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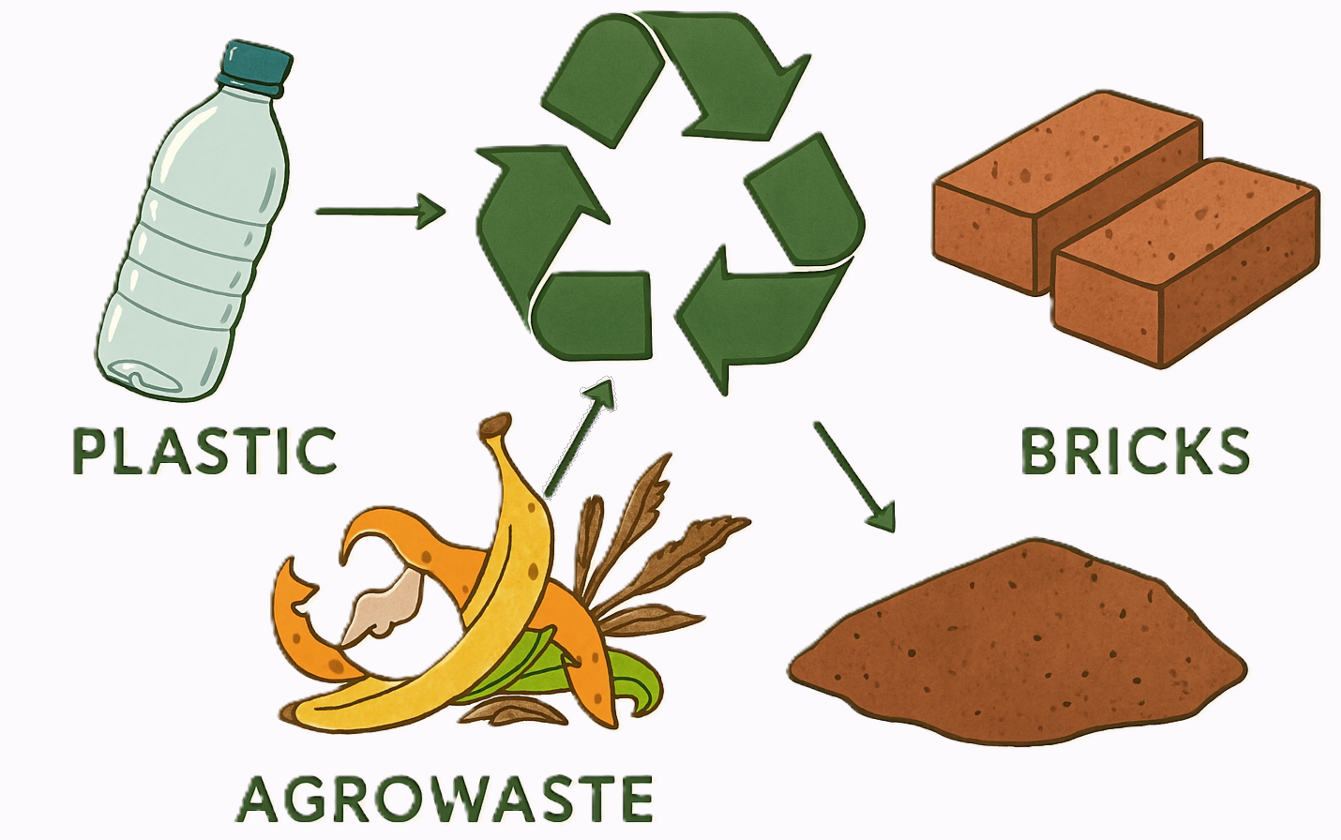

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Table of contents:

Chief Editor's Message

Editorial

Prof R K Kotnala
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Earth Sustainability & Reinforcing Circular Economy through Plastic & Agro Waste Recycling

At global level plastic waste and Agro-Industrial byproducts are being used in thermal insulation bricks or other innovative applications for sustainability? It is well known that India generates over 3.5 million tonnes of plastic waste annually and India recycles only ~35% of its plastic waste. Also a very large quantity of rice husk, bagasse, and sawdust from agro-industrial waste in which more than 500 million tonnes of agricultural residues are generated annually. Moreover, a significant fraction of these wastes is either landfilled or openly burned to contribute to severe air pollution, GHG emissions for public health at stake. Hence it poses a big challenge, how to mitigate it?

In this direction a Govt Policy has been framed on the use of Plastic Waste and Agro-Industrial By-products for Sustainable Thermal Insulation Materials such as bricks to be used in affordable houses in place of conventional bricks. This policy brief proposes the systematic utilization of plastic waste combined with agro-industrial by-products to manufacture thermal insulation bricks, blocks, and panels for affordable and urban housing. Such composite materials bricks can reduce building energy demand, lower construction costs, and fulfil circular economy objectives of UN SDGs also.

The production of conventional construction materials such as concrete, cement and bricks, has contributed significantly to the high environmental footprint associated with the construction industry. Moreover, there is a global push to deviate from the linear take-use-dispose model to a circular economy model, which incorporates up cycling and reuse of materials. For example: use of 1 ton plastic + 1.5 ton agro waste can produce approximately 2,500 insulation bricks. It results in a cost reduction: ~30–40% vs AAC blocks, finally resulting in CO_2 reduction of: ~1.5 tCO_2 per ton plastic used in it. Finally, it results in huge environmental & sustainability benefits for living beings.

This issue of CNS&E Journal published a manuscript on "Sustainable Thermal Insulation in Bricks Using Plastic Waste and Agro-Industrial Byproducts"

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Sustainable Thermal Insulation in Bricks Using Plastic Waste and Agro-Industrial Byproducts

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Abstract

This study investigates the feasibility of incorporating two agro industrial waste materials—wooden waste ash (WA) and rice husk ash (RHA)—as partial replacements for clay in the production of burnt clay bricks. These waste materials pose significant disposal challenges and contribute to environmental pollution. WA and RHA were sourced locally and added to clay in proportions of 5%, 10%, and 15% by weight. The mechanical properties (compressive strength and modulus of rupture) and durability characteristics (water absorption, porosity, sulphate resistance, and efflorescence) were evaluated. The results indicate that the inclusion of WA and RHA enhances sulphate resistance and reduces efflorescence, although mechanical strength decreases with higher replacement levels. The unit weight of bricks decreases with the addition of waste materials, which contributes to lightweight and economical construction. Overall, the incorporation of WA and RHA up to 15% can be recommended for sustainable and environmentally friendly brick production. Wooden waste ash and rice husk ash were procured from nearby locations in Greater Noida and Bulandshahr, respectively, and utilized as supplementary materials in clay brick production. The ashes were blended with clay at replacement levels of 5%, 10%, and 15% by weight. The manufactured bricks were assessed for mechanical performance, including compressive strength and modulus of rupture, along with durability characteristics such as water absorption, resistance to freeze–thaw cycles, and sulphate attack. The experimental results revealed a noticeable improvement in sulphate resistance and a reduction in efflorescence in bricks containing wooden waste ash and rice husk ash. In contrast, the incorporation of these waste materials did not produce any significant variation in the mechanical strength properties. Additionally, the inclusion of ashes led to a reduction in the unit weight of the bricks, thereby decreasing the dead load of structures and contributing to cost-effective construction. Hence, the use of such waste-derived materials in brick manufacturing offers an effective approach to reducing environmental impact while promoting sustainable and economical building practices.

Keywords: Plastic waste, Thermal insulation, Composite material, Rice husk, Sawdust, Glazed powder, sustainable construction.

1. Introduction

The construction industry has long relied on conventional materials such as cement, concrete, and burnt clay bricks, which contribute significantly to carbon emissions, resource depletion, and environmental degradation. With increasing concern about sustainable development and circular economy practices, the reuse of waste materials in construction has emerged as a promising solution.

Plastic waste and agricultural by products such as rice husk and wood residues pose major environmental challenges due to improper disposal methods. Recent studies [6–10] highlight the potential of converting such wastes into value added building materials, including composite bricks, geopolymer binders, and eco-friendly blocks. Biomass ash, in particular, has shown promise as a pozzolanic material capable of enhancing insulation and reducing unit weight of masonry products.

Researchers such as Chen et al. (2011), Yongliang et al. (2017), and Zhao et al. (2011) have explored the use of various ashes and industrial by products in brick manufacturing, with results indicating improved insulation properties and reduced environmental impact. However, limited research has focused on combining WA and RHA together for enhancing the thermal performance of bricks.

The objective of the present investigation is to address the existing research gap through an experimental assessment of the mechanical and durability characteristics of clay bricks containing wood ash (WA) and rice husk ash (RHA) at varying replacement levels. The manufacture of conventional construction materials, including cement, concrete, and bricks, has played a major role in increasing the environmental burden of the construction sector. In addition, there is a growing global emphasis on transitioning from the traditional linear model of resource consumption toward a circular economy approach that encourages material reuse and upcycling. Recent studies have explored the utilization of agricultural residues and plastic wastes in construction applications, evaluating their influence on essential performance parameters such as compressive strength, tensile strength, flexural strength, density, and thermal conductivity [6].

Improper disposal of plastic waste remains a serious environmental concern worldwide. Integrating plastic waste into building materials has emerged as a viable and economical strategy to mitigate this issue while improving material sustainability. In this context, research efforts have focused on developing composite construction materials by combining plastic waste with natural and waste-based constituents to achieve improved thermal insulation properties [4]. Furthermore, rapid urbanization over the past decade has significantly increased the demand for housing, leading to a corresponding rise in the consumption of building materials and a consequent shortage of natural resources [5–7]. This scarcity has compelled the construction industry to seek alternative raw materials capable of meeting the growing demand.

As a result, the conversion of industrial and agricultural wastes into functional construction materials has gained attention as a practical substitute for conventional resources [8–10]. Such practices not only promote effective waste recycling but also contribute to cost-efficient building design. In particular, the disposal of incinerated biomass ash can be effectively managed by its incorporation into engineering materials, especially fired clay bricks. Clay bricks remain one of the most widely used masonry materials due to their durability, strength, and availability. Consequently, the inclusion of waste materials in brick production has been extensively investigated over the years, with varying degrees of success depending on the type of waste used [11–13]. The fired clay bricks were manufactured on a large scale using a conventional brick kiln. The incorporation of these waste materials contributes to the conservation of natural resources while promoting cost-effective and sustainable construction practices [14–16].

Figure 1. Wooden Waste Ash (WHA) used for experimentation

Figure 2. Rice Husk Ash (RHA) collected from milling industry

2. Literature Review: First of all, various books and journals were collected for reference and were studied before starting the project work for having an idea about how the project should be. In this project an alternative building bricks are introduced. So, first the basic and essential characteristics of bricks were studied.

Biomass ash has been successfully used as a partial clay replacement [Chen et al., 2017].

Studies have found that 10% rice husk ash and 20% wood ash are optimal replacement amounts to achieve properties similar to control clay bricks. Other research indicates that up to 30% olive pomace fly ash can be incorporated into clay bricks fired at 900 or 1000 °C, yielding good mechanical values. Some studies suggest the integrity of bricks is reduced with ash amounts above 20%, though the acceptable limit can range from 10% to 30%. The inclusion of biomass ash generally tends to increase porosity and water absorption while potentially reducing compressive strength at higher percentages; however, the resulting products often still meet standard requirements for construction materials.

RHA improves insulation properties due to its high silica content [Purwanto & Darmawan, 2005].

High Porosity and Low Density: RHA has a large number of pores, which trap air. Air is an excellent insulator, and the high volume of these pores significantly reduces heat transfer by conduction. This results in low bulk density for the material produced.

Amorphous Structure: When RHA is produced under controlled combustion temperatures (typically below 700°C), the silica remains in an amorphous (non-crystalline) state. Amorphous materials have a disorganized structure that inhibits the movement of phonons (lattice vibrations which carry heat), thus leading to lower thermal conductivity compared to crystalline materials.

Low Thermal Diffusivity: The disorganised, porous structure of amorphous RHA limits the rate of heat transfer through the material.

High Melting Point and Thermal Stability: The high silica content provides resistance to high temperatures and thermal shocks, making RHA a durable insulator for high-heat applications, such as in steel casting and refractory bricks.

WA helps reduce density and enhances sustainability [Chilukuri et al., 2021].

Concrete remains one of the most widely used materials in the construction industry. Rapid industrial development and accelerated urban growth have significantly increased the demand for concrete, leading to extensive extraction of natural resources for cement production, as cement relies heavily on raw materials obtained from nature. Simultaneously, developing nations are witnessing a substantial rise in the generation of industrial and agricultural wastes, which poses serious threats to environmental sustainability and public health. The incorporation of such waste materials as supplementary constituents in construction practices offers a practical solution by reducing the dependence on natural resources and mitigating the adverse impacts associated with waste disposal. Numerous studies have demonstrated that the use of waste-derived materials in construction not only meets performance requirements but also enhances sustainability. This paper examines the scale of waste generation and its associated environmental consequences, while also identifying potential waste materials suitable for construction applications, including the production of blocks and insulating components. Furthermore, the study summarizes existing research on the utilization of agricultural and industrial wastes in the construction sector and presents examples of their application in real-world construction practices.

Composite bricks with waste materials show lower strength but improved durability and lightweight characteristics [Anbarasu et al., 2024; Chin et al., 2022].

The construction business is critical to building contemporary civilisation by providing the infrastructure needed for housing, transportation, and industry. However, its fast expansion, fuelled by urbanisation, population growth, and industrial development, has caused considerable environmental issue (Maraveas and Chrysanthos, 2020). Among construction materials, bricks are fundamental. They are widely used for their durability, availability, and versatility. Unfortunately, traditional brick manufacturing is resource-intensive, relying heavily on the extraction of natural clay and the firing process, which contributes significantly to greenhouse gas emissions. The extensive use of clay leads to the depletion of fertile topsoil, a critical resource for agriculture, and disrupts local ecosystems. Additionally, the high energy consumption of kiln operations, often powered by fossil fuels, exacerbates air pollution and global warming (Chin et al. 2022).

