaOH, deionized water, and ethylene glycol.

AAO has an extensive variety of applications in biology, environment and energy. In biology applications, AAO is utilized widely in protein recognition and bacteria recognition. In environmental applications, the AAO is utilized widely in desalination and toxic pollutants recognition. In energy applications, AAO is utilized widely in solar cell setups, capacitors and photonic crystals [6].

### 2 Anodization: Working and Types

### 2.1 Working Principle

Anodization is an electrochemical process in which the surface to be anodized is immersed in an electrolyte of a certain concentration. The surface on which the oxide layer should be formed is considered as an anode and coupled to the positive half of the DC power source and suitable material is used as a cathode and is coupled to the negative half of the DC power source. The selected cathode must be unreactive in the acidic electrolyte bath [7].

So, after the circuit is closed, the electrons from the aluminum anode are released and the aluminum ions are created at the surface. The ions created on the surface further react with the water in order to form the oxide layer on the surface of metal. At cathode, the hydrogen ions receive the electrons and are further reduced to form the hydrogen gas. The electrolyte solution releases oxygen ions which tend to combine with aluminum ions, here the development of aluminum oxide film (AAO) takes place on the surface of the metal. It can be completed in a precise way for finest results [8].

The overall equation is given below:

$$2\mathrm{Al} + 3\mathrm{H}_2\mathrm{O} \to \mathrm{Al}_2\mathrm{O}_3 + 3\mathrm{H}_2 \tag{1}$$

## 2.2 Barrier and Porous Type Layer Formation

AAO has two types of layer formation based on the nature of the electrolyte as shown in (Fig. 1). When the anodization is carried out in neutral electrolytes, the barrier kind of layer is formed, which is non-porous in nature. In neutral electrolytes, the oxide layer is formed both at aluminum oxide and oxide-electrolyte boundaries.



Whereas, when the anodization is carried out in an acidic electrolyte, a porous kind of layer is formed. In acidic electrolytes, the oxide film is created next to oxide-metal interface. Barrier layer acts as an initial layer before the formation of the porous layer [5, 8].

## 2.3 Mild and Hard Anodization

They are used for many applications in industries. The growth of oxide layer in hard anodization (HA) is 25–35 times faster than mild anodization (MA). Though, in mild anodization the growth of oxide layer is slower when compared to the hard anodization, but the formation of nano structure and arrangement of nano pores is well-defined. Whereas, the growth of oxide layer is faster in hard anodization but the nano structure formation and arrangement of nano pores are not well-defined [5].

Lower temperatures and higher currents are used to perform HA. But in a few cases, a satisfactory oxide layer can be attained at slightly higher temperatures. The pores formed due to hard anodization are smaller when compared to the standard anodization [10].

## 2.4 One-Step Anodization

One-step anodization [11], the name itself indicates that the anodization is performed only once. Before anodization procedure is carried out, the sample is degreased and then it is electropolished. Then the sample is anodized with the current supply at



Fig. 2 a Pre-treated aluminum, b Porous AAO-barrier AAO-unanodized aluminum, c Porous AAO-barrier AAO, d Porous AAO [11]

certain voltage, which in turn results in the formation of porous oxide layer on the surface of the sample along with the barrier layer and unanodized aluminum. Further, the unanodized aluminum and the barrier layer are removed, which results in porous AAO as shown in (Fig. 2).

# 2.5 Two-Step Anodization

There are several techniques that are identified for anodization. Two-step anodization is one among those techniques. In one-step anodization, the anodization procedure is performed once. Here, in two-step anodization, the anodization procedure is performed twice with the same conditions that are utilized for the first step. In two-step anodization, the material which is to be anodized is considered as anode and it is coupled to the positive half of the DC power source. Whereas, suitable material is considered as cathode and is coupled to the negative half of the DC power source. Next, the aluminum material is ultrasonically cleaned and electropolished for the better surface quality of the material. By applying the anodization conditions like a choice of the electrolyte type, concentration, applied potential, temperature and anodization time the oxide layer is formed. The formed oxide layer has asymmetrical arrangement and construction of the nano pores. The barrier layer is removed from the aluminum surface and the additional anodization is accomplished with similar conditions as shown in (Fig. 3). After completion of the anodization, the formed oxide layer has a systematic arrangement and construction of the nano pores. Twostep anodization is considered as the better technique for the proper formation of the nano porous structure on the aluminum [6].

# **3** Influence of Various Electrolytes on Surface Morphology of AAO

Lee [5] discussed about three kinds of anodization likely mild, hard and pulse anodization. They have used a potential of 25 V for sulphuric acid, 40 V for oxalic acid and 195 V for phosphoric acid. The arrangement of the pores was in hexagonal arrangement and square arrangement as shown in (Fig. 4).



Fig. 3 Two-step anodization [5]



Fig. 4 SEM top view of Al samples anodized in a Sulphuric acid at 25 V, b Oxalic acid at 40 V, c Phosphoric acid at 195 V [5]

Chung and Lee [12] presented about two anodization methods they are DCA and HPA. The experimentation was performed at 5-15 °C in 0.5 M of oxalic acid for 1 h. The effect of changing temperature and voltages on the AAO films for one-step anodization is been studied. By increasing the temperature better porous structure is formed with a widening of the pores.

Sulka and Parkoła [13] have discussed about the influence of temperature on the well-ordered nano porous structures of aluminum. Sulphuric acid is used as an electrolyte and the temperature ranges are -8, 1, 10 °C. The temperature of 1 °C and

**Fig. 5** SEM top view of Al samples anodized at 0 °C in phosphoric acid at 160 V after the second step for **a** 14 h, **b** 40 h, **c** with adding of methanol [14]

potential of 25 V depicted the rise in the homogeneity of pore diameter and interpore distance.

Zaraska et al. [14] stated the effect of the procedure time, anodizing voltage and addition of methanol on the physical features of oxide layer formed in a 0.3 M of  $H_3PO_4$  solutions by two-step anodization. The porous nature improves with a rise in voltage and time. With adding of methanol there was well regularity of pore size as displayed in (Fig. 5).

ZHOU Jian-Hua [15] discussed the impact of the chemical etching procedure done in acid and alkaline solution. The anodization of aluminum sheets is performed at 17 °C for 4 h. On performing chemical etching in an acidic solution, nano wires are formed. In alkaline solution, nano tubes are formed as shown in (Fig. 6).

Rahman et al. [16] presented a comprehensive examination of the pore-widening rate of nano porous anodic alumina layers as a function of the potential applied. The voltage is altered and electrolyte, concentration is kept constant. It is revealed that in pore-widening method, the porosity upsurges at a quicker rate for lower anodization potentials.

Lisenkov et al. [17] represented two different methods for anodization likely potentiostatic and discharge approaches. Deionized water is used as an electrolyte.



Fig. 6 SEM images when chemical etched in a Acidic solution, b Alkaline solution [15]



**Fig. 7** SEM top view of Al anodized for 24 h/2 h (1st step/2nd step) in **a** Sulphuric acid at 1  $^{\circ}$ C at 25 V, **b** Oxalic acid at 2  $^{\circ}$ C at 40 V, **c** Phosphoric acid at -1  $^{\circ}$ C at 160 V [18]

The determined thickness of the anodic film improved with cumulative voltage, but at a potential above 1800 V oxide layer will not be organized by any method due to film collapse.

Dobosz [18] discussed about anodization of aluminum in sulphuric, oxalic, and phosphoric acids as electrolytes. Each maintained at 1, 2 & -1 °C. Results were studied for different voltages. It was observed that the nanostructures have the determined order underneath certain quantified conditions as shown in (Fig. 7).

Chernyakova [19] deliberated about how the anode temperature affects the morphology of the AAO and also the growth rate. The potential and electrolyte temperature were kept constant. Highly ordered porous structure is shaped by changing the temperature of the anode.

Chowdhury et al. [20] discussed about the Influence of process parameters on pore dia. and growth rate of the structure. The temperature and voltage are varied. Experiment was conducted in 0.3 M of oxalic acid at a temperature of 5, 10 and 15 °C and voltage of 30, 45 and 60 V. It is observed that with voltage, temperature and time the pore sizes were affected. The calculated pore size displays a linear difference with anodizing potential. Better porous structure is formed at optimum conditions as shown in (Fig. 8).

Bruera [21] discussed about formation of nano structure by two-step anodization in sulphuric acid, changing the concentration and temperature of the electrolyte and



Fig. 8 SEM image of Al sample prepared at 10 °C in 0.3 M of oxalic acid at 45 V [20]
200 nm a b

Fig. 9 SEM image of Al sample produced at a 10 °C in 0.3 M of  $H_2SO_4$  at 20 V, b 5 °C in 0.3 M of  $H_2SO_4$  at 15 V [21]

anodization voltage. The best ordering conditions (Fig. 9) are at 10  $^{\circ}$ C and 0.3 M sulphuric acid at 20 V, 5  $^{\circ}$ C and 2 M sulphuric acid at 15 V.

Zhang [22] presented three step anodization following 1st step for 10 min, 2nd step for 0.5-12 h and 3rd step for 3 min for the perfect hexagonal arrangement of the pores. Here the anodization was performed at 0.3 M of oxalic acid with 40 V [DC] at 0 and 15 °C.

Zaraska et al. [23] have discussed about AAO films produced by a two-step anodization in 0.3 M of oxalic acid under several anodizing circumstances. The impact of anodizing temperature on physical topographies and porous structure of AAO was examined at -1, 3, 7 and 10 °C. With the increase of temperature, the growth of pore size, porosity of oxide layer and decrease in thickness is observed.

Refer (Table 1) for proper understating of the anodization parameters used and their effect on the surface morphology of AAO i.e., their effect on the Pore diameter (nm), Interpore distance (nm) and Porosity (%).