3. Material Used

3.1 Clay

The clay used in this study was sourced from the Greater Noida region. After collection, the material was air-dried under natural conditions, crushed to break down lumps, and passed through a sieve to eliminate unwanted particles and impurities. Clay is a fine-textured, cohesive soil that becomes plastic when mixed with water and can be shaped easily. Upon drying and firing, it develops sufficient strength and durability, making it suitable for the manufacture of bricks and ceramic products. The processed clay was subsequently used as the base material for brick preparation in this investigation.

3.2 Wooden Waste Ash (WA)

Wooden waste ash was obtained from an industrial boiler where timber residues were combusted at temperatures ranging between 750°C and 800°C. The collected ash was allowed to cool, finely ground, and sieved using a 90-micron IS sieve to achieve uniform particle size. Wooden waste ash is the fine particulate residue produced after the burning of wood in domestic or industrial systems such as fireplaces, bonfires, and power generation units.

3.3 Rice Husk Ash (RHA)

Rice husk ash was produced by controlled combustion of rice husks at a temperature of approximately 650°C for a duration of 3–4 hours, ensuring the formation of ash with a high amorphous silica content. The resulting ash was then sieved through a 90-micron sieve before use. Rice husks are the tough outer shells of rice grains that are separated during the milling process. Initially, the husks are removed to obtain brown rice, and further milling eliminates the bran layer to produce white rice. The combustion of these husks generates rice husk ash, which is widely recognized for its potential use in construction materials.

3.4 Chemical Composition

Table 1. Chemical Composition of WA and RHA (XRF Analysis) (Values inserted as per standard literature ranges).

Oxide	Rice Husk Ash (RHA)	Wooden Waste Ash (WA)
SiO_2	76.7% - 98.9%	45% - 48.6%
Al_2O_3	0.18% - 4.9%	5.9% - 12.4%
CaO	0.8% - 1.4%	14.5% - 18.1%
Fe_2O_3	0.2% - 1.0%	3.3% - 4.6%
K_2O	2.0% - 5.0%	1.85% - 15.9%
MgO	0.6% - 1.8%	3.2% - 4.8%
LOI (Loss on Ignition)	15.6% - 17.8%	12.5% - 15.6%

4. Results and Discussion

The mechanical and durability test results demonstrated the following:

- Compressive strength decreased as waste content increased due to higher porosity.
- Water absorption and porosity increased with RHA and WA addition.
- IRA values increased, indicating higher permeability.
- Sulphate resistance improved due to reduced clay content and presence of stable silica.
- Lower density contributes to improved thermal insulation.

Compressive Strength Test: The compressive strength of the specimens was determined using a compression testing machine equipped with a spherical ball-seated compression plate, designed to ensure uniform load distribution by allowing the center of the applied load to align with the center of the specimen.

Figure 3. Sample preparation for making of brick

Preconditioning: Any surface irregularities present on the bed faces of the specimen were eliminated through grinding to obtain two smooth and parallel loading surfaces. The specimens were then immersed in water at room temperature for a period of 21 hours. After soaking, the samples were taken out and allowed to drain excess water under ambient conditions [1]. Where a frog was present, it and all surface voids were completely filled with cement mortar prepared in a proportion of 1:3 (cement to clean coarse sand passing 3 mm sieve). The specimens were subsequently covered with damp jute bags and stored for 24 hours, followed by immersion in clean water for three days. After curing, the samples were removed and surface moisture was wiped off prior to testing.

Table 2. Compressive strength Test Results

Mix	Sample 1 (kN)	Sample 2 (kN)	Sample 3 (kN)	Average Compressive Strength (N/mm^2)
M1	81	78	77	4.59
M2	82	91	85	5.02
M3	98	102	99	5.82
Conv-ention-al mix	150	115	163	8.34

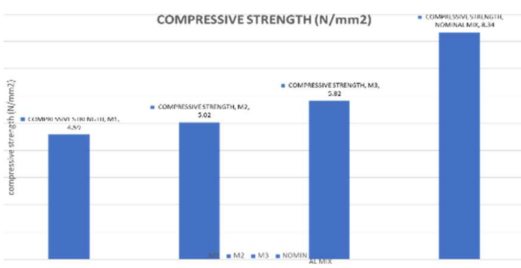

Figure 4. Compressive strength test result graph

Water Absorption Test: The specimens were dried in a well-ventilated oven maintained at a temperature between 105°C and 115°C until a nearly constant mass was achieved. After drying, the samples were allowed to cool to ambient temperature before recording their mass (M_1). Specimens that were still warm to the touch were not considered suitable for weighing or further testing.

Table 3. Water Absorption Test Results

Mix	Dry Weight (kg) M1	Wet Weight (kg) M2	Water Absorption (%)
W1	2.913	3.182	9.23
W2	2.805	3.167	12.90
W3	2.790	3.192	14.40
Conventional mix	2.885	3.389	17.46

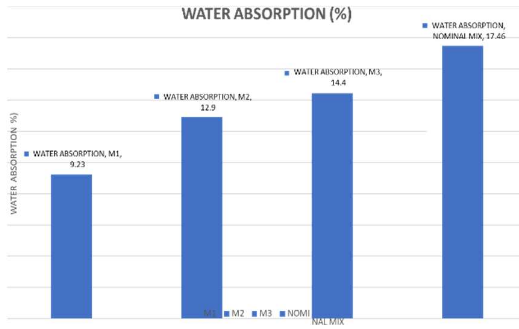

Figure 5. Water absorption test result graph

5. Conclusions:

- The incorporation of agricultural by-products such as rice husk ash (RHA) and wood ash (WA) into fired clay bricks provides an efficient solution for waste management while supporting environmentally responsible construction practices. The addition of these materials results in the production of lighter bricks.

- The reduced unit weight of the bricks contributes to overall construction economy. However, test results indicated a reduction in compressive and flexural strength in brick specimens containing RHA and WA when compared to conventional bricks.

- An increase in porosity, water absorption, and initial rate of absorption was observed with higher waste content. Increased porosity is generally associated with improved thermal insulation performance.

- Based on water absorption characteristics, bricks containing up to 15%

waste material were found to be suitable for use in regions with moderate climatic conditions.

- Efflorescence performance of the modified bricks was found to be satisfactory. Overall, the study concludes that fired clay bricks incorporating RHA and WA up to a replacement level of 15% can be safely and effectively utilized in construction, contributing to sustainable and resource-efficient building
- WA and RHA can be effectively used in burnt clay bricks up to 15% replacement.
- Waste incorporation reduces density and enhances insulation performance.
- Mechanical properties decrease but remain acceptable for non-load bearing and moderate weather applications.
- Porosity and water absorption increase, contributing to better thermal behavior.
- The approach supports sustainable construction and waste management.

Figure 6. Final product

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Conflict of Interest:

The author declares that there is no conflict of interest associated with the publication of this manuscript. The research work did not receive any financial support from any funding agency, and no personal or professional relationships influenced the research outcomes.

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Implication of AI in Transforming Human Resource Development

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Abstract

This paper presents a systematic conceptual review of the application of Artificial Intelligence (AI) in Human Resource Management (HRM). Human resources form the backbone of organizations, and the integration of AI technologies is transforming key HR functions such as recruitment, training and development, performance management, compensation, grievance redressal, and retirement planning. This study synthesizes peer-reviewed literature published between 2018 and 2024 drawn from databases such as Scopus, Web of Science, Google Scholar, and major academic publishers. The review identifies how AI enhances efficiency, reduces bias, supports strategic decision-making, and improves employee experience, while emphasizing that human judgment remains essential in ethical and relational domains.

Keywords: Artificial Intelligence recruitment, management, balance scorecard, regulatory

1. Introduction: Human resources are central to organizational effectiveness. It has the capacity to develop and build knowledge.

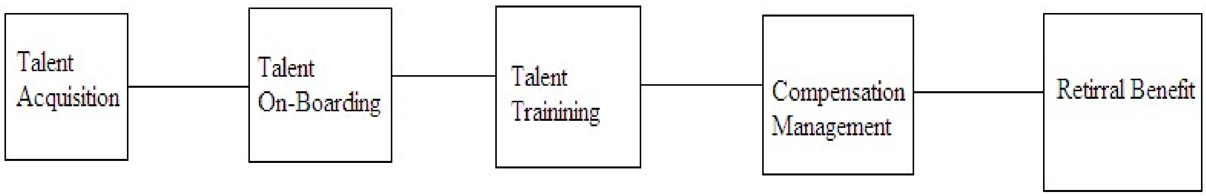

Figure 1. Stages of process involved in Human Resource department

It can bring out the application from their knowledge base and work for the advancement of society. Human resource department has the power to frame regulatory policy for the employee in an organization. It has many stages in its whole process. A block diagram on the process involved in human resource management has been mentioned below:

It mainly keeps a check on the following key performance metrics of the organization:

a) No. of candidate on-boarded as per qualification
b) How many varied candidates have been employed based on geography and qualification?
c) To settle inter-departmental conflict
d) Compensation and benefit sanctioning from higher management
e) No. of candidates promoted to higher level department-wise
f) No. of retiree
g) No. of candidates exiting the organization
h) Benefits to the retiree
i) Participation of the organization in Corporate Social Responsibility (CSR) activities

This paper is positioned as a systematic conceptual review that synthesizes existing academic literature to analyze the implications of AI across the HR value chain.

2. Literature Review: AI in Recruitment and Selection Human Resource Management (HRM) is a crucial function within organizations, focused on acquiring, motivating, and retaining a skilled workforce. The recruitment process is a fundamental component of HRM, aimed at minimizing costs, shortening recruitment timelines, and strategically deploying a competent workforce. With the integration of Artificial Intelligence (AI) technologies, traditional recruitment methods are evolving [1] (Sharma & Malik, 2020; Garg et al., 2021; Manthena, 2021).

AI is revolutionizing recruitment processes through tools like Applicant Tracking Systems (ATS), AI-powered chatbots, video chat analysis, and social media scanning. These technologies enhance efficiency by automating repetitive tasks, improving candidate engagement, and analyzing candidate features (Mukherjee & Krishna, 2022; Hemlata et al., 2021; Ulfa et al., 2021). However, organizations must carefully consider the challenges presented by the implementation of AI in recruitment, such as high costs, data privacy concerns, and uncertainties regarding candidate acceptance (Flack et al., 2022; Sorre et al., 2024).

The integration of AI in recruitment is reshaping the industry, leading to a transformation in recruitment roles and processes. While some roles may benefit from fully automated processes, human interaction remains essential in other scenarios. Recruiters emphasize the importance of staying updated on technological advancements to remain competitive [2]. The future of recruitment processes is envisioned to be data-driven, with AI aiding in decision-making based on analyzed data (Geetha & Reddy, 2018; Muthukumar & Garwal, 2023).

3. Human–AI Collaboration in HR

Despite the advancements in AI, human recruiters continue to play a vital role in recruitment processes. Humans excel in tasks requiring emotional intelligence, relationship-building, talent identification, and interpreting candidates' qualities beyond technical skills [4]. The ability of human recruiters to assess candidates based on personal chemistry and social interactions remains irreplaceable in the recruitment process (Jarrahi, 2018; Basu Choudhury et al., 2025a; Chamorro-Premuzic et al., 2019).

The integration of AI in recruitment processes presents opportunities for efficiency and innovation. While AI technologies enhance various aspects of recruitment, the human touch in recruitment remains indispensable for tasks that require empathy, intuition, and a deeper understanding of candidates beyond technical qualifications. Balancing AI tools with human expertise is crucial for optimizing recruitment processes and ensuring successful candidate placements.

4. Research Methodology: This study adopts a systematic conceptual review approach to examine the role of Artificial Intelligence in Human Resource Management.

4.1. Data Sources: Peer-reviewed articles were collected from Google Scholar, Scopus-

Figure 2. Process involvement in Balance Score Card (BSC).

indexed journals, Web of Science, Elsevier, Springer, Emerald, and Taylor & Francis.

4.2. Search Keywords: “Artificial Intelligence in HRM”, “AI in recruitment”, “digital HR”, “AI in performance management”, “AI and employee engagement”.

4.3. Screening Process: An initial pool of 87 articles was identified. After removing duplicates and screening abstracts for relevance, 42 articles were retained. A final set of 26 articles was selected for detailed thematic analysis.

4.4. Analysis Technique: The selected literature was coded thematically across recruitment, learning and development, performance management, compensation, governance, and ethics. Patterns, benefits, challenges, and future implications were synthesized.

4.5. Integration of AI in the Balanced Scorecard (BSC):

The BSC is a strategic tool that measures organizational performance across four perspectives: Financial, Customer, Internal Processes, and Learning & Growth. AI enhances the BSC by providing predictive analytics, automating data collection, and offering real-time insights, thereby improving decision-making and strategic alignment (Kaplan & Norton, 2007; Marr, 2016).

5. Results and Discussion: In all AI has simplified the process involved in human resource department. It has leveraged benefits both for the employer and employee. Employees can even check the review on various performance parameters of any organization before appearance of interview to get employed. Sometimes, shortlisting the candidates based on job description manually becomes hectic. As there are many qualifications which may closely align with the job description.

AI helps in removal of these types of problems using SVM (Support Vector Machine) or CNN (Convolution Neural Network) machine learning algorithms. Sometimes measuring the efficiency of workers in any department manually is difficult as there will be different personal interpretations of the same as per different people. AI helps mitigate such situations by removal of personal biases.

7. Future Scope: Artificial Intelligence (AI) is revolutionizing Human Resources (HR) by automating tasks, enhancing decision-making, and improving employee experience. In recruitment, AI streamlines processes by screening resumes and identifying top candidates efficiently, reducing time-to-hire and improving the quality of new hires.

Also, AI-driven tools provide real-time feedback and personalized development plans, enhancing performance management and employee growth. AI also plays a crucial role in promoting diversity and inclusion by minimizing biases in hiring and promotion decisions, leading to more equitable workplaces. Thereafter, AI enhances employee engagement by analyzing feedback and predicting turnover risks, enabling proactive retention strategies (Davenport & Ronanki, 2018; Tursunbayeva et al., 2018).

In compensation management, AI ensures fairness and competitiveness by analyzing market data and employee performance, aiding in the design of equitable salary structures. Overall, AI's integration into HR functions leads to more efficient, fair, and effective human resource management.

6. Conclusion: The implementation of Artificial Intelligence in Human Resource Management has fundamentally transformed organizational processes, from recruitment to retirement planning. AI has demonstrated significant advantages in streamlining talent acquisition, delivering unbiased results, facilitating proper promotions through learning and development, and upgrading Balance Scorecard metrics. Through machine learning algorithms like SVM and CNN, organizations can now more effectively match candidates to job requirements, eliminating the traditional challenges of manual screening. The integration of AI into the Balanced Scorecard framework has enhanced performance measurements across all perspectives, providing real-time insights for strategic decision-making. AI-driven tools have simplified employee grievance redressal systems and improved the management of benefits like overtime and travel allowances. While AI brings technological advantages, the human element remains crucial in HR management, serving as an enabler rather than a replacement. The technology has benefited both employers and employees, with the latter now able to research organizations and their performance parameters before interviews. Organizations that effectively integrate AI into their HR processes while maintaining human-centric values will likely see enhanced operational efficiency and improved employee satisfaction. Looking forward, AI's continued evolution in HR promises even greater potential for automation, personalization, and strategic workforce management. The future of HR lies in the strategic combination of AI capabilities with human expertise, creating more efficient, fair, and effective human resource management systems.

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Conflict of interest:

There is no conflict of interest among any of the co-authors of the manuscript.

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Biodegradation of maneb, a Fungicide by a γ-*proteobacterium Pseudomonas psychrotolerans* Strain SDS18

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Abstract

The present study reports the isolation and identification of a γ-proteobacterium which is capable of degrading maneb and its photolytic product ethylene thiourea. The strain SDS18 was isolated from the surface of the most common weed *Parthenium hysterophorus* growing in agricultural field. Based on molecular systematics the strain SDS18 was identified as *Pseudomonas psychrotolerans*. Our study first time revealed that a single bacterial strain is capable of metabolising the toxic fungicide maneb and its carcinogenic photolytic product ethylenethiourea. We found that the strain SDS18 can tolerate upto 150ppm of maneb and 200 ppm of ethylene thiourea and ethylene urea as sole carbon sources. The optimum conditions for degradation were in the presence of ammonium sulphate as nitrogen source at 30°C at pH 7.0. Interestingly, the strain SDS18 exhibited activities like phosphate solubilisation, production and assimilation of ammonia, ACC deaminase activity, production of indole acetic acid and siderophores which are plant growth promoting activities and antifungal activities for *Alternaria citri* and *Cladosporium cladosporioides* indicating it could be beneficial for plant growth and maturation. The isolated strain can be used for bioremediation of maneb and its photolytic products.

Keywords: Degradation, maneb, ethylenethiourea, plant growth promoting

1. Introduction: Fungicides are important agrochemicals of present-day agriculture which are employed to kill, destroy, repel or mitigate fungi and fungal spores [1,2]. Dithiocarbamates (DTCs) based fungicides are widely used organosulfur molecules. DTCs are represented by a common structure (R_1R_2N)-(C=S) - SX, where R can be replaced with an alkyl, alkylene, aryl or related other groups and X is generally a metal ion [3,4]. World Health Organisation (WHO) estimates that approximately 25,000 to 30,000 metric tonnes of DTCs are used annually [5]. Ethylene bisdithiocarbamtes (EBDCs) are extensively used DTCs based fungicides because of their wide range of antifungal activity [4,6]. EBDCs are complexes of dithiocarbamates in which the R group of two DTC molecules form an ethylene bridge [7]. Most commonly used EBDCs are mancozeb, maneb, metiram and nabam. They are effective in preventing fungal diseases of crop and ornamental plants [8]. Manganese ethylene bisdithiocarbamate (MANEB) is Mn containing EBDCs[9]. Approximately 2.5 million pounds of maneb are annually used on potatoes, almonds, walnuts, lettuce and peppers to inhibit fungal diseases [10]. Maneb is most effective against different species of *Fusarium* and *Alternaria* , the causal organism of early and late blight of potato and tomato [11]. Extensive agricultural application of maneb is a cause of concern as it is known to induce the production of nitric oxide, lipid peroxidation and Parkinson like disorder in mice [12]. There are reports for the increase in the incidence of Parkinson disease by 75 % when the agricultural workers of California were exposed to both maneb and paraquat [13]. Toxicity of maneb is primarily due to inhibition of mitochondrial complex III [14] ; as a result of which Reactive Oxygen Species (ROS) and Reactive Nitrogen species (RNS) are formed which lead to mitochondrial DNA damage and retarded ATP synthesis [15]. Among Mn containing organic and inorganic compounds, maneb exhibits greater cytotoxicity (about eight times more) due to the presence of manganese ions and dithiocarbamte moiety [16]. Maneb was ranked as the most hazardous pesticide for overall persistent health effects in research conducted at Yuma County, Arizona [17]. Under environmental conditions maneb undergoes photolytic degradation into Ethylene thiourea (ETU) [18]. ETU is known to cause thyroid disorder by impairing thyroid hormone synthesis and liver damage [19].

The bacteria which facilitate plant growth directly or indirectly are termed as “Plant growth promoting bacteria (PGPB)”. The use of PGPB in the agricultural field can lead to an increase in the productivity in an environment friendly manner. It is envisioned that in the near future PGPB can replace the chemical pesticides and fertilizers and can also be used for environmental cleanup practice [20]. Therefore, if a bacterial strain/consortium exhibits bioremediation and PGP potential, it could be a potential boon in agriculture.

The present study explored the feasibility of isolating maneb and ETU degrading bacteria for developing biological means of eliminating their environmental toxicity. To the best of our knowledge there are no reports available for utilisation, biodegradation of maneb and ethylene thiourea; PGPR and antifungal activities by a single bacterial strain.

2. Materials and Methods

2.1. Chemicals and media

The chemicals, maneb and potential degradation intermediates were purchased from Sigma- Aldrich, Co. USA and other chemicals, microbiological growth media were procured from Hi Media, India. Mineral salt media(MSM)(pH=7±0.5) used in the present study was composed of Na_2HPO_4(4g/l); KH_2PO_4 (2g/l); $(NH_4)_2SO_4$ (1g/l); $MgSO_4$ (0.8g/l); trace element solution consisting of $Al(OH)_3$(0.1g/l); $SnCl_2$ (0.05g/l); KI (0.05g/l); LiCl (0.05g/l); $MnSO_4.4H_2O$ (0.08g/l); H_3BO_3(0.05g/l); $ZnSO_4.7H_2O$(0.1g/l); $CoCl_2.6H_2O$(0.1g/l); $NiSO_4.6H_2O$(0.1g/l); $BaCl_2$ (0.05g/l); $(NH_4)_6Mo_7O_{24}.4H_2O$ (0.05g/l); $FeSO_4$ (0.001g/l). The media was autoclaved at 121°C temperature and 15lbs pressure. After autoclave, the media was supplemented with 50-200 parts per million (ppm) concentrations of maneb, ethylene thiourea and ethylene urea as mentioned in the text.

2.2. Sampling Site

Aerial parts of *Parthenium hysterophorus* plants were collected from agricultural fields located on outskirts of Chandigarh, India. The samples were collected at the end of month of June and were immediately transported to laboratory for analysis.

2.3. Isolation and selection of maneb and ethylenethiourea utilising bacteria

The plant parts were dipped in 5 ml of sterile normal saline for overnight and the saline was serially diluted and spread plated on mineral salt media (MSM) containing 50 ppm of maneb, ethylene thiourea and ethylene urea respectively as sole carbon sources. The plates were kept at 30°C for further observation for the growth of bacterial colonies. The isolated colonies on these plates were further screened for utilisation of maneb as a Carbon source in MSM broth.

2.4. Identification of the isolated bacterial strain

The selected bacterial isolate strain SDS18, positive for utilisation of maneb as a Carbon source was identified by polyphasic taxonomy [21]. DNA extraction, amplification and sequencing were performed by methods as described by Mayilraj *et al* [22]. Using EZ Biocloud 16S database, 16SrRNA sequences of the species closely related to SDS18 were obtained and a phylogenetic tree was prepared using Mega 7.1 software [23].

2.5. Growth profile of strain SDS18 in presence of maneb and its intermediates

Growth profile of strain SDS 18 was studied in MSM containing maneb, ethylene thiourea (ETU) and ethylene urea (EU) as the sole sources of carbon respectively. The concentration of these compounds ranged from 50 ppm to 220 ppm. The strain was inoculated in ¼ diluted nutrient broth. After 24 hours, the cell suspension was pellet down and the cells were suspended in autoclaved double distilled water. For growth and degradation studies, 2% of the strain's inoculum was used for inoculating the MSM media and the flasks were maintained at 30°C at 180 rpm. The growth of the strain was monitored by measuring optical density of the culture broth in Spectrophotometer (UV 1800, Shimadzu) at a wavelength of 600 nm at different time intervals. The flasks without inoculums served as blank or control.

2.6. Plant growth promoting activities of strain SDS18

The strain SDS18 was examined for several activities contributing to plant growth. The strain was checked for activities including catalase, ammonia, phosphate solubilisation, 4-amino-1-cyclopropane carboxylate (ACC) deaminase, siderophore, and for production of hormones like auxin. The methodology used for determination of activities was performed as methods described by Singh *et al* (24). Antifungal activity of SDS18 was checked against *Alternaria citri* (MTCC 4875), *Cladosporium cladosporioides* (ATCC 16022), *Fusarium oxysporum* (MTCC 7229) and *Alternaria alternata* (MTCC 2724). The bacterial strains *Pseudomonas aeruginosa* (MTCC 7903 and MTCC 4682) reported for antifungal activities were obtained from Microbial Type Culture Collection and Gene Bank (MTCC), Chandigarh, India. These strains and SDS18 were inoculated in Tryptic Soy Broth (TSB) for 48 hours.

1mM 0.5M EDTA was added in the culture broth and the cells were lysed by sonication in ultrasonics (Sonics Vibracell, VCX750) for 30 minutes at a pulse rate of 10 seconds on and 10 seconds off. The cell suspension was centrifuged at 9000 rpm for 5 minutes. The supernatant was made to concentrate in speed vacuum concentrator (Eppendorf AG,22331) for 4 hours till 2 ml of the solution remained. 100µl of fungal spore suspension (10^5-10^6) was spread plated on PDA plates (20ml). Wells were cut by use of micro tips. Approximately 150µl of the concentrated supernatant was added into each well. The plates were kept at 28- 30°C to observe the presence of zone of inhibition around the wells.

2.7. Extraction of putative intermediates of maneb degradation

For degradation studies, nine amber colored flasks with 100 ml MSM (pH7±0.5) with 100 ppm maneb as Carbon source were prepared. The strain SDS18 was inoculated at 2% inoculums density as described above in all the flasks. The flasks were kept in rotary shaker (Innova44, Brunswick) at 180 rpm at 30°C. At a regular interval of 24 hours, 3 flasks were removed from shaker and the culture broth was combined and centrifuged at 10,000 rpm at 4°C (6K16, Sigma).The supernatant was extracted thrice with 100ml ethyl acetate in a separatory funnel. The layer of organic solvent was collected each time. The pH of the supernatant was made acidic (pH 2.0) and alkaline (pH10.0) by the addition of concentrated 10N HCl and 10N NaOH respectively. The supernatants were extracted three times with ethyl acetate. The organic layer was collected after every extraction. The collected ethyl acetate layers of different pH were mixed and concentrated in the rotary shaker (Nutronics, 1263) at 35°C. The concentrated residue was suspended in 1ml ethyl acetate and kept at 4°C for analysis. Heat killed cells and uninoculated media were taken as control.

2.8. Analytical techniques

2.8.1. Fourier Transform Infrared Spectroscopy (FTIR)

The intermediate extracted in the ethyl acetate was mixed with 100 mg of dried potassium bromide (KBr) powder and a thin pellet was formed. The pellet was subjected to FTIR analysis in the spectrometer Bruker Optik GmbH, Model

Vertex 70. The spectra were recorded in the transmittance mode within the range 400-4000 cm^1. The spectrum was processed with the Opus 6.5 software. The resolution of the measurement was 4 cm^{-1}. The identity of the extracted intermediate was confirmed by comparison with the spectrum of the procured standards.

2.8.2. Electrospray Ionisation Mass Spectroscopy (ESI-MS)

For determining the mass of the extracted intermediates of maneb degradation, the extracted intermediates were subjected to mass spectrometer (Waters, QTOF Micromass) in both positive and negative modes. The spectra were recorded in both positive and negative mode in the mass to charge (m/z) range of 50-500.

2.8.3. ^{1}H Nuclear Magnetic Resonance (NMR)

The extracted intermediate dissolved in ethyl acetate was evaporated to dryness in the concentrator (Eppendorf AG, 22331). The concentrated residue was dissolved in 600 µl deuterated chloroform ($CDCl_3$) and subjected to Jeol ECX 300MHz NMR Spectrometer at 25°C. The results were processed with Delta 4.3.6 software.

2.8.4. High Performance Liquid Chromatography (HPLC)

In order to confirm the structure of extracted intermediates/metabolites, HPLC analysis was performed with an Ultimate HPLC System (Thermo Fisher, USA) connected with a UV detector (Thermo Fisher, USA). The column used was Thermo Acclaim C18 (5µ, 4.6x250 mm) while mobile phase was acetonitrile and water at a ratio of 10:90 (v/v) at a flow rate of 1ml/minute. The injection of samples at a volume of 20 µl were done manually (Rheodyne) and detected at 232nm. Identification of compounds was revealed by comparing the retention times with the external calibration curves prepared with authentic standard solutions between 62.5 ppb to 1 ppm.

2.8.5. Genome mining of strain SDS18

Genomic DNA of the strain was isolated by fungal/ bacterial DNA isolation kit (Zymo research, USA) by using manufacturers' instructions. The isolated DNA of strain SDS18 was dispatched for sequencing at Genotypic Pvt Ltd (Bengaluru, India,). Following quality check, library preparation and further processes were carried out as methods described by [25]. Sequencing was done using the Illumina Miseq paired-end technology (2x300) and the obtained raw data was used for genome assembly with MaSuRCA [26] genome assembler version 2.3.2 The genome of the strain formed a total of 7,369,198 reads. The data was processed to trim and eliminate low quality sequences using CLC Bio Workbench v7.0.5 (CLC Bio, Aarhus, Denmark). A total of 7,368,052 high quality, vector filtered reads (~568 times coverage) were used for assembly (at word size of 45 and bubble size of 98). The sequence was deposited to NCBI. The final draft genome was used for genome annotation employing RAST server and RNAmmer 1.2server [27].