### 4 Conclusions

There are various parameters like electrolyte concentration, temperature, voltage and anodization time that have an effect on the surface morphology of AAO. But, the applied voltage in various electrolytes is of most importance for the well-ordered arrangement of the nano pores. The temperature and anodization time is main to obtain better pore density as well as interpore distance. For sulphuric acid, the voltage range varies between 15 and 25 V because it cannot withstand higher current densities. The optimum potential of 25 V was recorded for sulphuric acid in order to achieve well-defined nano porous structure and systematic arrangement of the nano pores. The potential of 40 V for oxalic acid is considered as optimum value in order to achieve uniform pore size and well-defined arrangement of the nano pores. The higher potentials are considered for phosphoric acid when compared to sulphuric acid and oxalic acid. In phosphoric acid, anodization carried out at 180 V showed a

Table 1 Illustrati	ion of anodizing	parameters and the	eir effect on the	Pore diameter	(nm), Interpo	ore distance (nm)	) and Porosity (%)	
Concentration (M)	Temperature (°C)	Potential (V)	D <sub>P</sub> (nm) Pore diameter	D <sub>INT</sub> (nm) Interpore distance	α (%) Porosity	Time	Remarks	Reference
0.3 M of Oxalic acid	1	40	20-400	100	10–30%	1	Mild and hard anodization	[5]
0.5 M of Oxalic acid	5-15 °C	2-40	$40 \pm 5, 35 \pm 5$	1	82.9% 92.6%	1 h	One-step DCA, HPA	[12]
0.3 M of Oxalic acid	17 °C	40	50-1st step, 100-2nd step	I	1	4 h	Two-step anodization	[15]
0.3 M of Oxalic acid	5-7 °C	1st step-40 V, 2nd step-20 to 50 V	202	I	28%	20 h/ 10–20 min 1 st step/2nd step	Two-step anodization	[16]
0.3 M of Oxalic acid	2 °C	30-60	$30 \pm 5 \text{ to } 65 \pm 4$	<u>9</u> 9 ± 17	8–39%	1st/2nd step 24 h/2 h	Two-step anodization	[18]
0.4 M of Oxalic acid	5-60 °C	40	31	104–111	1	1 st/2nd step 30 min/45 min	Two-step anodization	[19]
0.3 M of Oxalic acid	5, 10 and 15 $^{\circ}C$	30,45&60 V	85	133	I	1 st/2nd step 5 h/2 h	Two-step anodization	[20]
0.3 M of Oxalic acid	0 and 15 $^{\circ}$ C	40	60	104	31.6%	1 st/2nd/3rd 10 min/ 0.5–12 h/3 min	Three step anodization	[22]
0.3 M of Sulphuric acid	1	25	20-400	63	10–30%	1	Mild and hard anodization	[5]
								(continued)

# Influence of Various Electrolytes on Surface Morphology ...

Table 1 (continu	ed)							
Concentration (M)	Temperature (°C)	Potential (V)	D <sub>P</sub> (nm) Pore diameter	D <sub>INT</sub> (nm) Interpore distance	α (%) Porosity	Time	Remarks	Reference
20 wt% of Sulphuric acid	$^{-8}$ , 1 and 10 $^{\circ}$ C	15–25	6.3–14, 4.2–6.3, 1319.6	30.1–37, 2.4–3.7, 31.4–35.7	1	10 min	Chemical vapor deposition	[13]
0.3 M of Sulphuric acid	1 °C	15–30	$\begin{array}{c} 18 \pm 4 \text{ to } 39 \\ \pm 4 \end{array}$	66 土 4	7–32%	1 st/2nd step 24 h/2 h	Two-step anodization	[18]
0.3 M of Sulphuric acid	5, 10, 20 and 30 °C	10, 12, 15 and 20 V	15.8–34	28.6–56.0	14-34%	1 h for each step	Developing structures using diff. electrolyte conc., temp., and voltage	[21]
0.3 M of Phosphoric acid	I	195	20-400	500	10–30%	I	Mild and hard anodization	[5]
0.3 M of Phosphoric acid	0 °C	160	95–210	310–480, 340–440, 330–430	1	8 h, 14 h, 8 h [mixed with methanol]	Increasing anodization potential and process duration	[14]
0.17 M of Phosphoric acid	-1 °C	120-300	105 ± 12 to 232 ± 15	$425 \pm 98$	6–27%	1st/2nd step 24 h/2 h	Two-step anodization	[18]

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significant improvement in the uniform arrangement of the pores and pore roundness but the circularity of pores is not well-achieved.

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# **Impact of Protein Nanoparticles on Beer** Foam



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# 1 Introduction

In terms of global consumption, beer falls short of only water and tea [34]. The average per capita consumption of beer in the world is 22.6 L as of 2020 [31]. In 2020 beer brought in revenues amounting to US\$522,299 million. It has been estimated that the beer market will grow at a rate of 9.4% [31]. This shows that the beer industry is growing rapidly and has a very huge market. India's overall consumption of alcohol has moved to around 6.5 billion liters by the year 2020 [12]. Indian beer industry generated revenue of USD 13,770 million in 2020. The market is expected to grow annually by 11.5% [30].

Beer is a very complex combination of over 450 different compounds viz water, yeast, etc. each having a characteristic impact on the taste, texture, or visual aspects of beer. Proteins, nucleic acids, etc. are some of the components present in the beer. Generally, protein is the main ingredient that influences the brewing process of beer. There are other ingredients that help in maintaining beer quality such as carbohydrates (from malt), hops, yeast, and water. Good quality beer has many health benefits if taken in considerable amounts regularly. It improves white blood cell counts in humans [25].

A foamy layer is the main characteristic of the quality of the beer. It is one of the primary characteristics that create an impression of the beer in the consumer's mind even before drinking. This foamy layer can have varying stability, texture, density, color, bubble size, and flavor. Foam is the most important part of the beer- it has a great advantage such as it prevents blotting by releasing  $CO_2$  gas. Stagnant surface behavior results in the formation of small bubbles and droplets in the formation of foam [23].

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Variations in the types and concentrations of lipids and proteins exert different effects on the stability of beer foam. Each macromolecule has its own unique effect on the beer. Thus varying the concentration of different macromolecules impacts the beer foam. Protein content in the final product is determined by the raw materials and processes which are used during the production of beer. Foam stability is affected by two types of compounds, one that stabilizes it and others that degrade it. Proteins are foam stabilizing compounds, foam stability increases with the increase in the amount of protein production [24].

Protein nanoparticles (PNPs) possess several advantages such as biocompatibility, non-toxic nature, etc. which can be used in improving food nutrition. Generally, protein-based nanoparticles (NPs) have many applications such as foam stabilization, emulsion stabilization, and encapsulation of bioactive molecules. Brewers are interested in the beer foam stability as it impacts the consumers. The beer foam stability is affected by the protein nanoparticles and also the beer brewing conditions. Mostly, the studies regarding PNPs are focused on the extraction of proteins from various food sources for better nutrition properties in different environmental conditions. Desolvation is considered the best process for synthesizing PNPs. The pH plays a major role in the foaming studies. At neutral pH, heat treatment increased foamability.

The uniqueness of this paper is that here the impact of PNPs on beer foam stability will be discussed which has not been discussed before. Proteins improve the foamability of the beer. They tend to get adsorbed to air/water interfaces [17]. This review paper also discusses the beer bubble formation and growth. This field is open for research and there is no review paper related to beer that talks about different aspects related to beer including the beer foam stability, beer quality, and factors affecting the beer foam. This paper also covers future perspectives.

## **2** Beer Bubble Formation and Growth

### 2.1 Formation of Bubble

Beer is supersaturated with  $CO_2$  during packaging, but to initiate bubble formation, external stimulation is needed such as a dispenser like a bottle or a tap. These sites are called nucleation sites. Nucleation sites ideally should be small to generate tiny bubbles that form a thick and consistent foam layer, most appealing to the consumer [1]. After few seconds, drainage is witnessed in the foam layer due to the lack of any protein particles. This draining of beer from the foam layer creates drainage streams that weaken the bubble layer eventually leading to the collapse of the foam layer. This phenomenon is termed "Drainage". Bubble formation takes place at nucleation sites in a repetitive manner, providing a "creaming" effect [1, 16].

### 2.2 Growth

Once the bubble is nucleated, the bubble grows in size collecting gasses, and finally detaches from the nucleation site [13]. The detached bubble size is a function of numerous parameters namely rate of molecular diffusion, nature and degree of nucleation sites, viscosity, and surface tension [3]. The size of bubbles generated contributes to the visual appeal of the beverage. Bubble size also impacts the sensory impact of beer; smaller bubbles transport  $CO_2$  more efficiently which causes a "tingling" sensation on the tongue surface. Smaller bubbles also don't disturb the foam layer, leading to a long-lasting foam layer over the beer surface. Therefore, smaller bubbles are favored in a glass of beer which is achieved by the addition of surfactants [3].

# 2.3 Gushing of Bubbles

While so many factors help in stabilizing the foam and facilitating bubble growth in the foam layer, over foaming may occur. The phenomenon of carbonated beverages like beer, wine, etc. vigorous over foam on opening the container is termed "gushing" [27]. This occurs due to chain nucleation and growth of bubbles- this phenomenon is favored in ceremonial containers of wine and sometimes in beer also [6, 26]. Most of the time, beer or wine is purposefully highly pressurized to produce microbubbles in the liquid which explode when the pressure is removed by removing the cork of the container initiating the chain reaction [6]. It thus enhances gushing and is generally used in ceremonial wine or beer bottles [28]. Also, protein nanoparticles may be introduced to increase foam stability and foamability in beer.

# 3 Factors Affecting Beer Foam Stability

Beer foam stability depends on many components of the beer like cations, hop acids, protein, lipid, polyphenol, Lipoxygenase-1,  $\beta$  Glucan, Malt source, etc. [8, 11, 15, 28]. As a raw material for brewing, white-skinned, low polyphenol cultivars of sorghum are most likely used [19]. Out of these components, protein is the most important factor in determining foam stability. Foam is an emulsion of gas in a liquid containing soluble surfactants [14]. During the foaming process a series of events, in sequence, take place. These are namely formation, growth, and detachment of foam bubbles. In terms of persistence, there are two types of food foams. The ones concerned with the products like coffee and beer have poor persistence as these items are consumed in a short time window. Whereas the foam related to food items like ice cream and mousse requires much longer foam persistence, as these items are to be preserved for a much longer duration [5]. Particle surfaces are intimately linked to particle

size. With increasing particle size there is a reduction in the number of surface particles. These impact the interface phenomena associated with surfactants [17]. Proteinaceous compounds called hydrophobin give rise to highly persistent foam and are therefore looked at as competent surfactants [28].