3. Results and Discussion

3.1. Isolation of maneb and ethylene thiourea utilizing bacterial isolates

The MSM plates were observed after 5 days of incubation. Based on morphology and pigmentation 10 different colonies were observed. The results of phylogenetic analysis of the isolates suggested that these isolates fall into two major groups

Firmicutes and *Proteobacteria* (Figure S1). The isolated strains were further screened for growth and degradation of maneb. For screening, MSM broth supplemented with the maneb as sole Carbon source was used. The strain(s) showing growth in the presence of maneb were screened for utilisation of ethylene thiourea and ethylene urea as a Carbon source. One strain designated as SDS18 was able to utilise maneb, ethylene thiourea and ethylene urea respectively as Carbon sources. The strain SDS18 was used for further studies.

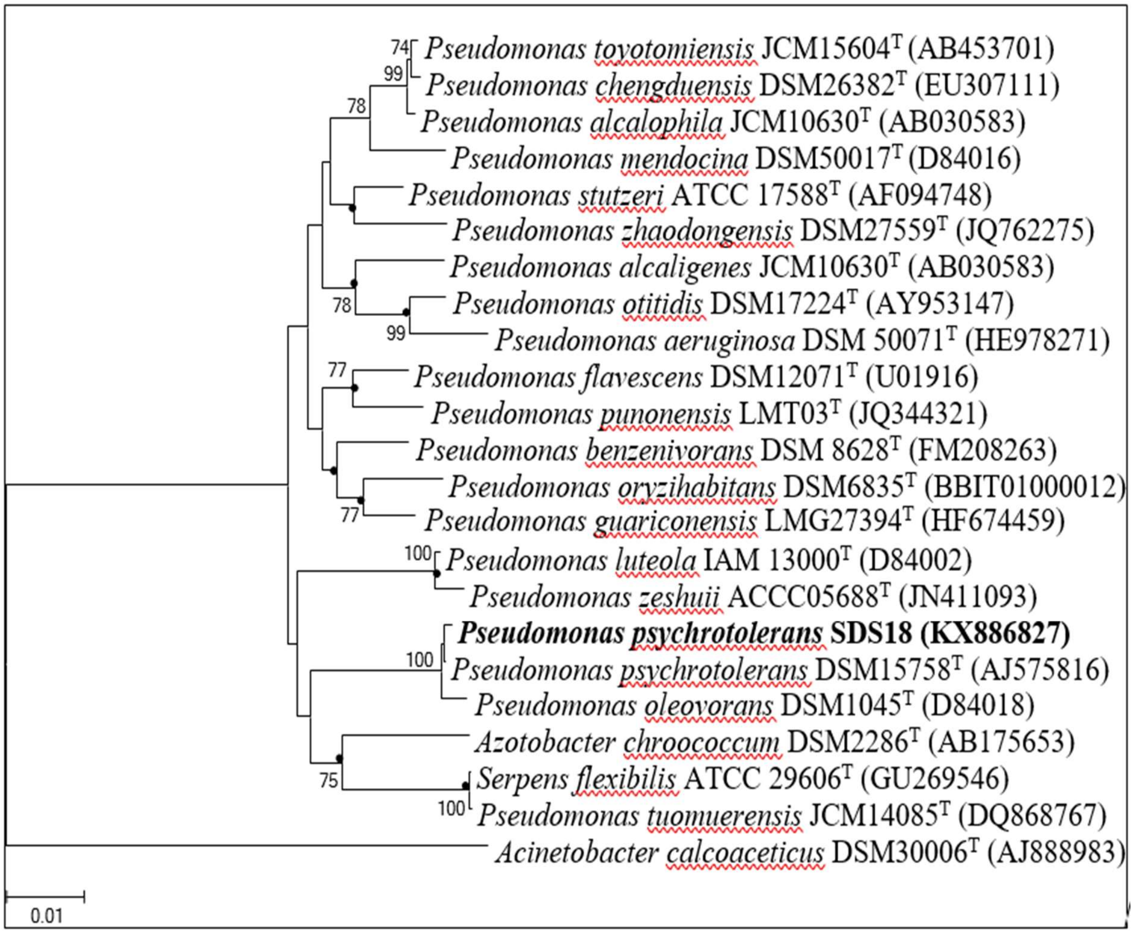

Figure 1. Phylogenetic neighbour-joining tree based on 16S rRNA gene sequences showing the relationship between strain SDS18 and other closely related members of the genus Pseudomonas. Acinetobacter calcoaceticus DSM30006T (AJ888983) was used as an outgroup. Bootsrap values (expressed as percentages of 1000 replications) greater than 70% are given at nodes. Filled circles corresponding to the nodes were recovered in the tree generated with maximum parsimony and maximum likelihood algorithms. Bar, 0.01% sequence variation. Gen Bank accession numbers are given in parentheses

3.2. Identification of the isolated bacterial strain

Microscopic studies suggested the bacteria to be Gram-stain negative, non-spore forming, motile and rod shaped. Biochemical and physiological tests indicated that the bacterium belongs to the genus *Pseudomonas*. Further, 16S rRNA gene sequence analysis (~1500bp) indicated the closest hit to be *Pseudomonas psychrotolerans* DSM 15758^{T} with 99.93% similarity followed by *Pseudomonas* *oryzihabitans* NBRC 102199^{T}, *Pseudomonas oleovorans* IAM 1508^{T}, *Pseudomonas stutzeri* ATCC 17588^{T}, *Pseudmonas toyotomiensis* HT-3^{T} and *Pseudomonas chengduensis* MBR^{T}. The 16S rRNA gene sequence was submitted to the GenBank database under accession number KX886827. The draft genome sequence of strain SDS18 is deposited to the NCBI database with accession number MTLN 00000000.

The combined phylogenetic tree constructed by Neighbor joining (NJ), Maximum parsimony (MP) and Maximum likelihood (ML) algorithms (Figure 1) shows that the strain SDS18 forms a distinct clade with *Pseudomonas psychrotolerans* (DSM 15758^{T}) and *Pseudomonas oleovorans* (DSM 1045^{T}). The genus *Pseudomonas* is known for various biological activities including the utilisation of several agrochemicals [28, 29]. However, there are no reports for degradation of ethylene bisdithiocarbamates by the genus *Pseudomonas*.

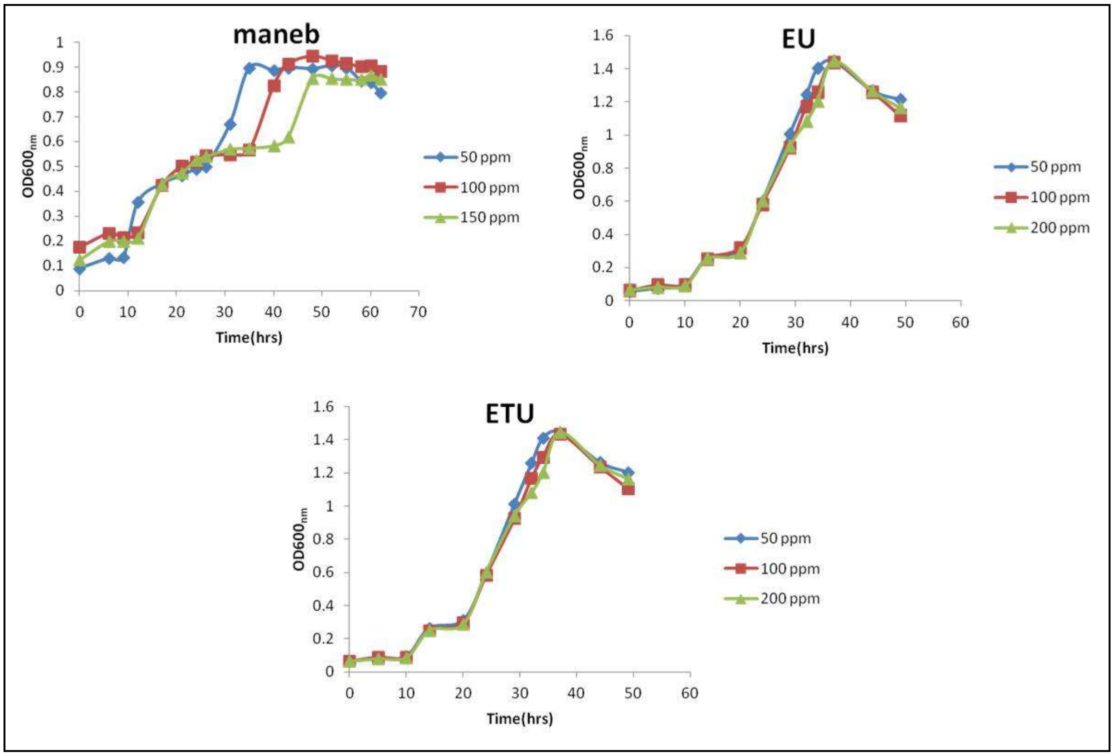

Figure 2. Growth curve of strain SDS18 on maneb, ETU and EU. The values represent an average value of three independent experiments

3.3. Growth profile of strain SDS18 on maneb and ethylenethiourea

The growth of a bacterial strain is measured by the increase in the turbidity and the optical density of the inoculated liquid broth [30]. Growth was absent in uninoculated controls. The increase in the optical density of MSM indicated the growth of strain SDS18 in MSM with the utilisation of maneb, EU and ETU as sole sources of Carbon. The growth curve revealed that the strain SDS18 utilises 50 ppm to 150 ppm concentration of maneb and 50 ppm to 200 ppm concentration of EU and ETU (Figure 2).In case of maneb the lag phase was seen at (10-25hours); log phase(28-40hours) and stationary phase at 40-60 hours. In case of EU and ETU the strain showed lag phase at 10 hours followed by log phase at 12-35 hours and stationary phase at 35-40 hours. The possible reason for a long lag phase in case of maneb could be due to the toxic and recalcitrant nature of the compound. Maneb can inhibit microbial growth, activity and proliferation. Hence, the strain(s) requires comparatively longer duration to adapt and overcome its toxic effects before they can actively grow and reproduce. This observation correlates with the previous reports of pesticide degradation [31]. Growth in the presence of such toxic compounds as sole Carbon source indicates transformation of the molecules to simpler ones via metabolism. In case of maneb, OD reached a value of 0.945 in 62 hours at 100 ppm concentration while in case of ETU and EU, maximum OD (1.446) was attained in 48 hours at 50 ppm concentration. However, the strain does not show much variation in the growth curve at different concentrations of maneb, ETU and EU. No significant change in pH of media was observed because the concentration of Na_2HPO_4 was quite high which acted as a buffer in the MSM.

3.4. Plant growth promoting activities of strain SDS18

There are some studies suggesting the isolation of bacteria conferring both pesticide degradation and plant growth promoting characteristics [32, 33]. The strains of *Pseudomonas psychrotolerans* are reported for plant growth promoting traits [34, 35]. The isolate SDS18 was checked for plant growth promoting activities namely production of HCN, catalase, ammonia, siderophore, auxin, ACC deaminase activity and phosphorus solubilisation. The strain SDS18 was positive for all, except HCN production.

In plants, catalase helps to get rid of H_2O_2, which is generated under oxidative stresses like salinity, high or low temperature, strong light, drought and various chemicals including particulate matter of air causing air pollution and herbicides [36]. Microbial strains exhibiting catalase activity are resistant to different types of stress [37]. The strain SDS18 produced effervescence upon addition of H_2O_2 indicating it to be positive for catalase production.

HCN is a gaseous secondary metabolite inducing negative effect on root growth and root metabolism. Thus, HCN producing bacteria are termed as 'deleterious rhizobacteria'. These are non-parasitic plant pathogens with the ability to secrete phytohormones and phytotoxins affecting the metabolism of plants negatively [38]. The strain SDS18 did not produce HCN even after4 days of growth as colour of filter paper remained similar to the control. The unchanged colour of the filter paper indicates that the strain did not produced HCN, conferring plant growth promoting feature to the strain.

N is required to synthesise bio molecules like proteins and nucleic acids. Since atmospheric N is inaccessible to plants [39], PGPB converts N to ammonia (assimilable by plants) known as biological N fixation [40]. Ammonia production also hampers the growth of phyto pathogens [41,42] reported ammonia production in rhizospheric isolates belonging to *Bacillus*

(95%) followed by *Pseudomonas* (94.2%). In fact, the endophytic strain *Pseudomonas psychrotolerans* PRS08-11306 possess 'turnerbactin' a biosynthetic gene cluster for nitrogen fixation [43]. In the present study, the strain SDS18 was able to produce ammonia in peptone water, as addition of Nessler's Reagent changed colour to brownish yellow.

Siderophores are small molecules having high affinity for iron which aid in scavenging iron by formation of soluble Fe^{3+} complexes which can be easily taken up by the mechanism of active transport [44]. CAS shuttle assay indicated that strain SDS18 was able to produce siderophores within 24 hours of growth. The percentage of siderophore production was found out to be 60.98%. Literature suggests the production of siderophores by *Pseudomonas* spp. Amongst the species of *Pseudomonas*, *Pseudomonas fluorescens* and *Pseudomonas aeruginosa* produce pyoverdins which are fully characterized, while *Pseudomonas stutzeri* is known to produce ferrioxamine E, also called nocardamine [45,46]. Importance of siderophores producing bacteria in phytoremediation has been mentioned in numerous studies [47,48].

Phosphate solubilisation is one of the most important criterions for PGPB [49]. PGPB possess the ability of solubilising the inorganic phosphorus (P) such as calcium phosphate [$Ca_3(PO_4)_2$], ferric phosphate [$FePO_4$] and aluminium phosphate [$AlPO_4$] of soil and make it available to the plants by secreting organic acids and acid phosphatases [50]. Members of genus *Bacillus* and *Pseudomonas* are reported as the most efficient phosphate solubilising bacteria [51].The phosphate solubilising activity of strain SDS18 was checked by growing the strain in Pikovaskaya's broth for 4 days and the amount of soluble phosphate was calculated (Figure 3a) as described by [52]. We found that the concentration of phosphate increased from 1.36mM to 3.682mM after 4 days of incubation, whereas in control the concentration remained unchanged.