# 3.1 Impact of Protein and Protein Nanoparticles on Beer Foam Stability

Proteins affect the metabolism of yeast and the beer characteristics such as its quality and foam head and thus are of primary importance in wort and beer [9, 21]. Protein normally originates from barley malt in the brewing process. Surface active protein and polypeptides are beer foam stabilizers and their hydrophobicity is a major supporter of the rise in beer foam stability [33]. Protein must be capable of unfolding at the surface and rapid adsorption to have good foam making ability [1]. Proteins are natural surfactants that can stabilize the interface between any two phases. A part of the durability of protein films is attributed to their interfacial rheological characteristic. They stabilize foam and are responsible for flavor stability and mouth feel in protein-protein linkage [32]. Up to 80% of the beer polyphenol is said to have originated from the malt depending on the type of beer and the remaining part originated from hops. There are 4 types of proteins derived from barley and involved in foam formation such as LTP1p (Lipid transfer protein), 9.7-kDa polypeptide, Protein-Z, and 40 kDa polypeptide. Some polypeptides are obtained from yeast during the fermentation and brewing process. Among all, Protein-Z was found to be the prevalent protein in beer foam. This protein was found to be positively correlated with foam stability [18]. For better foam stability, protein nanoparticles play a major role in beer foam. Increasing PNP concentration tends to improve foam stability by decreasing the liquid flow within the lamella region [10]. Also, the foam production methods like bubbling, shaking, etc. may have an impact on the beer foam stability. Foams which are produced from bubbling are generally unstable due to lesser protein concentrations. The pH conditions are also very important to affect the protein surface properties related to the foam stabilization. The solubility of the proteins can impact the stability of the foams produced. Proteins in the form of solid particles and their effects are important in this context. The protein foam stability tends to increase with increasing liquid viscosity. The beer foam stability may be influenced by different interface properties due to protein molecule interactions. The chemical structure of the protein molecules may also impact the interfacial properties. Unwanted proteinic particles can be discarded during the brewing process in two ways. First is the yeast stress and the second is the high gravity brewing which results in the release of proteinase that lowers hydrophobicity and gradually decreases the foam stability [4].

### 3.2 Other Factors Which Affect Beer Foam

### Haze

Haze formation is bad for beer as it affects the product and makes the beer foam look less attractive visually. Beer haze is normally formed due to the complexation of polyphenolic beer ingredients. Beer haze doesn't look good on beer and is judged by the consumers. Polyphenol and beer protein are the factors that contribute to the formation of haze [22]. Unwanted haze can come into the beer by the pasteurization of beer containing albumen [2]. This problem can be solved by lowering protein and/ or polyphenol levels or by minimizing their sizes. Haze-active materials are generally removed to preserve the colloidal stability [29].

#### Mashing Temperature

To produce a stable foam, maximum amount of protein should be extracted from the malt. These proteins are then extracted out to form protein nanoparticles and then put in the beer in the later brewing process before packaging. If the mashing temperature is lower than 55 °C, it causes a loss in foam promoting proteins because proteolysis remains active [7, 20]. If the mashing temperature is high (>71 °C), protease activity is inhibited and proteins assist in the stabilization of beer foam.

## 4 Conclusion and Future Perspective

Beer is consumed all around the world, and its overall consumption is less than only water and tea. This has led to beer being developed in an enormous market, where beer quality, visual appeal, and flavor have become extremely important. Also, flavor, consistency, and the quality of beer are essential for a good consumer experience. The first thing that plays a role is the visual appeal of the product. Visual appeal includes the color, consistency of beer, and beer foam. Beer foam helps in determining the beer quality and is one of the factors responsible for creating a good or bad impression on the consumer. Beer foam serves two purposes:- firstly, it provides a delicious look to the drink. Secondly, it protects the flavor of beer by preventing CO<sub>2</sub> escape and it also prevents quick oxidation of beer, thus acting like an airtight seal over the beer and preventing blotting which is harmful for human health. It has been found from literature studies that protein nanoparticles help in the stabilization of foam for a little longer time without much drainage in malt beer. The pH plays a major role here. At both low and high pH, foam remains stable due to protein NPs used with a combination of any secondary foam enhancer according to various literature. If the foam of the beer stays for a longer time, then it's a benefit for consumers' health. More foam leads to more release of carbon dioxide from beer. As it has been previously reported that Protein-Z plays a major role in beer foam stability, thus all other proteins derived from barley must be worked more to obtain better foam

stability in beer. Various protein nanoparticles can be used for foamability in food. These are not only applicable for beer but also for different proteinaceous products (milk, egg, coffee, etc.) and, for different cosmetic applications such as shampoo, soap, face wash, etc.

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# Numerical Simulation of High Efficiency Perovskite Solar Cell for Indoor Application



Km. Neeraj, Brajendra Singh Sengar, and Saurabh Mishra

# 1 Introduction

The remote sensors, actuators, and communication devices are all electronic devices that consume little power. The amount of power required to effectively operate these devices is decreasing on a continuous basis. An indoor photovoltaic cell is used to provide power to billions of wireless devices connected by the internet. The Internet of Things (IOT) predicted in the future, a large network of low-power electronic devices will be able to collect large amounts of data, thanks to the Internet of Things. At the moment, indoor photovoltaics can significantly reduce the amount of battery power required to power these devices, [1–3]. A device which converts indoor light into electrical power or energy known as Indoor Photovoltaic device, organic photovoltaic devices are some of the types of PV that are applied to change Indoor light into electrical energy. A metal halide perovskite material based Photovoltaic device is the best addition of Photovoltaic device family.

A popular newcomer to the PV market, PSCs has high energy conversion efficiency (ECE), low recombination rate, high absorption coefficient, and long carrier life time when compared to other types of solar cells [4–9]. Power conversion efficiency is the parameter that plays an essential role in performance and can be defined as the ratio of output power to incident power. Indoor light is less intense and has a narrower spectrum than natural light. Research scientists had reported 1000 lx fluorescent light design as a good light source for indoor solar cells [3, 10, 11]. The efficacy of perovskite solar cells was investigated using various artificial known light

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devices such as illuminants, halogens, fluorescent, Light Emitting Diodes [12–14]. Fluorescent and LED lights, on the other hand, were used due to their higher ECE and economy.

Metal halide perovskite-based PV devices (third-generation solar cells) have been used and gained interest in indoor applications in recent years [15–17]. The perovskite solar cell (PSC) is a device that is made of combining organic and inorganic semiconductors to cater for the limitations of a single semiconductor and to make the device highly efficient. The Metal halide perovskite solar cell (MHPSC) device is a hybrid halide device with disruptive technology, having an inverted planar structure has been reported to achieve high ECEs than under 1 sun illumination.

Being an area of interest, in continuation, the researchers and scientists endeavored diverse tactics like device design, and controlling the recombination phenomenon in bulk and at the interface to improve the indoor energy conversion efficiency (i-ECE) of device structure [18–21]. With these efforts, MHPSCs had described to approach their theoretical efficiency value.

To achieve a greater, indoor- ECE with an increasing voltage in open circuit condition ( $V_{oc}$ ), minimize the current density of short circuit, ( $J_{sc}$ ) MAPbI2-xBrClx PSCs with a customized bandwidth, and stifled defect density is desirable for application. The low absorption of active layer of perovskite material in indoor light spectrum is an essential consideration to achieve a high open circuit voltage and ( $V_{oc}$ ) high i-ECE.

For analysis, the simulated tool is used to design and numerically simulate the MAPbI2-xBrClx (methylammonium lead iodide bromide chloride)- based metal halide perovskite solar cell device with an inverted planer structure for indoor application. The modeled structure of the device was investigated and confirmed by comparing it with the experimental research work reported in the scientific literature [22]. The parameters like layer's thickness and imperfections at the different interfaces were also investigated using numerical modeling and simulation techniques for their impact on the energy conversion efficiency.

### 2 Device, Design, and Model

SCAPS-1 dimensional simulation tool was utilized to model and simulate a thirdgeneration metal halide perovskite solar cell structure. This simulator utilizes two basic mathematical equations: (1) Poisson's equation and the (2) continuity equation [23] for design and simulation. The equations are as follows:

$$\frac{\partial}{\partial x}(\varepsilon(x)\frac{\partial\psi}{\partial x}) = -q[-n+p-N_A^-+N_D^++\frac{1}{q}(\rho_{def}(n,p))$$
(1)

$$\frac{\partial j_n}{\partial x} + G - U_n(n, p) = \frac{\partial n}{\partial t}$$
(2)

Numerical Simulation of High Efficiency Perovskite Solar Cell ...

$$\frac{\partial j_p}{\partial x} + G - U_p(n, p) = \frac{\partial p}{\partial t}$$
(3)

where  $\varepsilon$  is the dielectric permittivity, p, n are free carrier concentration, q is charge on electron,  $N_A^-$ ,  $N_D^+$  are charge dopant,  $\rho_{def}(n, p)$  is charge defect density,  $\varphi$  is electrostatic potential,  $J_n$ ,  $J_p$  are carrier density, G is generation rate,  $U_n$ ,  $U_p$  are recombination rate, x is thickness and t is time. SCAPS-1D uses finite difference method for discretization and the boundary condition are taken at interface and contact. The boundary conditions are given below:

$$J_n = D_n \frac{dn}{dx} + \mu_n n \frac{d\varphi}{dx}$$
$$J_n = D_p \frac{dn}{dx} + \mu_p p \frac{d\varphi}{dx}$$

where  $J_n$  represent the Electron current density,  $D_n$  represent electron diffusion coefficient  $\mu_n$  represent electron mobility,  $J_p$  represent Hole current density and  $\mu_p$  represent Hole mobility (Fig. 1).

Chang et al. (2019) and co-researchers<sup>[22]</sup> have reported an investigation on triple-anion Perovskite-based photovoltaic cell with tailored bandwidth of 1.7 to 1.8 eV. They fabricated MHPSCs with inverted planer structure  $[In_2O_5Sn/NiO_x/$ MAPbI<sub>2-x</sub>BrCl<sub>x</sub>/PC61BM/Ag] for examining it for indoor light harvesting, and recorded high efficiency of 36.2%. The basic properties for our simulation study, like light intensity (Lux); temperature;  $J_{sc}(mAcm^{-2})$ ;  $V_{oc}$  (V); FF (%) etc. were taken from the experimental study conducted by Chang et al. [22]. Moreover, with the exploration of the literature, we collected the available data for our modeling and simulation study. The neutral defect (Gaussian) was located above intrinsic energy level for the defect states in MHPSC device (MAPbI2-xBrClx). A single level defect had been placed above intrinsic energy level in the charge transport layer. 1000 lx fluorescent light has been chosen as the standard light source for indoor photovoltaic cell. In the above simulation study, we attempted the investigation on MHPSC device with the parameters affecting the energy conversion efficiency (ECE) like current density of short circuit, voltage in open circuit condition and FF of the circuit. Moreover, investigation results have been compared and well matched with the experimental research works in the scientific literature [22]. The lower trap-state of the perovskite active layer, as well as less carrier recombination at the perovskite active layer, may explain why the inverted planar structure has a higher efficiency.

The basic properties that are utilized for the simulation study are listed in Table 1. However, the interface imperfections are shown in Table 2 (Fig. 2).





# **3** Results and Discussions

# 3.1 Thickness Variation

Absorber layer thickness is an essential parameter, it is considered for fabrication of photovoltaic cell. With the variation in thickness, many other parameters can be improved resulting in an enhancement in further output performance of the solar cell. A Perovskite layer thickness variation had investigated, found by increasing thickness brought an increment in current density of short circuit as shown in Fig. 3. It had examined that for a thickness of 1.1  $\mu$ m, the rate of increase in the value of  $J_{sc}$  was 1.266 mA/cm<sup>2</sup>. Further, it was also observed that after a certain thickness value, if we increase the thickness, we observed a decreasing trend in  $J_{sc}$ . However, the rate of increment was high, due to low absorption coefficient of Perovskite material. Indoor light with low incident power can only generate a few electrons. Because of

Layer property	NIO <sub>x</sub>	MAPbI <sub>2-x</sub> BrCl <sub>x</sub>	PC <sub>61</sub> BM
d(nm)	50	700	60
$E_g$ (eV)	3.8 [24]	1.9	1.8
χ (eV)	1.9	3.75 [25]	4.1
$N_a (\mathrm{cm}^{-3})$	$3 \times 10^{18}$	0	0
$N_d (\mathrm{cm}^{-3})$	0	$1 \times 10^{13}$	$1 \times 10^{17}$
Er	11.7	13	4
$\mu_e (\mathrm{cm}^2/\mathrm{Vs})$	2.8 [24]	5	$1 \times 10^1$
$\mu_h (\mathrm{cm}^2/\mathrm{Vs})$	2.8 [24]	5	$1 \times 10^1$
$N_c ({\rm cm}^{-3})$	$2.5 \times 10^{20}$ [24]	$1 \times 10^{15}$	$1 \times 10^{20}$
$N_v ({\rm cm}^{-3})$	$2.5 \times 10^{20}$	$1 \times 10^{20}$	$1 \times 10^{21}$
Contact properties	Front		Back
Surface recombine speed of the electron $(cms^{-1})$	107		10 <sup>6</sup>
Surface recombine speed of the hole $(cms^{-1})$	107		107
qφB	0		0
Reflectivity	0.06		0.7

Table 1 Attributes Include In the simulation study

**Table 2** Attributes utilized inthe interface defects

Defect type	Neutral
Defect density $N_t$ (cm <sup>-2</sup> )	Varied 10 <sup>11</sup> -10 <sup>20</sup>
Electron cross section area (CSA) $\sigma_n$ (per cm <sup>2</sup> )	10 <sup>-16</sup>
Hole cross section area (CSA) $\sigma_p$ (per cm <sup>2</sup> )	10 <sup>-17</sup>
Distribution	Gaussian
Defect with reference (energy level)	Upper valance band energy level $(E_v)$
Characteristic energy(eV)	1.1

this, an indoor Metal halide Perovskite-based solar cell (MHPSC) device can have a thicker absorber layer than a single SUN device. Because the diffusion length of the carrier is high in indoor devices, less recombination occurs, and the depletion layer moves away from the back contact, resulting in fewer electrons captured by the back contact for recombination. Furthermore,  $V_{oc}$ , increase with thickness.  $V_{oc}$ , increase confirms lower charge recombination in thicker film. The increase in  $V_{oc}$ , is less than the increase in  $J_{sc}$ . The Simulation results show that a thicker Perovskite absorber layer improves the performance of MHPSC device.



## 3.2 Bulk Defect Variation

The device's efficiency is dynamically affected by both the number of defects and characteristics of those defects. When it comes to perovskite, having a solid understanding of the function that bulk defects play in device performance is of the utmost importance. The bulk defect density was investigated and the investigation resulted in current–voltage characteristics with the variation in defect density displayed in Fig. 4. As seen in the plot of a metal halide perovskite solar cell, a high defect density leads to a decrease in charge carrier diffusion length. In exchange, the carrier's life expectancy will be reduced. The diffusion length and carrier life time have a significant impact on device performance. Figure 4 demonstrates a significant decrement in





open circuit voltage ( $V_{oc}$ ) when defect density was varied from  $10^{11}$  to  $10^{12}$ . However, Short circuit current ( $J_{sc}$ ) was not affected by this variation. It is possible because perovskite materials have a high crystallinity, which leads to a lower defect density. This is something that has been reported by a number of researchers [25].

In addition, as we increase the defect density from  $10^{12}$  to  $10^{13}$  the value of  $V_{oc}$  remains the same while  $J_{sc}$  is decreases. Following the increase in defect density from  $10^{14}$  to  $10^{17}$ , a significant decrease in both  $V_{oc}$  and  $J_{sc}$  is observed.  $V_{oc}$  remains constant while  $J_{sc}$  decreases from  $10^{12}$  to  $10^{13}$  because  $10^{13}$  cm<sup>-3</sup> is the minimum number of defects in the active layer. The recombination rate in a perovskite solar cell is high due to an increase in defect density.  $V_{oc}$  and  $J_{sc}$  both decrease as defect density increases from  $10^{14}$  to  $10^{17}$  because diffusion length and carrier life time are reduced. As defect density increases, the parameters of perovskite solar decrease.

# 3.3 Interface Defect Variation

The recombination rate is increased by occurring different types of defects at the interface, resulting in needy device quality. Researchers had faced limitations and problems in modeling recombination at the interface. However, the best way to model recombination at the interface is by inserting a fine film of a material and studying the imperfection at the intersection.

 $NiO_x$  (TL1) and PC<sub>61</sub>BM (TL2) were then separated by two thin interfacial layers. The amount of defect varied from 10<sup>11</sup> to 10<sup>20</sup>. This investigation analyzes the importance of interface for contributing to the efficiency of MHPS device. Figure 5 shows the consequences of interface defect on the efficiency, current density of short circuit and voltage in open circuit conditions. From these results, it can be observed that the defects occur on the interface of TL1 resulted in negligible consequences on the device quality. However, the device's quality is significantly impacted by the defects that occur on the TL2 intersection. This dramatic behavior at the interfaces may be the effect of generating a higher number of hole-electron pairs at TL2 interface than at the TL1 interface.



Fig. 5 Efficiency,  $J_{sc}$ ,  $V_{oc}$  variation with interface defects at a  $NIO_x$ /Perovskite b Perovskite/ PC<sub>61</sub> BM

# 4 Conclusion

SCAPS-1D simulation tool was utilized to construct a stable MHPSC device with customized bandgap. The following conclusions can be drawn as follows:

• This material has a wide bandgap for indoor light spectrum and it also inhibits trap-states and nonradiative recombination.

- The simulated device structure of MHPSCs has a lower defect density and also a lower absorption coefficient with absorber material can divulge both the high voltage in open circuit condition and current density in short circuit condition.
- The consequences of defect density are lower for the transport layer first interface than for TL2 interface
- The efficiency of IPV devices was obtained at 35.48% when the different parameters were optimized.

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# Check for updates

# **Computational Validation and Nanofabrication of** *Withania Somifera* Extract for CNS Targeting Against Alzheimer's Disease

Divya Jindal, Pranav Pancham, Shalini Mani, Rachana, Shazia Haider, and Manisha Singh

# 1 Introduction

According to World Health Organization (WHO), neurological disorders contributed to the highest percentage (6.2%) of the total index among all diseases. Globally, Alzheimer's disease (AD) is the second-highest (12%) neurological disorder (NDD) after cerebrovascular diseases. The NDDs are a heterogeneous group of disorders that are characterized by the progressive degeneration of the central nervous system (CNS) primarily along with the peripheral nervous system (PNS) which in turn affects their functions [1]. AD has been investigated extensively and is characterized by two major neuropathological hallmarks leading to the initiation and disease progression-the first one is the accumulation of amyloid B (AB) plaques and the second is neurofibrillary tangles (NFTs) of tau ( $\tau$ ) proteins associated with neuroinflammatory changes [2]. Additionally, it has been observed that insoluble amyloid fibrils aggregated in AD conditions are the primary contributor to its pathogenesis. The amyloid fibrils are composed of Aß peptide 39-42, derived from a transmembrane glycoprotein amyloid precursor protein (APP) [3]. The popular understanding of tau  $(\tau)$  is that it is a protein that undergoes aberrant phosphorylation before forming the toxic aggregates linked to AD and other tauopathies. Phosphorylation of  $\tau$ , on the other hand, could be a normal but disruptive activity and degradation of the

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protein [4]. Subsequently,  $\tau$  is subjected to a variety of Post-translational Modifications (PTMs) along with various phosphorylation activities such as acetylation, ubiquitination, glycation, glycosylation, SUMOylation, methylation, oxidation, and nitration [5]. A comprehensive understanding of how these PTMs regulate  $\tau$  in a balanced physiological mechanism and what are the various possible related causes that cause AD pathogenesis is still lacking.

There are certain unexplored targets in a neuronal system that can be inhibited and eventually helps in decreasing the effects of associated proteins in the signalling pathway. TSPO (Translocator Protein) [6] and ADNP (Activity-Dependent Neuroprotective Protein) [7] are two amongst all proteins that can act as potential exclusive targets for limiting neuronal damage. These proteins further get dysregulated, causing neurodegenerative and neuropsychiatric disturbances. The 18-kDa protein TSPO is found in the contact regions between the outer and inner mitochondrial membranes. Owing to its ability and affinity to bind with diazepam, it was previously known as the peripheral benzodiazepine receptor (PBR). And due to the presence of a cholesterol recognition amino acid consensus (CRAC) domain in its C-terminal region, TSPO has a high affinity for cholesterol. It is made up of 169 amino acids grouped in five alpha-helical domains TSPO expression in the brain, on the other hand, is modest, with the protein present mostly in glial cells and at lower levels in neurons [8, 9]. TSPO expression, on the other hand, is known to rise in reactive astrocytes and microglia cells at regions of neuroinflammatory diseases, such as AD [10]. The fact that TSPO can be employed as a target for neuroprotective techniques stems from its location and functions. Compounds that act on the mitochondria have been proposed as potential therapeutic agents in neurodegenerative diseases since one of the most important functions of this organelle is to regulate cellular metabolism and energy production. The neuroprotective effects of TSPO ligands in experimental models of AD have been studied further. Tan et al. (2018) found that lower levels of TSPO are related to higher A $\beta$  deposition in rats chronically treated with lorazepam, implying that TSPO may be involved in the regulation of A $\beta$  levels [11]. The original drug-based peptide design technique was used to create these novel dipeptide TSPO ligands that used alpidem as a non-peptide prototype. The illuminating open-field and elevated plus-maze tests in outbred laboratory mice ICR were used to explore the anxiolytic actions in Balb/C mice (CD-1) [12].

Furthermore, the other ADNP is an activity-dependent neuroprotective protein that has been linked to a variety of diseases like schizophrenia, and multiple sclerosis including AD—where ADNP protein levels were found to be lower in patient serum samples compared to controls [13]. Furthermore, downregulation of ADNP has recently been hypothesized as an early pathogenic alteration in Parkinson's disease (PD) too, potentially contributing to dopaminergic neurodegeneration.