Ethylene is the only gaseous phytohormone regulating the processes of plant growth, development and senescence. Under stress causing conditions like flooding, drought, action of heavy metals, phytopathogens, and high salt, the production of the hormone increases and negatively affects the development of a plant [53]. One of the mechanisms involving the regulation of ethylene production is the activity of an enzyme '1- aminocyclopropane-1-carboxylate (ACC) deaminase' found in bacteria. The enzyme ACC deaminase converts ACC which is the direct precursor of ethylene to α-ketobutyrate and ammonia helping in the growth of plants [54]. The PGPB exhibiting ACC deaminase activity stimulates plant growth, mainly in unfavourable conditions [54]. When the strain SDS18 was cultured in the DF MSM medium with ACC as the sole N source, the strain was able to use ACC as sole nitrogen source implying its ACC deaminase activity. The activity was 8.625±1.25 µM of α-ketobutyrate/h/mg protein. Literature reports the existence of ACC activity in *Pseudomonas* spp [55]. Phytohormones are chemical compounds enacting as messengers and coordinating the cellular functions of plants. In plants, five major phytohormones namely auxin, gibberellins, cytokinin, ethylene and abscisic acid are present. The most abundant occurring auxin is indole-3-acetic acid (IAA). It is a major signaling molecule

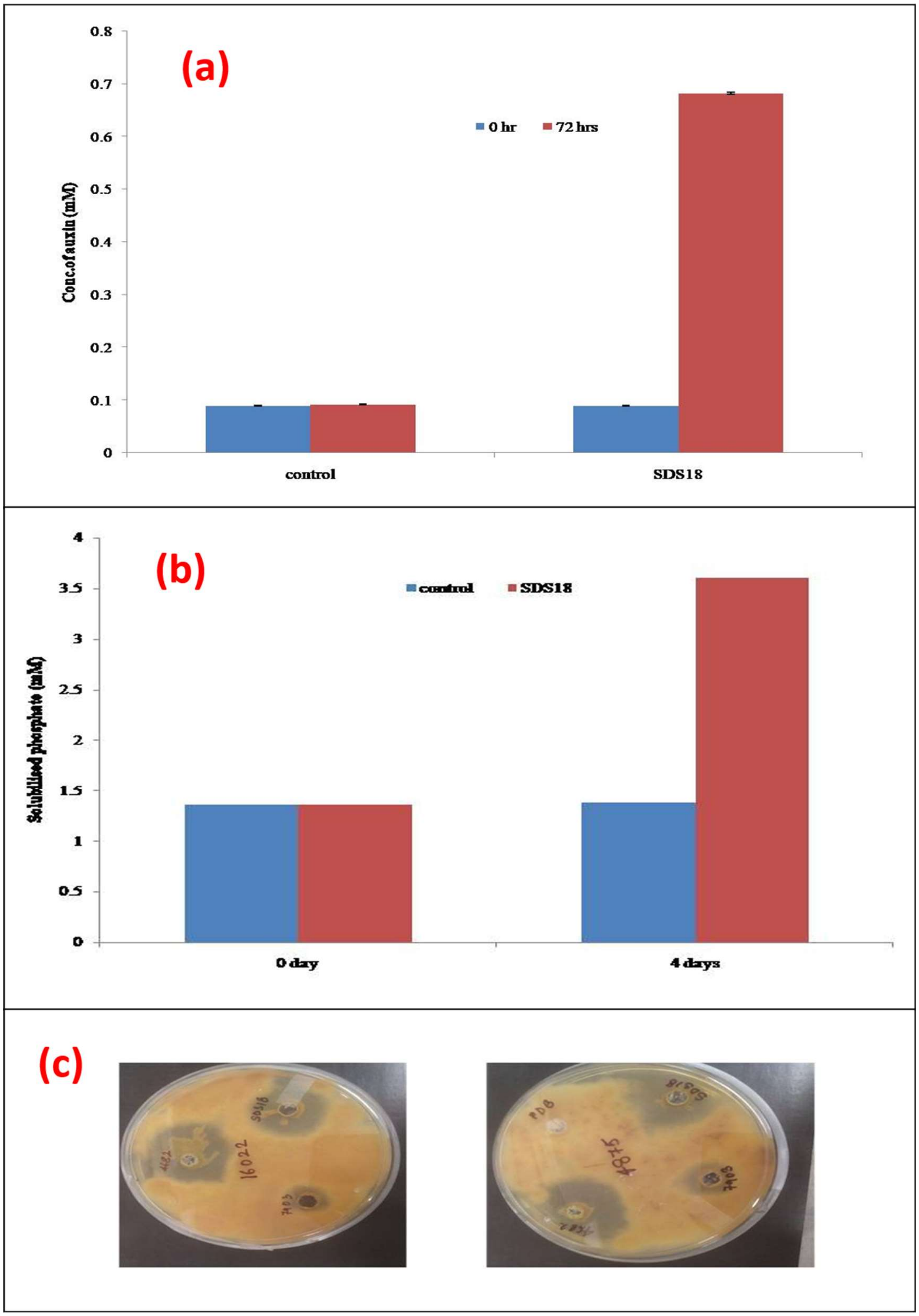

Figure 3. Plant growth promoting traits of strain SDS18: (a) Phosphate solubilisation activity. The values represent an average value of three independent experiments. (b) IAA production, the values represent an average value of three independent experiments. (c) Antifungal activity of SDS18 on Cladosporium cladosporioides and Alternaria citri; MTCC4682-Pseudomonas aeruginosa IC230; ATCC16022- Cladosporium cladosporioides; MTCC 4875- Alternaria citri; MTCC7903-Pseudomonas aeruginosa PfD1.

since it regulates the process of plant development together with organogenesis and cellular responses like cell division, cell expansion, differentiation and gene regulation [56]. Interaction between IAA producing organisms and plants results in positive effects on the plant side, ranging from phytostimulation to pathogenesis. IAA producing bacteria use this hormone to interact with plants as a part of their colonization approach. L tryptophan is considered as the precursor of IAA synthesis in bacteria [57]. The strain SDS18 produced IAA in the presence of tryptophan (Figure 3b). The results presented in Figure 3b indicates that the concentration of auxin increased from 0.089mM to 0.682mM after 72 hours of growth in case of flasks inoculated with the strain SDS18, whereas the concentration of auxin remains unchanged in uninoculated control.

Several bacteria have been recognized as prospective biological control agent of fungal phyto pathogens due to their ability to guard plants against various important agronomical fungal diseases like black rot of tobacco, pea and wheat, damping off sugar beet. *Pseudomonas* secretes a variety of antibiotics like pyrrolnitrin, 2,4-diacetylphloroglucinol(2,4-DAPG) and Pyoluteorin [58]. Antifungal activity experiments confirmed that the strain SDS18 was capable of inhibiting the growth of *Cladosporium cladosporioides* and *Alternaria citri* (Figure 3c). The zone of inhibition in case of *Alternaria citri* was 26 mm comparable with the positive control *Pseudomonas aeruginosa* IC230. The strain SDS18 showed 28 mm zone of inhibition in case of *Cladosporium cladosporioides*; while the positive control *Pseudomonas aeruginosa* showed 33 mm.

3.5. Comparative genomic analysis of the PGPR genes

In silico studies of plant growth promoting bacteria suggested the presence of genes in the selected bacterial strains conferring plant growth promoting traits [59]. The genome mining of the strain SDS18 revealed the presence of genes related to plant growth and development. Further to confirm the plant growth promoting ability of the strain SDS18, comparative genomic analysis between the γ-*Proteobacteria* strains reported for plant growth promoting traits was done. For analysis, recently reported plant growth promoting strains *Pseudomonas fluorescens* PS006 [60], *Klebsiella* sp. D5A [61] and *Pseudomonas putida* S11 [62] were chosen. The comparison (Table 1) shows that the strain SDS18 contains the necessary genes attributed for plant growth promoting characteristics.

Table 1. Comparative plant growth promoting genomic features of Pseudomonas psychrotolerans SDS18, Pseudomonas fluorescens PS006, Klebsiellasp.D5A, Pseudomonas putida S11.

S.No.	Plant growth promotion traits	*Pseudomonas psychrotolerans* SDS18	*Pseudomonas fluorescens* PS006	*Klebsiella*sp. D5A	*Pseudomonas putida* S11	Genes with Potential for conferring PGP traits
1.	Phosphate solubilisation	Yes	Yes	Yes	Yes	Glucose dehydrogenase, *pqq*dependent
2.	IAA production	Yes	Yes	Yes	Yes	Indole-3-glycerol phosphat e synthase
3.	Siderophore production	Yes (Achromobactin, Enterobactin)	Yes (Pyoverdine)	Yes (Enterobactin, Aerobactin)	No	acsA, acsB, acsC, acs D, acsE, acsF
4.	Catalase	Yes	Yes	Yes	Yes	Catalase gene homolog
5.	Acetoin & butanediol synthesis	Yes	Yes	Yes	Yes	Acetoin dehydrogenase cluster
6.	Peroxidases	Yes	Yes	Yes	Yes	
7.	Superoxide dismutase	Yes	Yes	Yes	Yes	
8.	Ammonia production/ assimilation	Yes	Yes	Yes	Yes	Glutamate synthase gene cluster

3.6. Comparative genomic analysis of the stress response genes

Stress response is stimulated in bacteria when the bacterial cell encounters unfavourable conditions in the immediate environment. In order to cope with the stress, certain genes are activated which controls molecular pathways [63]. Maneb and ETU are toxic compounds. The compounds causes oxidative stress [64]. Literature suggests that increase in oxidative stress leads to Parkinson disease, Alzheimer's disease, heart failure, cancer, and atherosclerosis. In response to oxidative stress, cells are known to produce antioxidant enzymes like catalase, superoxide dismutase, heme oxygenase-1 and glutathione-S-transferases. These enzymes are known to protect the cells against oxidative stress/damage [65].

Literature suggests some bacteria like *Pseudomonas aeruginos* [66], *Micrococcus* sp. S2 [67] and *Bacillus subtilis* [68] produce superoxide dismutase especially manganese superoxide dismutase which plays a significant role in resistance towards oxidative stress.

The annotated genome of the bacterial strain *Pseudomonas psychrotolerans* SDS18 contains fifty six genes for oxidative stress. Some of the important genes are glutathione-S-transferase, NAD dependent glyceraldehyde-3-phosphate dehydrogenase, NADPH dependent glyceraldehyde-3-phosphate dehydrogenase, manganese superoxide dismutase, superoxide dismutase [Cu-Zn] precursor, catalase, hydrogen peroxide-inducible genes activator, ferroxidase and peroxidase. There are no reports for maneb and ETU degrading genes apart from the presence of cytochrome P_{450}.

3.7. Analytical techniques for identification of putative intermediates of maneb degradation

There are some reports which state the transformation of maneb to ETU and EU [9]. The sample extracts obtained at 24 hours indicated no formation of metabolites. The sample extracts obtained at 48 hours and 72 hours indicated formation of ETU. Hence, the two sample extracts were combined. Further work of identification was carried out with this sample extract. No growth was seen in case of both the control flasks.

3.7.1. HPLC Analysis

The extracted intermediate was subjected to HPLC in order to compare its retention time with that of the authentic standard ETU. The HPLC profile of the intermediate showed the retention time of 3.973 minutes identical to that of the standard of 500 ppb ETU (Figure 4a and Figure 4b). The HPLC results suggest the extracted intermediate as ETU.

3.7.2. FTIR Analysis

In order to determine the functional groups, present in the extracted intermediate, FTIR analysis was done. The similarities revealed between the FTIR spectra of the standard and extracted intermediate as shown in supplementary figure 2a and 2b indicates that the extracted intermediate is ETU. The medium peak within the range 3250-3400 cm^{-1}represents the N-H stretch of ETU. C-N stretch is represented by the variable peak within the range 2210-2260cm^{-1}. A strong peak within the range 3000-3100cm^{-1} represents the C-H stretch

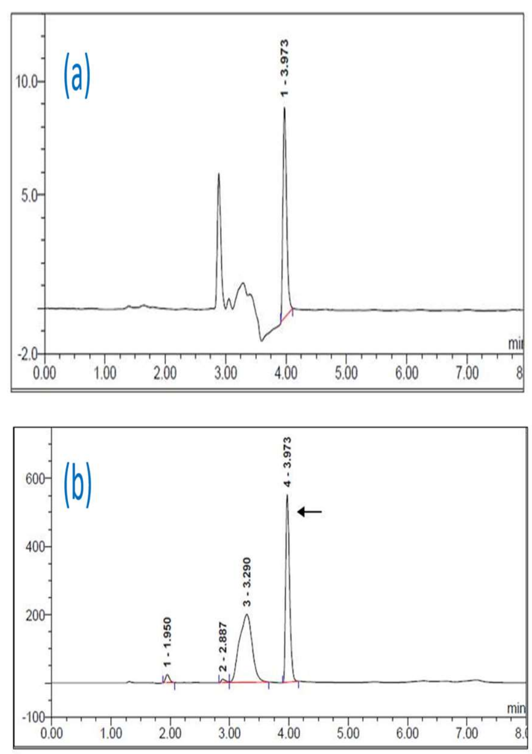

Figure 4. HPLC for structure determination of the extracted intermediate. (a) HPLC chromatogram of 500ppb ETU showing a peak at 3.973 minutes. (b)

of aromatic compounds [69]. The FTIR results finally revealed the presence of ETU in the extract.

3.7.3. [1]HNMRAnalysis: To find out the position of protons, [1]HNMR is a useful technique. We performed and analysed the proton NMR spectra for both the standard and sample. The [1]HNMR spectra indicated that the compound ETU has one singlet at δ 4.86 due to the symmetrical environment (Figure 5a). Similar NMR spectrum is obtained for the extracted intermediate too (Figure 5b). The [1]NMR results revealed the compound to be ETU.

3.7.4. LC/Q-TOF-MS Analysis

For finding out the percentage of transformation of maneb to ETU, LC/Q-TOF-MS studies of the culture supernatant were done at different time intervals. The m/z peak for maneb is at 265.01 (Figure 6a). After75 hours the culture supernatant showed a reduction in m/z peak at 265.01 (Figure 6b). Hence, 35.78% reduction of maneb occurred.