For AD, various drugs have been designed since 1968 and since then FDA has approved commercial formulations such as donepezil, alpidem, rivastigmine, galantamine, memantine, and aducanumab (most recently) date. However, they have some adverse effects and lesser efficacy to bypass blood brain barrier (BBB). Moreover, enzymatic action in the drug absorption and kinetics transforms these formulations into non-therapeutic intermediary molecules, resulting in extended side effects [14,

15]. The last few decades have seen an upsurge in Phyto therapeutics research interest against NDDs and the utilization of phytochemicals for the same. Since, efficient pharmacological treatment of dementia utilizing drugs (Donepezil, Galantamine, cholinesterase inhibitors, and benzodiazepines) is frequently lacking and has many incidental side effects. And it is quite evident from the various research studies done so far to identify phyto therapeutic drugs to improve neuronal functioning in the human brain. Natural products are thought to be safer, more affordable, and more readily available to the general public and thus, preferred more in recent times. Similarly, Tonics, rejuvenators, and vitalizers of Ayurveda seem to relieve disease and instigate resistance and life span in the patients [16]. One such neurologically important ancient aged tree variety Withania somnifera (Ashwagandha) is widely reported for treating and improving various neuronal ailments like dementia, multiple sclerosis, and hepatitis along with other cognitive impairments. Besides this, it is also utilized for several other disease conditions like glaucoma, vertigo, macular degeneration, etc. [17, 18]. It is used both as a nutraceutical and therapeutic agent, in Europe and most South Asian countries [19]. Many studies have shown Ashwagandha eases, inhibits, changes, or eliminates neurotic decay and synaptic dysfunction [20] and subsequently, can be utilized to treat NDDs significantly.

### 2 Methodology

### 2.1 In Silico Analysis of Phytocompounds of Selected Plant

The pharmacological success of a drug compound/extract depends on various facets of qualitative or semi-quantitative relationships between molecular structure of the same and its effect on the cerebral function. Thus, the standard consistently used pharmacological testing tools such as in vivo and in vitro models are extensively used since long. However, during the last decade, there is an increase in the development, growth, and implementation of computational (in silico) techniques for pharmacological hypothesis generation and testing. These in silico methods are primarily utilized in association with the production of in vitro data to both build and test the model. The development and optimization of novel compounds with their affinity for a specific target, as well as the elucidation of ADMET feature, with physicochemical characterization, have all benefited from such models [21].

### 2.1.1 ADME of Selected Compounds

The ADMET-related properties were determined by utilizing the Molinspiration tool running in typical mode. This tool produces truly significant descriptors and utilizes

them to perform ADME forecasts arranged by ADME-score—drug-similarity property, which was utilized to evaluate the pharmacokinetic profiles of the phytoconstituents present inside the library. The properties considered were—physicochemical analysis, number of heavy atoms, rotatable bonds, hydrogen bond receptors, hydrogen bond donors, molar refractivity, and TPSA [22].

# 2.1.2 Molecular Structures of the Target and Ligands

Molecular Docking of ligands of *Withania somnifera* (WiS) was carried out on specific targets of AD i.e., ADNP (Activity-Dependent Neuroprotective Protein) and TSPO (Translocator Protein). The PDB files of the required proteins were downloaded from the RSCB protein database (PDB, NCBI) and structure of all the phytocompounds of WiS is downloaded from the PubChem database.

# 2.1.3 Preparation of Target Proteins and Ligands

To estimate the binding affinity for the Receptor-ligand complex, binding energy was calculated for all the docked structures using GLIDE (Schrödinger). The proteins were prepared with a ligand to check the active site, further cleaned, and optimized using the protein preparation wizard tab in Schrödinger. The active site is selected as a site of ligands present in all these proteins. The proteins were prepared by the Prime program of the Schrödinger Suite. Then the proteins were minimized for stabilization to RMSD at 0.30 Å to unite heavy atoms with the OPL5\_2005 force field [23]. The phytocompounds of WiS were prepared by utilizing the Ligprep program in Schrödinger [24].

# 2.1.4 Receptor Grid Generation

Receptor Grids were set up after preparing the protein structure using the Receptor grid generation panel under Glide Tab to find all the probable active sites for all forms of ligands. For site-specific docking, the grid is formed around the active site where ligands were present.

# 2.1.5 Ligand Docking and Visualization

Ligand docking was done using the Extra Precision (XP) tool of the Glide program in the Schrodinger suite. The prepared protein and ligand were taken from the Ligand Docking panel of Glide to search for interactions between the protein and ligand. The poses were automatically generated by Glide. The 2-D representation of ligand and protein interaction was visualized by using a ligand interaction diagram. The diagram provides the types of interaction involved with different amino acids in varied colour representations [25].

## 2.2 Fabrication of Extract-Loaded Nano-Emulsions

### 2.2.1 Development of WiS Loaded Nano-Emulsions

Because of their varied lipophilic, hydrophilic, and amphiphilic phases, NE formulations essentially comprises of 3 types of excipients (oil, surfactant, and co-surfactant) to form different kinds of nano-emulsions (water in oil (w/o), oil-in-water (o/w), and bicontinuous types) making them more flexible drug carrier and delivery systems. For the listed phases, WiS extract phytocompounds were encapsulated based on their physicochemical features, HLB (hydrophilic and lipophilic balance) value of the chosen emulsifiers, nano-emulsion type selection (i.e., O/W and W/O), and GRAS (Generally Regarded as Safe) limits of selected excipients. So that the developed formulation can be clearer and more stable without causing any toxicity or irritation.

The solubility of extracts in various types of oils (Oils—isopropyl myristate (IPM), Castor oil, Linseed oil); Surfactants (TPP, Triacetin (glycerol triacetate), PEG, Pluronic acid, Cween 20, Cween 80); Co—surfactants (Ethanol, Isopropanol) was taken by mixing them with WiS extract [26]. To prepare the NE system first of all the oil phase was supplemented with different Smix ratios of surfactant and co-surfactant (1:0, 1:1, 2:1, 3:1, 4:1, 5:1, and 6:1) followed by vigorous vortexing. Further, this mixture was titrated with an aqueous phase with vigorous vortexing and mixing. All the steps of adding various listed excipients were accomplished under continuous stirring and shortlisted on the basis of visual inspection, for any phase separation, cracking, precipitation, transparency, and frothing/creaming effect.

### 2.2.2 Phase Studies

Based on the solubility analysis results; excipients (oil, surfactants, and cosurfactants) showing maximum solubility were proceeded for the construction of Pseudo Ternary Phase Diagrams using Origin Pro 2021 software. Experimentally, the surfactants and co-surfactants were taken in different ratios and were considered as Smix, further 16 different combinations of Oil and Smix ranging from 1:9 to 1:2 (9 combinations), 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, and 9:1 were taken for the study [27, 28].

#### 2.2.3 Thermodynamic Stability

Many concepts, such as interfacial/free energy (Gm) created in NE formulation, negative interfacial tension, and entropy of NE production, influence the thermodynamic stability and droplet size analysis of formulated nano-emulsions. The thermodynamic stability of created micelles is regulated by the free energy, surface charge, and double-layer interaction potentials of formed micelles. As a result, thermodynamic stability tests were performed on the optimized formulations that cleared the aqueous titration process and remained transparent under optical observation. Various optimized nano-emulsion formulations of extracts were subjected to fourstep analytical processes (heating cooling, freeze–thaw cycles, centrifugation, and dispersibility cycles) [29].

# 2.3 Characterization of Nano-Emulsions

### 2.3.1 Measurement of Particle Size, Poly Dispersity Index, and Zeta Potential

Nanometric size ranges of the particles are known to make their passage easier through different biological barriers, during targeted delivery therefore; we aimed to make the formulation in the nanometric size range. Particle size and Polydispersity Index of the sample were analysed by Particle Size Analysers which analyse the Brownian motion, gravitational settling, and light scattering of the particles. The surface charge of the particles draws a layer of oppositely charged ions, on their surface and forms a double layer of ions as the particles diffuse in the solution. This electric potential generated onto the edge of the double layer is called the zeta potential of the particles which ranges between  $\pm 100$  mV. The zeta potential analysis was performed to analyse the charge present on the surface of the particles in the colloidal solution using a particle size analyser [30].

#### 2.3.2 Transmission Electron Microscopy (TEM)

TEM is a frequently used method in nanomedicines and material science as they are capable of enhancing the imaging process with higher resolution and magnification than other types of microscopes. The sample was prepared by diluting the optimized microemulsions (1: 100 with mili Q water) and placing it in the centre of the carbon-coated copper grid with 2% phosphotungstic acid; the dried coated grid was taken on a slide and covered with a cover slip. The slide was observed under the electron microscope [31].

# 2.3.3 Measurement of Rheological Parameters (Viscosity, Conductivity, and pH)

Various other parameters like viscosity, conductivity, and pH were analysed for the optimized formulation. These parameters are the ones that are macroscopically observable and are used to characterize the given nano-emulsions. The rheological properties are used to detect the lamellar phase, which is suitable for drug delivery. It is reported that nasal irritation gets lower if any source gets delivered with a pH range between 4.5 and 6.5 [32]. The rheological parameters are the parameters that are macroscopically observable and are used to characterize the given nano-emulsions. One of the most easily noticed macroscopic properties of the colloidal systems is their rheology parameter: viscosity. The viscosity is an appropriate quantity for various plausible applications of nano-emulsions. The viscosity of nano-emulsions indicates the consistency of the fluid and is a measure of the internal resistance to the flow [33]. The conductivity measurement of nano-emulsions reflects its continuous phase or nature and due to the presence of an aqueous phase in either O/W or W/O types of nano-emulsion, it tends to either increase or remain almost equivalent to water. Generally, oil in a water nano-emulsions system with ionic amphiphiles shows a level of conductance at low temperature and low water content [34].

### 2.3.4 Release Kinetics

Franz diffusion cell-assisted release kinetics analysis was carried out using a pretreated dialysis membrane (D9652, Sigma Aldrich, Singapore) and the recipient compartment was loaded with phosphate buffer saline to analyse the release of extract from the prepared nano-emulsion system (PBS, 20 mL, pH 7.4). The formulations were added through the donor membrane, and after every 30 min, 2 mL of test samples (*Withania somnifera* and *Withania somnifera* loaded nano-emulsion) were removed and replaced with an equal volume of PBS to maintain the equilibrium. The experiment lasted 12 h, and the active phytoconstituents were measured by LC–MS analysis [34].

# **3** Results and Discussion

# 3.1 In Silico Analysis of Withania Somnifera

Various descriptors have been used to analyse the pharmacokinetic properties of the compounds. TPSA is the Topological surface area that a ligand covers on the protein surface while miLogP is the octanol–water partition coefficient. The tool checked their miLogP, natoms, molecular weight, number of OH atoms, and nrotb values. The ligands also checked for the rule of five signifying the Lipinski Rule. The ADME properties of selected phytocompounds of *Withania somnifera* is mentioned in Table 1.

Table 1 ADME of selected phytocompou	unds of Witho	mia somnife	ra						
Withania somnifera Phytocompounds	MiLogP	TPSA	Natoms	MW	HON	HNHON	Nviolations	Nrotb	Volume
17-Alpha-Hydroxywithanolide D	2.67	119.75	35	488.62	7	4	0	2	455.37
Somnifericin	2.77	124.29	35	490.64	7	4	0	3	466.46
Withanolide Q	3.48	104.06	34	470.61	6	3	0	3	446.01
Quercetin	1.68	131.35	22	302.24	7	5	0	1	240.08
Withanolide R	4.18	96.36	34	470.61	9	2	0	2	442.16
Withanolide E	3.18	116.59	35	486.61	7	3	0	2	449.16
Withanolide A	4.15	96.36	34	470.61	6	2	0	2	441.81
Withanolide J	3.75	104.06	34	470.61	9	3	0	2	445.1
6-Thioguanosine 5'-Diphosphate	-3.35	235.52	28	459.27	15	8	2	6	326.23
Alpidem	5.81	37.62	27	404.34	4	0	1	7	356.62

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Phytocompounds of Withania somnifera	XP GScore	Glide energy	Glide emodel
TSPO			
17-Alpha-Hydroxywithanolide D	-9.862	-47.589	-65.12
Somnifericin	-9.717	-26.557	-40.347
Withanolide Q	-9.358	-37.96	-32.949
Quercetin	-9.27	-38.624	-50
Withanolide R	-8.979	-41.998	-45.13
Withanolide E	-8.849	-41.564	-39.825
Withanolide A	-8.769	-47.389	-60.425
Withanolide J	-8.715	-43.569	-49.645
Alpidem	-8.563	-38.568	-39.805
ADNP			
6-Thioguanosine 5'-Diphosphate	-10.038	-52.421	-62.829

 Table 2
 Binding affinities of proteins with phytocompounds of Withania somnifera with different protein targets ADNP & TSPO

By using the Glide program of Schrodinger, docking of ADNP & TSPO is performed with all the phytocompounds of *Withania somnifera* and their respective controls. Out of all, few compounds have shown good binding affinities with the proteins and are stabilized by the same amino acids as their respective controls. It is assumed that the lower the energy, the more stabilized and stronger is the interaction between the two components. Site-specific docking was performed to the site where the native ligand is present. Site-specific docking was performed with selected proteins and Phytocompounds from *Withania somnifera* extract. For sitespecific docking with TSPO, Alpidem have been used as a control. The binding affinities of all the proteins and phytocompounds are mentioned in Table 2.

Additionally, other analyses were also performed after the visualization of the docked poses. Those interactions include the hydrogen bonds and the hydrophobic interactions formed between the protein and the ligands. It was observed that the residues that are involved in forming H-bonds and hydrophobic bonds were the same as those formed at the active site. Then the complex structures were checked for interactions based on their amino acid involved in the interaction of shortlisted top-scoring compounds out of them. The amino acids involved in the interaction are shown in Fig. 1.

### 3.2 Phase Studies

The excipients (oil, surfactant, and co-surfactant) were selected keeping in mind their Hydrophile-Lipophile Balance (HLB) values considering them to be in between the range of 7–17 in case of o/w nano-emulsions. Because of their lower bending



Fig. 1 Docking poses and ligand interaction diagram of the selected ligands of Withania somnifera with TSPO & ADNP



Fig. 1 (continued)



Fig. 1 (continued)

stress of interface, Co surfactants were added as the final layer of this colloidal solution, resulting in a more flexible interfacial film throughout a wide range of compositions. Linseed oil, Cween 20, and Ethanol were chosen for the oil, surfactant, and co-surfactant phases, respectively, based on these findings. The formulation of *WS* extract was analysed by aqueous phase titration method where, the extract was

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S.No	Combination	Smix ratios	Clear titration ratios
1	Linseed oil + Cween 20 + Ethanol [ASH-LCE-1]	1:0	1:5, 1:6, 1:7, 1:8, 1:9
2	Linseed oil + Cween 20 + Ethanol [ASH-LCE-2]	1:1	1:9, 2:8, 3:7, 4:6, 5:5, 9:1, 1:2, 1:3, 1:3.5, 1:5, 1:6, 1:7, 1:8
3	Linseed oil + Cween 20 + Ethanol [ASH-LCE-3]	2:1	4:6, 5:5, 6:4, 1:2
4	Linseed oil + Cween 20 + Ethanol [ASH-LCE-4]	3:1	6:4, 7:3, 8:2, 9:1, 1:2, 1:7, 1:8
5	Linseed oil + Cween 20 + Ethanol [ASH-LCE-5]	4:1	1:9, 1:2, 1:3, 1:3.5
6	Linseed oil + Cween 20 + Ethanol [ASH-LCE-6]	5:1	1:9, 2:8, 5:5, 1:2, 1:3, 1:3.5
7	Linseed oil + Cween 20 + Ethanol [ASH-LCE-7]	6:1	1:9, 2:8, 1:2, 1:3

Table 3 Clear titration ratios of linseed oil and smix

blended with the excipients having the highest solubility for the extract (Linseed oil, Cween 20, and Ethanol). Out of all the combinations tried (112 combinations); are listed below (Table 3) combinations of surfactant and surfactants with clear titration ratios were selected for further analysis. Here we have used the term "Smix" for a combination of surfactants and co-surfactants together. Also, out of all the combinations Smix ratio of 3:1 showed the maximum clear titration combinations, hence were considered further for testing (Fig. 2).

## 3.3 Characterization of Nano-Emulsions

# 3.3.1 Particle Size (PS), Polydispersity Index (PDI), and Zeta Potential (ZP)

Various formulations from WS were selected for additional analysis after all the Nano-emulsions were found to be thermodynamically stable. Using a zeta particle size analyser, the average droplet size of all the nano-emulsions examined is 50.11 nm, having droplet size varying from nano to micro. The polydispersity index and particle size were picked. The distribution width and type of dispersion are indicated by the polydispersity index, which spans from 0 to 1 and is discovered to be 0.335. The polarity and electric potential of the formulation are reflected in its ZP, which is dictated by the presence of charge on the particle's surface. The optimized WS formulation's zeta potential was reported at (-) 21.6 mV, suggesting the predominance of repulsive forces and preventing flocculation (Figs. 3 and 4).



Fig. 2 Psuedoternary phase diagrams of clear titrations ratios of Withania somnifera nanoemulsions (WSNE)
Results



Fig. 3 Particle Size Analysis and Polydispersity Index of WSNE

Record 281: ASH-LC20E 1



Record 282: ASH-LC20E 2



Fig. 4 Zeta Potential of WSNE ratio

Record 283: ASH-LC20E 3



Fig. 5 TEM analysis of WSNE ratio

# 3.3.2 Transmission Electron Microscopy (TEM)

TEM micrographs of the particles of improved formulations of *WS* are shown in Fig. 5. Finely scattered particles in the spherical nanometric size range were detected (25 nm). As a result, the globule sizes of WSNE obtained from TEM pictures are consistent with a particle size analyser analysis performed earlier.

# 3.3.3 Measurement of Rheological Parameters (Viscosity, Conductivity, pH)

The volume and effective number of carbons of the oil both have an impact on the viscosities of nano-emulsions. Since linseed oil has saturated long-chain and effective carbon numbers, which make it more flowable, it was chosen for the oil phase of this experiment. Because alcohols are believed to join the micelle interface by situating themselves amid surfactant heads, cween 20 is used in combination with ethanol as a co-surfactant in this study. It was discovered that nano-emulsions have a specific conductivity of 81.3 mS/m. WS has a pH of 5.35, which is slightly below the ideal pH needed in the brain region (pH-7.2). WS has a viscosity of 41.7 0.6 (Table 4).

Table 4   Summarization of rheological parameters of the optimized nano-emulsions	Sample	рН	Conductivity (mS/cm)	Viscosity (cP)
	ASH bare nano-emulsion	$4.12\pm0.8$	77.1 ± 0.4	37.5 ± 0.2
	ASH-ALGA	$5.35 \pm 0.7$	$\pm 0.5$	$41.7 \pm 0.6$

#### 3.3.4 Release Kinetics

Chemical release kinetics were assessed over the course of 18 hours using the Franz diffusion setup, with data being collected hourly. 80% of the drug was released during the first 14 h of the experiment, and just 20% during the final 14 h, according to the compound release pattern. To confirm the compound's sustained release, look at the graph of compound release % versus time (Fig. 6). The pattern of release for WS and WSNE showed an improvement in the release pattern of WS in the form of NE as compared to the pure extract form. The highest correlation coefficient can be shown in the data analysis and verification using standard release kinetics models (Fig. 6;  $R^2 = 0.9859$  for WSNE).

As shown in Fig. 6, the cumulative drug release (CDR) data for the nano-emulsion were found to follow various release kinetic models, which aid in understanding their distinct drug release pattern. As shown in Table 5, the WS extract follows the Korsmeyer-Peppas model, while the percentage CDR of the WSNE fits the zero-order model of release kinetics. This conclusion was drawn from the experiments' evaluation of the regression coefficient's ( $R^2$ ) value. The drug release pattern in a suspended state is explored and explained using kinetics linked to the Zero Order



Fig. 6 Release kinetics study of WS standard extract and WSNE

Table 5 Various kinetic   models for in vitro release analysis of WSNE		Kinetic model	Equation	R2
	WSNE	Zero order	y = 5.8298x - 1.2316	0.9878
		First order	y = -0.0804x + 2.2331	0.8626
		Higuchi's model	y = 0.0336x + 1.0594	0.9193
		Hixson Crowell's model	y = 0.1822x - 0.3765	0.9317
		Korsmeyer-Peppas model	y = 1.4408x + 0.3123	0.9207
	WS extract	Zero order	y = 3.1444x + 11.39	0.5808
		First order	y = -0.0225x + 1.9518	0.5556
		Higuchi's model	y = 0.0381x + 1.2704	0.5836
		Hixson Crowell's model	y = 0.0674x + 0.1755	0.5667
		Korsmeyer-Peppas model	y = 1.1659x + 0.4558	0.6952

model. Additionally, it has been found that matrix systems with water soluble pharmaceuticals work well for this kind of kinetic since they are more frequently observed in systems with small-sized medications. To explain the powder dissolutions or medication release pattern from a particular formulation, Korsmeyer-Peppas kinetic is much more appropriate. This model best describes the release from sustained release tablets made of an erodible matrix in medication dosage formulations.