The fungicide maneb is broken down to ETU. ETU is a well-known metabolite of dithiocarbamate fungicides. The molecular weight of ETU is 102.2. Since, the strain is able to utilise ETU as Carbon source, LC/Q-TOF-MS studies were performed to find out the percent reduction. The LC-MS spectrum of 0 hour (Figure6c) indicates the m/z peak of ETU at 103.03 while the spectrum of 75 hours (Figure 6d) reveals the complete disappearance of the peak of ETU. This suggests the transformation of ETU to simple molecules. There are reports suggesting the transformation of ETU to CO_2, H_2O [70]. However, in our study we could not detect the formation of small molecules formed as a result of ETU breakdown.

Further, identification of genes/enzymes involved in the biodegradation of maneb and ETU could lead to elucidation of the complete pathway. Maneb degradation ability and PGP traits of strain SDS18 suggest that bacteria can be used in field for eliminating fungicide as well as support growth of plants.

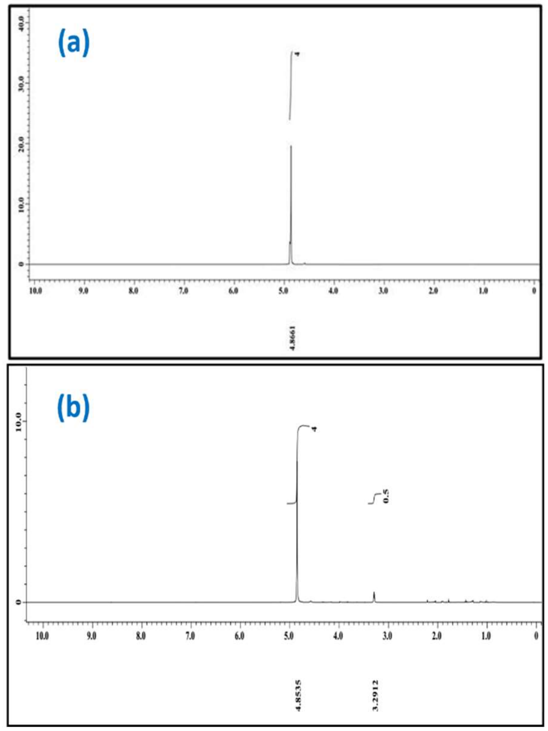

Figure 5. [1]HNMR for structure determination of the extracted intermediate. (a) [1]HNMR spectrum of 1 ppm ETU, (b) [1]HNMRspectrum of the extract.

4. Conclusions

This study reports the characterization and biodegradation potential of a plant associated bacteria for maneb and its photolytic product. The plant associated bacteria mainly consisted of *Firmicutes* and *Proteobacteria*. Of all the isolates, the most promising strain SDS18 was characterized as *Pseudomonas* *psychrotolerans* by polyphasic taxonomy. The strain SDS18 was able to utilise upto 150 ppm of maneb and 200 ppm ethylene thiourea as sole Carbon sources. The isolate was unique in its attribute of exhibiting all plant growth promoting features and possessing antifungal activities against *Alternaria citri* and *Cladosporium cladosporioides*. *In silico* studies of the strain SDS18 revealed that its genome has genes for phosphate solubilisation, ammonia production and assimilation, IAA production, siderophore production, acetoin and butanediol synthesis, peroxidases and superoxide dismutase which are also present in other plant growth promoting bacteria. The genes to combat stress response generated due to the toxic maneb were also present. *In vitro* biodegradation studies had shown that the strain could degrade 35% maneb to ETU. Further, ETU was completely degraded. Hence, the plant growth promoting strain SDS18 can prove to be a potential candidate for maneb and ETU degradation.

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Conflict of Interest

The authors declare that they have no conflict of interest.

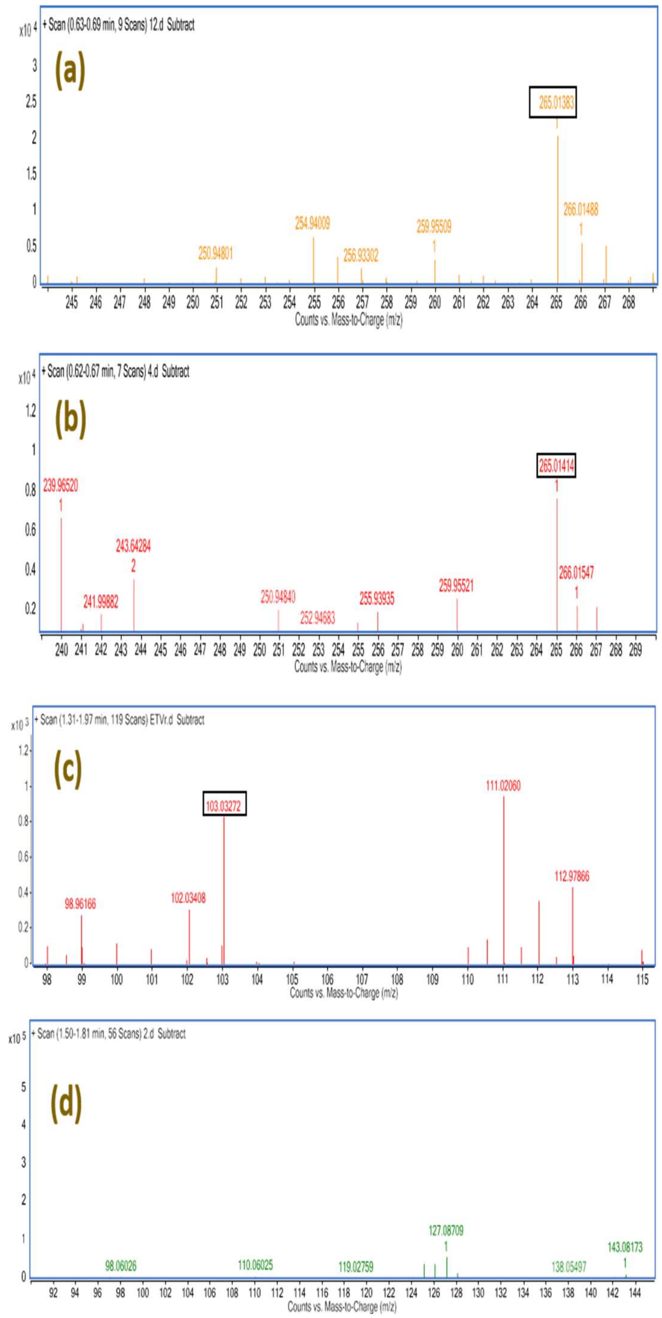

Figure 6. LC/QTOFMS studies showing reduction of maneb and ETU. (a) LC-MS spectrum for 0 hour culture supernatant showing the m/z peak of maneb at 265.01; (b) LC-MS spectrum for 75 hours culture supernatant showing the reduction (35.78%) in the m/z peak of maneb at 265.01; (c) LC-MS of 0 hour culture supernatant

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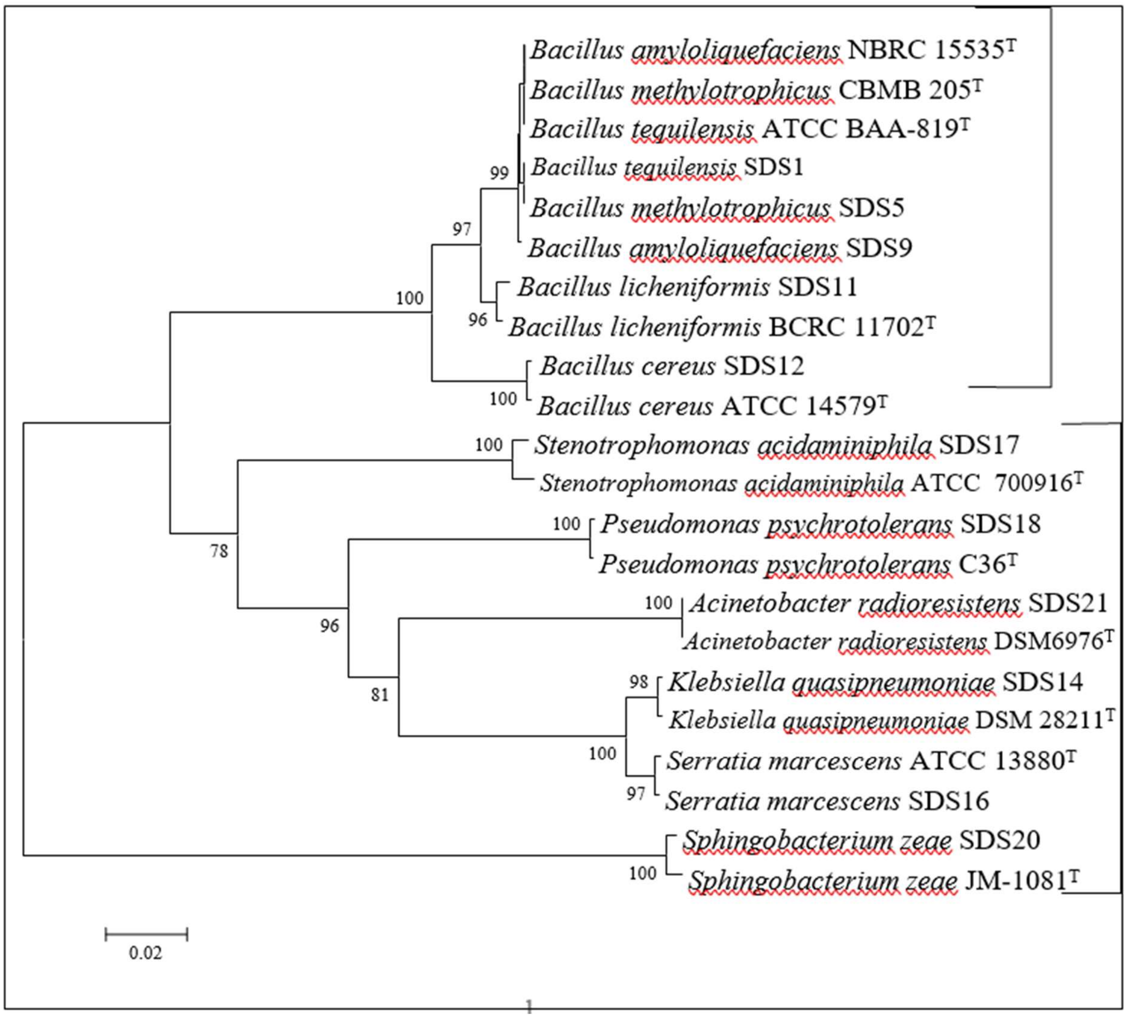
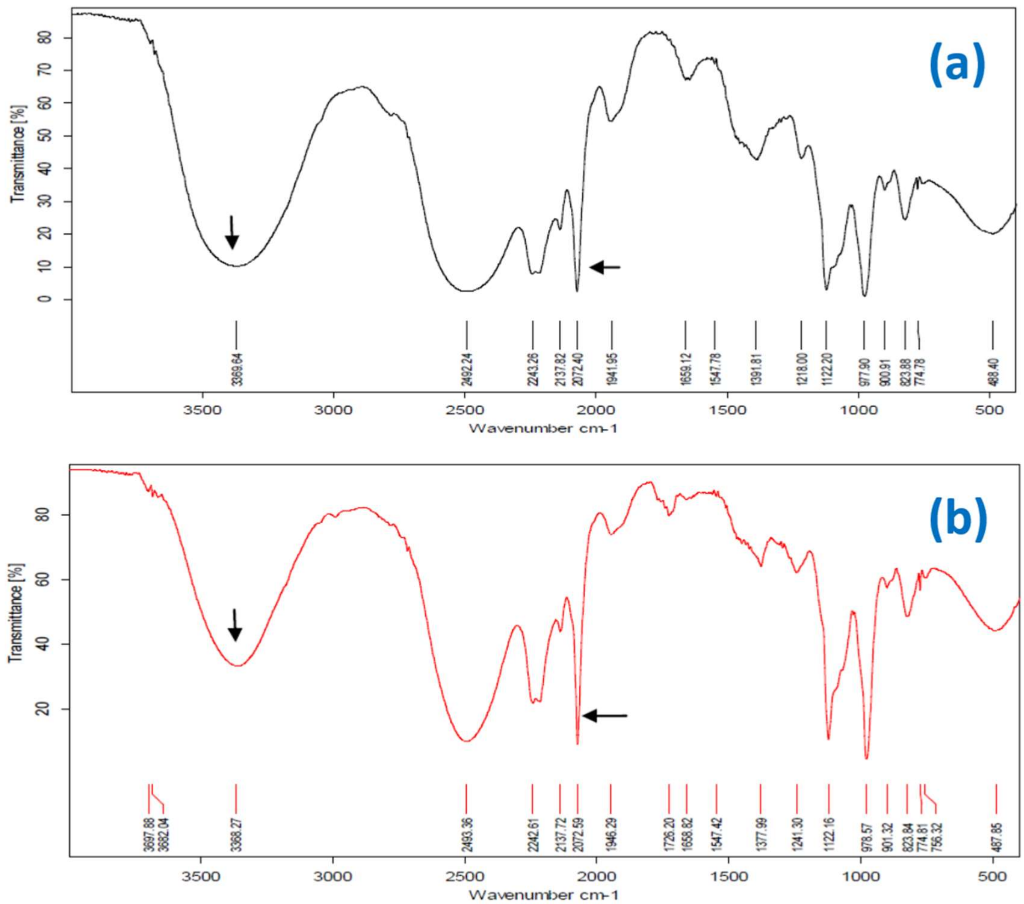
Supplementary Information



Supplementary Figure 1. Neighbour joining based phylogenetic tree of the plant associated isolates.



Supplementary Figure 2. FTIR Spectrum. (a) 1 ppm ETU, (b) Extracted intermediate.

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Memristor Functional Layer Dynamics in Real-Time Data Analysis and Its Applications: A Review

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Abstract

In the age of artificial intelligence, it is crucial to have high-speed capabilities for processing and storing data. Existing CMOS-based technologies encounter a bottleneck in achieving high-speed computing due to the separate storage and processing units, causing communication lag that impedes processing speed. Memristors, with their capacity for parallel data storage and processing, present a promising solution. This advanced capability is harnessed in state-of-the-art real-time data analysis to boost the processing speed. In this review, the utilization of memristors as computing hardware for real-time data analysis has been discussed. This review systematically explores different classes of materials considered for functional layers and delves into their characteristics, accompanied by a discussion on potential applications.