# 4 Conclusion

We can draw the following conclusion after discussing the current study's findings: WSNE are shown to be robust and stable under various thermodynamic and physiochemical analyses. They also have effectively created and described particles in the micro- to nanometric range. With confirmation from TEM and a zeta potential value of -21.6 mV, the characterization of the optimized nano-emulsion formulation shows that the size range of the formulation is 50.11 nm. The release kinetics investigation demonstrates that sustained release of WSNE improves the pathological condition of neurological diseases, and it may be pursued as a viable ligand potential for clinical studies to evaluate its efficacy in humans. Therefore, more in vivo animal model validation of the work is necessary.

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# Fabrication of Particulate Aluminum Metal Matrix Nanocomposites: A Critical Review



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Ashish Kumar, Ravindra Singh Rana, Rajesh Purohit, Anurag Namdev, and Madhusudan Baghel

## 1 Introduction

The limited source of automotive fuel makes a researcher more thoughtful to develop a material that consists of tremendous strength and is lighter in weight. Aluminum alloy-based particulate reinforced nanocomposites are a suitable replacement for traditional materials like steel due to their excellent wear, mechanical, anti-corrosion properties and most importantly higher strength-to-weight ratio [31]. The synthesis of particulate nanocomposites could be done using ex-situ and in-situ methods. If the reinforcing nanoparticles are added to the liquid or powdered matrix material, the synthesis is known as ex-situ. While in-situ method focusses on the generation of reinforcements (nano-compound) inside the melt itself by the result of a chemical reaction between matrix and inorganic salt. Various researchers prominently developed composites using stir casing [18], powder metallurgy [11], friction stir processing [2], disintegrated melt deposition [10] process and in-situ process [5]. Ceramic particles such as SiC, Si<sub>3</sub>N<sub>4</sub>, B<sub>4</sub>C, TiB<sub>2</sub>, TiC, Al<sub>2</sub>O<sub>3</sub>, CNT, and Gr are most prominently used as reinforcement to strengthen the aluminum alloy. Most of the reinforcing particles are solid and denser than the aluminum matrix so lower wettability between both phases is the prime issue.

The major challenges associated in nanocomposites fabrication are the clustering of nanoparticles due to the higher surface area, porosity content due to air entrapment and non-uniform distribution of nanoparticles. So, in this review various fabrication methods were discussed and a novel synthesis approach was suggested to overcome the above-mentioned issues.

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#### **2** Fabrication Techniques

The surface area and surface energy of nanoparticles are too high, so the agglomeration or clustering of nanoparticles and uniformity in particle distribution in the primary phase (matrix Al. alloy) are the main challenges in the fabrication. The frequently used fabrication methods are discussed.

#### 2.1 Stir Casting

Stir casting is a very traditional and easy processing technique. It is prevalent for fabricating ceramic reinforced particulate Aluminum metal matrix composites due to its simplicity, fabricating components in large quantities, and being suitable for more prominent and complex job fabrication. The schematic diagram of the stir casting technique is shown in Fig. 1. The argon gas provides an atmospheric gas shield over the molten material to avoid air entrapment and casting with minor defects. A metallic stirrer (with four blades at the bottom) is used for the particle distribution throughout the matrix alloy. The stir casting method was previously used to fabricate aluminum-based composites by using Silicon carbide [25], silicon nitride [14], graphene [1], titanium carbide [28], titanium boride [21], carbon nanotubes [24], aluminum oxide [26] as a particulate reinforcement to strengthen the Al alloy matrix. However, this technique is fundamental, and some challenges associated with the mixing of nanoparticles in molten Al alloy such as (i) lower wettability of ceramic nanoparticles with molten Al alloy, (ii) high tendency of agglomeration due to higher surface area and surface area, (iii) higher porosity content due to air entrapment by stirrer and large van der-wall forces [3, 12].

The challenges mentioned above could be countered by using advanced stir casting (ultrasonic-assisted stir casting) up to an extent. Herein, a sonicator (approx. 20 Hz) attached to a metallic horn reduces the porosity content and improves particle distribution by transferring low-frequency ultrasonic waves to the slurry. These low-frequency waves collapse the air bubble inside the slurry by the effect of cavitation. The formed cluster of particles breaks and is uniformly distributed throughout the molten alloy. The schematic diagram of ultrasonic-assisted stir casting is shown in Fig. 2. Thermocouples are mainly used to detect the processing temperature, and argon gas minimizes air entrapment by forming a shield over the molten slurry.

Rao [23] developed nano Sic reinforced Al 7075 nanocomposites via ultrasonicassisted agitation casting method. They mixed the nanoparticles with different weight percentages and observed a significant increment of 94.52% in yield strength for 2 wt.% nano SiC reinforced composites compared to base Al 7075 alloy. Microstructure analysis reveals that reinforcing particles are uniformly dispersed in a matrix up to 2 wt.% due to the combined effect of stirring and ultrasonication treatment. They noticed outstanding tensile and wear properties with the addition of nano reinforcement. The increment in strength is credited to the orowan



Fig. 1 Stir casting set-up



Fig. 2 Ultrasonic-assisted stir casting set-up

strengthening, fine grain strengthening, increased load-bearing capacity, and thermal mismatch-strengthening.

Significant improvement was observed in wear resistance of 2 wt.% Sic nanocomposites up to 2250 m sliding distance. Madhukar et al. [18] fabricated h BN reinforced Al 7050 nanocomposites using ultrasonic-assisted agitation casting method; the reinforcement was done in 0.5, 1, 1.5, 2, and 3% by weight. EDS and XRD characterization reveals the presence of reinforcement in the matrix without impurities. They observed a significant increment in hardness and tensile strength up to





2 wt.% due to nanoparticles' homogeneous distribution and strengthening mechanisms' contribution. The strength of composites starts reducing after 2 wt.% due to the clustering of particles and increased porosity content. Kumar et al. [13] examine the tensile strength of Al alloy (sample 1), AA–0 wt.% SiC-2 wt.% Gr (sample 2), AA-3 wt.% SiC-2 wt.% Gr (sample 3), AA-6 wt.% SiC-2 wt.% Gr (sample 4) fabricated through stir casting technique. Results reveal that the tensile strength directly depends on the reinforcement combination; the maximum value of UTS noticed for sample 4 is shown in Fig. 3.

Chak and Chattopadhyay [4] developed Al/ GNP nanocomposites with the help of a stir caster advanced with a noncontact ultrasonicator. GNP was mixed in a proportion of 0.1. 0.3 and 0.5% by weight; furthermore, T-6 heat treatment was performed on the casted composites and alloy to improve their mechanical and tribological properties. They noticed a significant increment of 37 and 27% in ultimate tensile strength and hardness, respectively, with the addition of 0.5 wt.% GNP credited to grain refinement and uniform distribution of reinforcement in matrix. Enhancement of 83 and 34% in tensile strength and hardness, respectively, for 0.5 wt. % GNP composites after performing heat treatment, the improvement in mechanical properties after T-6 heat treatment attributed to age hardening. The wear resistance also improved with the addition of reinforcement due to the self-lubricating quality of GNPs. Madhusudhan et al. [19] developed CNT reinforced Al6082 nanocomposites using ultrasonic-assisted stir casting technique. They examined the effect of different volume fractions of CNT (0.3, 0.6, 0.9, and 1.2% by weight) on the microstructure. They noticed significant grain refinement in grain size with an increment in wt.% of CNT (shown in Fig. 4).

Li et al. [17] reported the mechanical properties of Al-SiC (60 nm) composites fabricated through the stir casting method; the reinforcement is done in the proportion of 0, 1, 3, 5, 7, and 9% by weight in Al alloy. They observed that Sic reinforcement was homogeneously distributed throughout the matrix up to 7 wt.%. Significant grain refinement was noticed from the microstructure analysis; coarse Al dendrite of 270  $\mu$ m transformed to 90  $\mu$ m with the addition of SiC nanoparticles in it. It was noticed that the hardness and tensile strength of Al alloy improved by 135.7 and 155.4% with 7 wt.% SiC reinforcement. For 9 wt.%, the mechanical properties



**Fig. 4** Microstructure of CNT/Al6082 composites grain refinement with varying weight % of CNT at 200 μm **a** AA6082, **b** with 0.3 wt. %, **c** CNT with 0.9 wt. % CNT, **d** with 1.2 wt. % CNT

were reduced due to the clustering of nanoparticles. Yuan et al. [32] developed Al/ SiC<sub>P</sub> nanocomposites via ultrasonic-assisted stir casting combined with the squeeze casting technique. They observed that nano SiC particles were uniformly distributed in the matrix, and very less agglomeration of SiC was seen in the microstructure of 2 wt. % composite. The tensile properties were improved with increasing ultrasonication time and squeeze pressure due to the good mixing of particles and reduction of void content in the casting. Kumar et al. [15] developed Si<sub>3</sub>N<sub>4</sub> reinforced Al 7068 nanocomposites through ultrasonically advanced stir casting technique; the reinforcement is done such as 0, 0.5. 1, 1.5, and 2.0% Si<sub>3</sub>N<sub>4</sub> by weight. Microstructure analysis reveals significant grain refinement and uniform distribution of Si<sub>3</sub>N<sub>4</sub> nanoparticles in al matrix up to 1.5 wt.% shown in Fig. 5. After that, the clustering of particles at some locations was observed. The hardness, UTS, and yield strength of 1.5 wt.% Si<sub>3</sub> $N_4$  nanocomposites significantly improve compared to the base alloy. The improved mechanical properties are attributed to the combined effect of grain refinement, increased load-bearing capacity due to the ceramic Si<sub>3</sub>N<sub>4</sub> inclusion, and orowan strengthening. The fracture surface analysis discloses ductile and mixed (ductile and brittle) types of failure in the case of alloy and nanocomposites, respectively. Li et al. [17] reported the impact of ultrasonic treatment duration for 0, 1, 3, 5, and 7 min on the dispersion of 1 wt.% nano SiC particles in copper-rich Al alloy. They noticed the yield and tensile strength improved when ultrasonic waves were transferred for 5 min due to improved distribution of particles; the SiC more oversized agglomerates were broken into smaller ones due to the acoustic streaming and cavitation effect. Ultrasonic treatment for more than 5 min was insignificant for particle distribution and mechanical properties: the yield strength, ultimate tensile strength, and percentage elongation of 1 wt.% SiC composites were improved by 6.8, 7.6, and 29%, respectively, after 5-min ultrasonic treatment compared to base alloy (Al-5Cu).