Keywords: Memristor, Function layer, Switching, Real-time data analysis, Neuromorphic, Reservoir computing.

1. Introduction

Big data is a term often coined for massive data sets which are difficult to quantify in the general numerical system for accounting for the size of data. These data sets are massive and are sporadic in nature creating difficulties in storage, analysing and visualizing [1]. This has also been defined as data that is derived from copious sources such as satellites, social media, people, machines and more. This data can be something as specific and personal as phone numbers and bank details, and something as huge and public as movies, videos, weather information and more [2]. It can also be in the form of health and information like image sensing, scans and various reports curated for the purpose of expanding knowledge and disease management[3].

The management of this big data requires complex machinery, both hardware and software, involving statistical and mathematical theory concepts [4]. Big data is often characterized by the 7 Vs: Volume, Velocity, Variety, Veracity, Validity, Volatility, and Value [5]. These dimensions capture various aspects of modern datasets, including their scale, speed, complexity, reliability, accuracy, instability, and usefulness. Deep learning is one of the machine learning techniques that has successfully achieved face recognition, communication and sensor networks[6]. Data is a source of knowledge, information, and accountability; so now, more than ever, big data analysis is very important. The collection of this data helps gain a fundamental understanding of basic principles and scientific ideas [7]. Another side to big data is that the management techniques are not like regular data, as big data is unstandardized and highly unpredictable. The period of analysis is also very essential as, in a small amount of time, there can be a huge change in the environment [8]. With problems like analysing big data, there also seem to be questions about hardware. It needs to be considered how the hardware will be developed that is fast and accurate. Hence, in recent years, computer hardware and software have shifted from computing intensive to memory intensive [9]. It is popularly known as the 'memory wall' or von Neumann bottleneck, which refers to the limited data transfer rate between the processor and memory, restricting overall system performance.. To solve these, we see a growing interest in modern computing methods such as PIM (processing in memory), NN (neural networks) and ML (machine learning). The memory wall problem is caused due to slow memory access to the CPU and hence slowing down the speed of computing [10]. In 1965 Gordon Moore published a paper that observed a techno economic phenomenon that the number of transistors in computer chips is growing exponentially every two years [11]. This exponential growth resulted in doubling the functionality and productivity, but Moore's law is expected to fail by 2025 [12] because of miniaturization and reducing lithography to atomic level [13]. The memristor offers a viable solution to the challenges posed by the limitations of traditional data processing technologies, particularly in managing the growing demands of big data at scales where Moore's law falters. The memristor has emerged as a promising solution to the challenges posed by traditional computing architectures, particularly in the context of big data processing. By integrating memory and computation into a single device, memristors enable faster data transfer and significantly lower energy consumption. In the early 1970s, Leon O. Chua theorized the memristor as the fourth fundamental circuit element—alongside the resistor, capacitor, and inductor—based on symmetry principles in circuit theory [14]. Since the first experimental demonstration of a memristive device in 2008, extensive research has explored its potential applications, particularly in neuromorphic computing and artificial neural networks. [15-16].

Memristors have gained considerable attention as key components for next-generation computing systems due to their non-volatility, low power consumption, high density, and excellent scalability. As image acquisition, transmission, storage, and conversion become increasingly efficient, the volume of image data is growing rapidly. However, the limitations of conventional computational systems based on the Von Neumann architecture are becoming more apparent, making it essential to enhance the efficiency of processing—a challenge that has long concerned researchers in the field. Memristors, with their non-volatile, synapse-like properties and ability to integrate storage and computation, offer a promising solution. They are crucial for developing intelligent processing systems that mimic the structure and function of biological brains and for creating new image processing systems based on non-Von Neumann architectures, enabling integrated storage and computation of image data [17, 18, 19, 20].

The memristor behaves like a resistor that is non-linear, and it has the ability to remember its previous states of resistance. This change in resistance is based on the amount of current that flows through the memristor. Based on changes in polarity due to applied voltage, they can be classified into unipolar or bipolar memristors [21]. Bipolar can be set or reset with a change in polarity of an input signal, but in unipolar, the device can be set and reset with a change in the threshold value of current [22]. Now, we will analyse the importance of this fourth fundamental element for work in interdisciplinary fields. Within the field of bioimpedance and biotechnology, memristors can be of huge value, as electronic skin and neural networks and memory [23].

The memristor has a structure analogous to the synapse structure. The top electrode acts like the presynaptic neuron, the insulator as the synapse and the bottom electrode as the post-synaptic neuron. In nervous systems, the collective activities and firing patterns of neurons regulate functions, consciousness, and memory formation [24]. Understanding the encoded features in neural spike trains, the time series of electrical impulses used by neurons to communicate, within the neural network is essential for advancing our comprehension of the operational mechanisms of the nervous system [25]. This understanding can come from using memristors for real-Reservoir Computing (RC), a machine learning paradigm derived from recurrent neural networks (RNNs), uses a fixed dynamic system (reservoir) to process input data, allowing only the output weights to be trained, and has proven successful in accomplishing diverse tasks, including image pattern recognition, time series forecasting, and pattern generation [27]. A schematic representation of the memristor analogous to the biological synapse is depicted in Figure 1.

Real-time data analysis is important in scenarios where processing data immediately as it is generated is essential. This approach ensures that the information is rapidly processed and provides real-time output for analysis [28]. Real-time data analysis is particularly indispensable in situations requiring immediate action, such as surveillance. This methodology provides up-to-date information promptly, allowing for swift decision-making and response [29]. Despite being more complex and expensive compared to near real-time or batch processing methods, the benefits of instantaneous data analysis make it indispensable in critical, time-sensitive applications such as driverless cars, traffic surveillance and satellite monitoring [30].

2. Memristor

A memristor, which is short for 'memory resistor', is a thin 2-terminal electrical device that is specific for its ability to remember its state history even when voltage is drawn. It is referred to as metal insulator metal structure (MIM) [31].

2.1. Memristor characteristics

Endurance: Endurance of the device is determined by its stability after multiple switching cycles [32]. Endurance is affected by various intrinsic factors like process variations of the device and extrinsic factors such as electrical stress created by circuits [33] .

Resistance Ratio: Upon activating the device, the resistance is set at 100 ohms, and upon deactivation, it increases to 10,000 ohms. To switch the device off, a signal with opposite polarity is applied, causing the conduction filament to break and the resistance to increase, leading to the device's deactivation [34]. We utilize the same signal patterns as in the endurance case, ensuring a significant distinction between high resistance and low resistance, allowing for easily differentiable spacing or windows [35].

Retention: How long the device remains in either the on or off state is determined by applying a signal for initialization. The voltage is continuously monitored to observe the device's behaviour over an extended period in the low-resistance stage. In the high-resistance phase, a pulse is applied to assess the duration of the device's state [36].

Switching speed: In a memristor, the rate at which you can switch between the on and off states is determined by the movement of charged particles in the functional layer. Applying a positive voltage causes particles to move, facilitating the transition to the on state [37]. However, when the device is

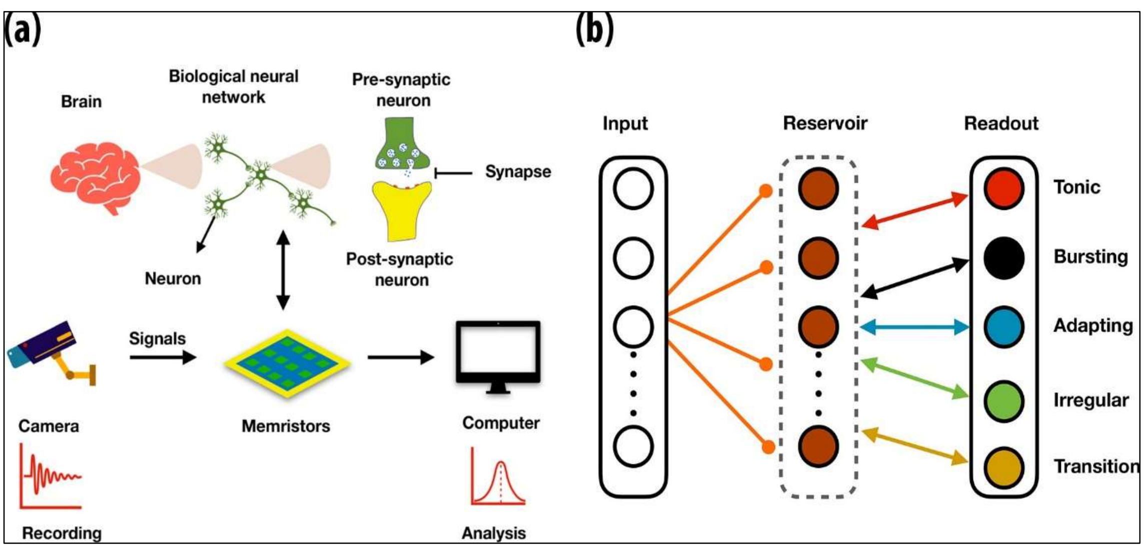

Figure 1. Schematic showing memristor-based real-time neural spike analysis. The input signal is generated based on the activity. The memristor is an analogy to biological synapses and is used for neural signal analysis [52].

reset, the process becomes abrupt and induces changes that may damage the device to some extent. The extent of damage and how the device retains depend on the specific characteristics of the device [38].

Power consumption: When a voltage is applied, the device operates at a power level determined by the set or reset process. The power at which the device is set or reset corresponds to the energy required to establish or disrupt the state of the device [39].

2.2. Electrodes

Memristive devices, relying on resistive switching (RS) phenomena, are promising for next-generation and the development of neuromorphic computing architectures. A straightforward method to create a memristive device is by placing an insulator material between two metal electrodes, forming a metal–insulator–metal (MIM) structure. In these devices, the switching mechanism depends not only on the insulator material but also on the choice of metal electrodes and the properties of the metal–insulator interface [40]. The electrode connects the functional layer through the top and bottom electrodes and probes the functional layer with different input signals [41]. These electrodes serve as pre and post-synaptic neurons in neuromorphic computation [42]. These are realized as a change in the size of the electrodes and a decrease in the memory conservation [43]. Even the effects of electrode materials and the operating environment show changes in the device. In some materials such as Ti/MgFx/Pt conducting or electroforming occurs better in vacuum because removing moisture makes the device more resistive [44]. Meanwhile, other materials conduct better in the open air. In further cases, the effect of different top electrode materials was analysed on the resistive switching effect of the memristor and results still have to be established [45]. The electrodes play a crucial role in determining the switching behavior of devices. Electrochemically active electrodes, such as Ag and Cu, can help form conductive channels within the devices, enabling the switching process. Under a high electric field, these metal atoms can oxidize into metal ions and diffuse into the functional layer matrix, creating a conductive pathway between the electrodes [46, 47]. In contrast, inert electrodes like Pt and Au do not directly contribute to the switching phenomenon. The work function of the electrode material is also a key factor in memristors, as it influences the contact between the metal and the functional layer. Depending on the energy band level of the functional layer, electrodes can form either ohmic or Schottky contacts [48]. In an ohmic contact, charge carriers experience minimal resistance and can move easily between the electrodes and the material. Conversely, in a Schottky contact, a space-charge region forms due to the diffusion of carriers, leading to the creation of a built-in potential barrier that restricts further carrier flow [49]. At low voltage, the device remains in a high-resistance state (HRS). However, as the voltage increases, the current rapidly escalates due to the breakdown of the Schottky barrier, resulting in a low-resistance state (LRS). When an opposite bias is applied, the potential barrier at the interface rises, keeping the device in the HRS. This behavior underscores the critical role of electrode selection and contact formation in the performance of memristor devices[50, 51].

2.3. RS Material

The resistive switching materials play a crucial role in the performance of the memristor device. These devices have different structural and functional characteristics based on their materials. They are of two types: organic and inorganic resistive switching materials. Organic materials have various advantages, such as availability, flexibility and low cost. On the other hand, inorganic materials have characteristics like high speed, stability and robust and accurate behaviour. The performance of memristors made from various types of materials is summarized in Table 1.

Table 1. Comparison table for different materials

Materials	Device Structure	Vset/ Vreset	ON/ OFF ratio	Endurance	Retention	Reference
Metal Oxide	Pt/TiO2/Pt	9.6/6.65	10^2	25	10^3	[54]
	Ag/TiO2/Pt	0.23/-0.12	-	-	10^4	[55]
	TiN/ZrO2/Pt	1.5/-2	10	600	10^4	[56]
	TiN/TiOx/ HfOx/TiN	1.5/-1.4	~ 10^3	10^4	10^4	[57]
	Ag/ZnO/Cu	1.2/-1.25	~ 10^3	~ 500	-	[58]
	Au/ZnO/Au	4/-4	10^2	-	-	[59]
	Pt/WO3/Pt	2/-2	10	50	$3×10^4$	[60]
	Au/CeO2/Au	2.4/-3	10^4	-	-	[61]
Polymer	Ag/PVK:1 TCNQ/ITO	0.69/-0.62	10^3	10^4	10^4	[62]
	Au/PEDOT: PSS@Ag/ PMMA/ITO	-10/+7	10^2	50	10^4	[63]
	Al/iPrP- PDI/ITO	-1.5/2	10^3	250	10^5	[64]
	Ag/2D Imine/ITO	+1/-3.3	10^5	200	$8×10^4$	[65]
Perovskite	Ag/MAPbI3/Au	0.32/0.13	10^7	10^3	10^4	[66]
	Au/MAPbI3− xClx/FTO	0.1/0.45	10^4	400	10^4	[67]
	Ag/PMMA/ CsPbI3/Pt	0.18/0.1	10^6	300	-	[68]
	Ag/PMMA/CsSnI3/Pt	0.13/0.08	$7×10^3$	600	$7×10^3$	[69]
	Ag/PMMA/CsPbBr3/PMMA/ ITO	2.6/2.8	10^5	5000	10^5	[70]
	Ag/FAPbI3/Pt	0.22/0.22	10^5	1200	10^3	[71]
	Ag/(PEA)2(MA)n−1Pbn I3n+1/ITO/ PET	1/1	$7×10^3$	2500	$6×10^2$	[72]
Proteins	Al/Silk/ITO	10.4/-11.5	10^{120}	10^{10}	10^3	[73]
	Ag/keratin/ITO	6/-6	10^{160}	150	$3×10^3$	[74]
	Al/gelatin/ITO	-0.7/+2.5	10	6	10^{120}	[75]
	Cu/rDnaJ/Pt	0.12/-0.08	10	6	10^{100}	[76]

2.3.1. Metal oxide: Metal or binary oxide materials have several benefits, such as easy and simple preparation, low cost, and stability, and they are compatible with the CMOS (Complementary Metal Oxide Semiconductor) process. Numerous oxide materials, including Al_2O_3[53], TiO_2[54], SiO_2[55], HfO_x[56], TaO_x[57], WO_x[58], SnO_x[59], NiO_x[60], ZnO[61], and others, have been studied for RS behavior. The RS phenomenon in oxide-based memristors is primarily attributed to the migration of oxygen vacancies [62, 63]. Utilizing engineering techniques to manage oxygen vacancies within the functional layer matrix offers a pathway for altering the properties and characteristics of oxide-based memristors, thereby enhancing their suitability for memory and neuromorphic applications[64, 65]. In one of the cases, a multifunctional trilayer was created of $HfO_x/Al_2O_3/TiO_2$. The trilayer helps in interchanging the properties of the materials and upgrading the quality of the device [66]. It has been observed that for highly reactive materials like Hf and Ti, long pulse endurance can be obtained [67]. Whereas materials like Ta, which are less reactive, have a longer retention time, suggesting a low resistance stage [68]. Many calculations and previous research show that Hf, Ti, Zr, and La metal caps exhibit superior thermodynamic efficacy in oxygen extraction from HfO_2[69]. This is attributed to the fact that the energy demand for these metals in the reaction is the lowest among all considered elements.