Similarly, yield strength, tensile strength, and percentage elongation improved by 9.5%, 27.4%, and 303% after 5 min ultrasonic treatment compared to untreated composites. The mechanical properties were improved due to the combined effect of grain refinement and uniform particle distribution. The average grain size of the Al–5Cu matrix (0 min UV), Al–5Cu/1wt. % SiC (0 min UV) and Al-5Cu/1 wt.% SiC (5 min UV) are 65  $\mu$ m, 59  $\mu$ m, and 28  $\mu$ m, respectively. Kumar et al. [15] Represented the effect of stirrer design on the microstructure of Al–MWCNT nanocomposites, the fabrication is done using an ultrasonic-assisted stir casting technique. They considered the various stirrer design such as four-bladed, U shape, and four-bladed disk turbine blade stirrers. Microstructure analysis revealed that the MWCNT homogeneously distributed in Al alloy when stirring was performed by using four-bladed disk turbine type at the speed of 400 rpm compared to other designs.

#### 2.2 In-Situ Method

The addition of ceramic particles in molten alloy externally or synthesis of reinforcing particles inside the matrix alloy itself is known as in-situ processing. In this process, ceramic particles are formed inside the melt by the chemical reaction of metallic powder or inorganic salts. The formed ceramic particles are contamination-free, strengthening the matrix alloy more prominently due to strong interfacial bonding. Moreover, the uniform dispersion of reinforcing particles is achieved effortlessly compared to the traditional stir casting approach [6]. The schematic diagram of the in-situ process is shown in Fig. 6.

Xu et al. [30] fabricated  $Al_2O_3$  reinforced Al metal matrix composite through an in-situ technique,  $Co3O_4$  powder was mixed in the molten alloy to form  $Al_2O_3$ particles inside the melt by the result of a chemical reaction between molten Al alloy



Fig. 5 Distribution of nano  $Si_3N_4$  particles in Al alloy 7068 matrices in the proportion of **a** 0.5%, **b** 1.0%, **c** 1.5%, **d** 2.0% by weight [15]



Fig. 6 In-situ process



and  $Co_3O_4$ . The microstructure study reveals the effect of  $Al_2O_3$  and cobalt particles on grains; the coarse eutectic Si transforms into a fine fibrous-like structure and refines the second dendrite arm spacing (SDAS) of the grains. The tensile strength and percentage elongation significantly improved by 43.6 and 85.7%, respectively, for 0.6%  $Al_2O_3$  reinforced composites.

Gao et al. [7] used salt reaction method to fabricate Al–4.5Cu/2.5 wt.% TiB<sub>2</sub> composites and ultrasonic treatment was done to improve the particle distribution in the matrix alloy. Results revealed that the large clusters of particles were broken into smaller ones by ultrasonic treatment for 30 s due to the cavitation effect and acoustic streaming to the slurry. The ultimate tensile strength was improved by 84%, and an improvement of 39% was noticed in the yield strength of 2.5 wt.% composites compared to the base Al alloy matrix.

Fig. 5 (continued)

It has to be noticed that the use of in-situ processes in composite fabrication is limited due to the unique nature of compound generation, and chemical reaction. It is majorly used for TiC and  $TiB_2$  reinforced composites.

#### 2.3 Disintegrated Melt Deposition Method (DMD)

This process is derived from the stir casting process to fabricate magnesium matrix nanocomposites [8]. The principle of this process is similar to stir casting, where the mixture of matrix and reinforcement is prepared through the stir casting method. Furthermore, the prepared slurry passed through a nozzle near 750 °C with the help of inert gas jet, and the processed slurry was collected on a metallic substrate. Due to the challenging fabrication route, the use of this process is restricted. The segregation of particles when the mixture passes through the nozzle is commonly noticed due to the difference in the density of reinforcement and matrix.

Ho et al. [10] developed hybrid AZ91A/Cu composites by using the DMD technique. Microstructure study reveals the uniform distribution of Cu particles in alloy with good interfacial bonding between reinforcing particles and alloy. The mechanical properties of the prepared composite are much better than AZ91A/SiC composites at the same and above reinforcement volume fraction. The ducitily is oppositely influenced and decreased compared to the base alloy. Srivatsan et al. [27] examined the mechanical properties of DMD processed AZ31/1 wt. % CNT composites followed by hot extrusion. They reported a tremendous increment in microhardness of composites compared to monolithic alloy, the increment credited to the synergism of finer and resultant ratio of intermetallic particles (Mg17A112) in magnesiumbased alloy and homogeneous dispersion of reinforcing phase in the matrix. The tensile properties are also enhanced compared to base alloy attributed to the combined effect of observable changes in microstructure, fracture modes (from brittle to ductile fracture), and uniform distribution of CNT particles.

#### 2.4 Powder Metallurgy Technique

The powder metallurgy technique involves four steps in fabricating metal matrix composites shown in Fig. 7. Initially, the raw matrix material powder and reinforcement particles are properly mixed using a high-energy ball miller followed by cold or green compaction of the prepared ball.

milled powder. The cold compacted samples were sintered in a furnace to strengthen the composite material. Nano, as well as micro composites, could be fabricated using this technique. Harichandran et al. [9] Examine the thermal conductivity of GNP strengthened Al metal composites using the finite element method; composites were fabricated using the powder metallurgy method followed by hot extrusion. GNPs were mixed in Al alloy by the volume fraction of 0.5, 1, 1.5, and



Fig. 7 Steps involves in the powder metallurgy method

2%. They noticed the thermal conductivity of alloy increases with the addition of reinforcing particles. The thermal conductivity increases as the reinforcing content increases from 0.5 to 2% in the matrix, [20] Used metallurgy technique to fabricate AA7075/6 wt.% B<sub>4</sub>C composite; initially, the ball milling on raw powder was performed and followed by cold compaction. Finally, three techniques were used in sintering: conventional, spark plasma, and microwave sintering. They examined the effect of sintering operations using microstructural characterization. They reported the optimum mechanical properties of spark plasma arc sintered composite due to the short sintering time and temperature and the better distribution of reinforcing particles. Ramachandra et al. [22] examined the microstructure, hardness, and wear characteristics of Al-ZrB<sub>2</sub> nanocomposites. Composites were fabricated using a powder metallurgy process. Homogeneous dispersion of particles at lower weight % ZrB<sub>2</sub>, whereas a small cluster of particles at higher reinforcement volume fraction was observed from the microstructure analysis. The wear resistance improved after reinforcement addition to the matrix alloy. The prepared composite is suitable for the connecting rod, and piston application.

There are certain limitations of this process such as part dimensions, the strength of the fabricated component, the cost of the final product, required specific die design. Due to the mentioned limitations the use of powder metallurgy is restricted.

## 2.5 Friction Stir Processing (FSP)

Friction stir processing is a single-step processing method to achieve homogeneity of the material, densification, and microstructural refinement. It is a solid-state processing method based on the solid-state thermo-mechanical process. In this process, a solid tool (attached with a rotating probe) travels along the pre-generated groove with a specific rotational speed; stirring action generates a localized thermo-mechanical plastically deformed zone due to the friction between the tool and base material. The thickness of the probe keeps lesser than the work plate and the diameter of the probe is near to the workpiece thickness. During the friction, process material gets plastically deformed due to temperature increment. Base material and reinforcement join together after the solidification, and the final composite possesses higher mechanical and wear properties [33]. The schematic diagram of FSP is shown in Fig. 8. This type of process is mainly used to make surface composites for nuclear reactor applications, so their use is restricted and could not able to make traditional composites.



Ardalanniya et al. [2] fabricated Alclad zinc rich Al alloy-based composites reinforced with GNP particles along with nano and micro copper particles through multi pass FSP. They noticed maximum hardness for composite reinforced with 1.5 wt. % GNP, whereas the tensile toughness and tensile strength minimize for this composition. A 26.3 and 28.8% increment was observed in tensile strength and tensile toughness respectively for composite developed with micro-size Cu particles due to the stronger interfacial bonding between Cu particles and matrix material (without GNP). Vijayavel et al. [29] noticed reinforcement clustering, porosity and other defects in stir cast metal matrix composite plate of 12 mm. whereas uniform distribution, and grain refinement observed in microstructure of the composite prepared through the Friction stir processing route. They considered different tool transverse speeds such as 20, 30, 40, 50, and 60 mm/min and examine the effect on microstructure, wear and mechanical properties. Results reveal microhardness, microstructure and wear rate were optimized at the transverse speed of 40 mm/min, in addition, uniform distribution of SiC particles and refined grain were also observed at this speed.

# 3 Suggested Fabrication Set-Up

Though various fabrication processes are available for the Al metal matrix nanocomposites, the stir casting route is best suited due to the advantages like the ease in processing, low-cost processing, and fabricating a large and complex component with large-scale production capability. But the main challenges of stir cast products such as the ununiform distribution of nanoparticles, casting defects, and agglomeration of particles. So, Fig. 9 shows the schematic view of the suggested casting set-up equipped with ultrasonic treatment, purging through inert gas, and a bottom pouring facility. The porosity content could be controlled by purging an inert gas, the unwanted segregation of nanoparticles could be minimized through the bottom pouring facility, and agglomeration could be controlled through the combined effect of stirring, ultrasonic treatment, and bottom pouring attachment. Some challenges were faced at the time of casting such as the distance between the crucible and mold should be optimized, the hole inside the crucible should be optimized and mold



Fig. 9 Suggested set-up of ultrasonically assisted stir casting equipped with bottom pouring and 5purging facility

should be designed in such a way that the mixture poured in the correct way without harm to the operator.

# 4 Conclusion

There are various processing techniques available for ceramic particle reinforced Al-based nanocomposites. For the stir casting route, ball milling of nanoparticles and matrix powder is advisable before mixing into the melt to avoid rejection of particles due to the density difference and lower wettability. The literature shows that ultrasonic treatment improves the mixing and reduces the clustering of particles. The powder metallurgy route is best suited for the fabrication of nanocomposites with a higher volume fraction of reinforcement due to its processing advantages but is limited to small jobs. All processing routes have their advantages and limitations; apart from this, stir casting is the most suitable technique due to its advantages like easy process route, cost friendly, and ability to develop large and complex shapes in masses. The issues related to the stir casting process could be minimized through suggested ultrasonic-assisted stir casting equipped with a bottom pouring and purging facility. The suggested fabrication method could be used to cast composites with better particle distribution, tensile and wear properties with dimensional freedom of product at lower cost compared to other methods. The cost of fabricated composite will be also lower or similar to other methods if compares with tensile and wear properties.

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