2.3.2. Polymer: Today, more than ever, there is a requirement and demand for high-performance and flexible memristor devices that mirror artificial synapses. Resistive Switching (RS) phenomena are observed in polymers such as PEDOT (Poly(3,4-ethylenedioxythiophene), iPrP-PDI (polydispersity index), PEDOT: PSS (Poly(3,4-ethylenediox-ythiophene) polystyrene sulfonate), PVK Poly(N-vinyl carbazole), imine, PBDTT (poly(2,2′-disulfonyl-4,4′-benzidine terephthalamide)), and others [70, 71, 72, 73, 74, 75]. Some polymers that have been used in memristor studies are organic, and some are inorganic[76]. The example of organic-inorganic is Ag/SU-8Ag/Pt [77]. These crystalline inorganic structures mentioned above are very strong due to thermally stable ionic bonds but are weak in flexibility and need to endure high preparation temperatures [78]. Whereas the organic materials mentioned have good flexibility because of comparatively weaker ionic bonds, due to these weak bonds, they lack thermal stability [79]. Hence, it is difficult to find a memristor material that satisfies all the conditions required for it to be a high-performance device. Therefore, an inorganic ionic memristor was proposed, which has both ionic and covalent bonds in its network [80]. Polymer-based materials also show drawbacks, such as creating weak and unstable conduction filaments, which leads to poor performance and inefficiency. In experiments to overcome this problem, a flexible polymeric memristor using polyethyleneimine incorporated with silver salt has been proposed [81]. This device showed high-quality results such as superior endurance, good retention and high ON/OFF ratio or switching speed and low operating voltage [82]. The paper further investigates the reasons for this success, and it is suggested to be due to the pre-existing Ag ions in the material, which create a strong or robust conducting filament [83]. Despite these changes that have been made, some memristor devices still show considerably weak performance due to the stochastic characteristics of the conduction filament. Hence the concept of interfacial load polymer (ILP) was considered, which brings stability and control to the growth of the conduction filament [84]. This provides self-reliance to the device and acts as an internal load resistor, which limits overgrowth of the conduction filament. Many polymers are created using nanoparticles ,which work on specific areas of improvement in the device.

2.3.3. Perovskites: Perovskites are materials with ABX_3 crystalline structure. The memristor performance and behaviour has been analysed with various materials, organic as well as inorganic perovskites and hybrid organic- inorganic perovskite devices [85]. Many advantages and increased efficiency have been shown of perovskite materials in photo-electric or solar devices [86]. They also have low cost, simple fabrication process, and low-temperature processibility[87]. Researchers have also explored a range of perovskite materials such as $MAPbI_3$, $CsPbI_3$, $CsPbBr_3$, and $(PEA)_2PbBr_4$ for the memristors based on their potential in neural network-based neuromorphic computing properties. In perovskite-based memristors, the RS behavior is mainly stimulated by the migration/diffusion of the halogen ions[88]. Perovskite materials can show low switching voltages, a high on/off ratio, a high endurance, and an analog switching behavior[89, 90, 91]. These features makes perovskites beneficial materials to use in pursuit of parallel computing and neuromorphic devices. It has also been reported that two terminal organometal perovskites can mimic human brain-like processes in the form of artificial synapses and perform activities such as remembering and learning [92]. Recent research shows that perovskites-based memristors can mimic the synapse with comparatively low energy consumption [93]. Among many memristors are those which are known for their scalability and high information processing. One of these was the halide perovskite (HP) memristor, which achieved low cost and real-time information processing. However, some drawbacks, such as toxicity and low stability were observed later [94]. Generally, halide perovskites are known for their photoelectric properties and defect tolerance. Except for superior photoelectric semiconductors, they also showcase excellent ion migration properties [95]. These properties, first found in perovskite solar cells, led to the discovery of the use of HP in memristors [96]. The biggest bottleneck is shown in lead HP-based memristors, which otherwise show outstanding characteristics but have low stability [97]. In addition to this, lead has some toxic and harmful properties whose effects on the environment and humans simply cannot be ignored. Organic-inorganic halides perovskites (OIHP) have also caught attention due to their exceptional optical and photoelectric properties [98]. They have been used for photoelectric purposes, achieving a significantly high power conversion rate of 26 percent [99]. Hybrid organic-inorganic metal halide perovskites (HOIP) are also emerging as solutions for non-lead-based HP memristors. As a prospective contender for the upcoming high-capacity data storage innovation, as well as a candidate for application in healthcare and the Internet of Things (IoT), these HOIP-based memristors exhibit distinctive attributes such as minimal weight, adaptability, extensibility, and minimal energy consumption [100].

2.3.4. Protein: Memristors can also be based on proteins, making them bio inspired so that they can process information analogous to the human brain. Naturally occurring materials such as protein also have the added factor of being green, sustainable, and biodegradable. Material research and engineering advancements today enable the manipulation of proteins through biotechnological and chemical methods, allowing their application in fields like synthetic biology and bioelectronics [101]. Proteins without metal ions can serve as the biopolymer matrix, contributing to stability for doped active units. To catalyse formation of conduction filaments, protein of bacterium G. sulfurreducens helps increase metal reduction following the catalysis concept used to stabilize and form conduction filaments faster in a memristor [102]. These protein- based memristors also operate at around milliwatt voltage with exceptional stability. In recent news, ferritin or iron-based protein has demonstrated memristor switching characteristics [103] . In a paper, a non-linear bio-inspired transparent memristor was made using fibroin from the silkworm- Bombyx Mori [104]. In addition to silk and ferritin, egg albumen (EA) is currently emerging as a promising biomaterial capable of meeting the requirements of next-generation non-volatile memory devices [105]. This is due to its biocompatibility, biodegradability, flexibility, and cost-effectiveness [106]. Building upon the previously discussed

LBL assembly technique, Cho's team investigated the utilization of specific proteins, namely catalase protein and lysozyme protein, in the creation of RRAM devices [107]. They achieved typical resistive switching (RS) characteristics, and the performance could be improvised through molecular manipulation. This discovery expanded the spectrum of applicable biomaterials for memristors [108].

2.4. Signal Processing

With the continuous advancement of cutting-edge technologies, including artificial intelligence (AI), robotics, and real-time data processing, the demand for highly efficient algorithms has become increasingly imperative. Researchers are dedicating efforts to develop new computer technologies that can effectively address these challenges. To overcome these issues, there is a need for automated monitoring of real-time data. Traditional algorithms have proven inadequate in handling big data and tend to lack accuracy. In a memristor based on reservoir computing, real-time data analysis is possible and relatively accurate. Reservoir computing is a concept that originated from recurrent neural networks (RNNs) [109] and only recently has been used in an array of tasks such as pattern and image recognition [110]. A reservoir is a constantly changing system that is capable of performing non-linear processing of input signals and projecting them into further reservoir states [111]. One of the key properties of reservoir computing is that the outputs depend not only on current inputs but also on inputs from the recent past, so the outputs are a cumulative result of most inputs. This property is known as fading memory, which means the system's output depends not only on current input but also on past inputs—with recent inputs having a stronger influence [112].

Brain computing-based automated system emerge as an innovative and promising approach. By emulating the computational capabilities of the human brain, this technology offers a promising solution to complex challenges in modern-day technologies. In biological systems, a synapse is used for the transmission of electrical signals from one neuron to another. They are responsible for the transmission of biological information through the nervous system. Long-term and short-term memory are distinguished by the difference in synaptic weight [113]. Various methods of neuromorphic computing and achieving a structure similar to the human brain led to the development of artificial neural networks (ANNS) [114]. These artificial neural networks consume less power and have several benefits, like parallel processing of data and information. In investigating the hardware implementation of reservoir computing, various physical reservoirs have been created utilizing electronics, photonics, spintronics, mechanics, material engineering, robotics, and biology [115] . Nevertheless, the progress in fully analogue reservoir computing systems has been limited or constricted [116].

To achieve this vision, a combination of various neural network models can be deployed, including a Spiking Neural Network (SNN), which models the timing of neuron spikes to better replicate brain-like behavior; Convolution Neural Network (CNN), which is effective at extracting spatial features from image data; or a custom-designed model that mimics the information processing abilities of the brain [117]. This study can explore the utilization of a memristor-based spiking neural network or RC (reservoir computing) system for real-time neural data analysis. By integrating advanced technologies such as memristors and brain-inspired computing, automated signal processing can enhance accuracy, efficiency, and responsiveness [118]. These advancements hold great promise in effectively addressing the challenges.

3. Applications

Memristors have revolutionized the application of deep learning, neural networks, intelligence sensing, security, and signal processing by integrating memory and processing capabilities into a single component[119]. Memristors have become a pivotal component in the advancement of deep learning and neural networks due to their ability to mimic the synaptic functions of the human brain, providing both memory storage and computational capabilities. In deep neural networks (DNNs)[120], particularly in models like multi-layer perceptrons (MLPs) [121] and convolutional neural net- works (CNNs), memristors enable efficient implementation of matrix-vector multiplication [122], a critical operation in neural network training and inference. For instance, memristor-based crossbar arrays, a matrix of intersecting wires with memristors at the junctions enables highly parallel computation and memory storage, significantly accelerating the computation of complex tasks such as image recognition and classification while reducing power consumption. This is exemplified in their application to CNNs, where memristors store weights and facilitate fast, low-energy processing of visual data, achieving high accuracy in tasks like handwritten digit recognition. Additionally, the analog nature of memristors makes them ideal for implementing recurrent neural networks (RNNs) and other deep learning models that require dynamic learning and memory [123], thus enhancing their applicability in intelligent sensing and real-time data processing. Furthermore, memristors are increasingly utilized in security applications, where their unique properties support the development of secure, efficient cryptographic systems and hardware-based security solutions.

The functional layer is a crucial part in the memristor. Changing the functional layer can bring about many differences in the application of the memristor. Considering real-time data processing applications, the Perovskite-based materials show promising characteristics with high on/off ratios, endurance, and retention. However, the choice depends on the specific requirements of your application. If low on/off ratios are acceptable and high endurance is crucial, the Metal/Binary oxide material might be considered. The Polymer-based material seems to be a good compromise with a moderate on/off ratio and endurance.

Many Oxide materials-based devices show the functionality of bio-inspired synaptic devices for neuromorphic computation [124, 125]. Researchers have studied the metal oxide-based synaptic device in various applications such as pattern recognition, temporal information processing, artificial nerve sensory systems etc. [126, 127, 128, 125] Kim et al. employed HfO2-based memristors to create an artificial nociceptor, which mimics receptors generating pain signals to aid the body in avoiding potential danger [128]. The device demonstrates four discernible nociceptive behaviors: threshold, relaxation, allodynia, and hyperalgesia, based on the strength, duration, and frequency of external stimuli. Yuan et al. presented a neuromorphic perception system that utilizes artificial sensory neurons based on VO_2 memristive device and operates on spike-based principles [129]. They showcase a cross-sensory neuromorphic perception component capable of converting optical, thermal, pressure, and curvature signals into spikes. This demonstrates its ability to simulate biological vision, temperature sensing, haptic feedback, and mechanical sensation capabilities. These perception components are further employed to track the curvature of fingers, enabling the classification of hand gestures. This underscores the device's efficacy in fostering the development of neuromorphic perception systems for electronic skin and neurorobotics. Yang et al.[130] introduced an innovative method for robotic obstacle avoidance by utilizing NbO_2 memristive devices to construct an H-H neuron circuit serving as the ascending neuron. Through the implementation of firing feature-driven neural networks, the study showcases a scalable and efficient approach for real-time obstacle detection and avoidance in robotics. The findings underscore the potential of memristive technology to enhance the adaptability and responsiveness of autonomous systems, offering significant advancements in the field.

Polymeric memristive devices are pivotal for the development of flexible wearable technology. [82]. Their versatility extends to mimicking synaptic functions inspired by the human brain. [70, 76, 131]. As a result, these devices are instrumental in modern life applications like real-time health monitoring and response systems [132, 133]. Healthcare is one of the main aspects of the world that technology still has not completely overcome. With recent developments in microbots and microtechnology, real-time transmission of data and disease monitoring has now become possible [134]. We can also consider wearable devices for instant recognition of gestures and movements for human-machine interaction. Recent advances in smart devices have served as a much better alternative than the previous heavy bulky electronics, for the design of human-machine interaction (HMI), because they are equipped with various sensors such as an accelerometer sensor, gyroscope sensor, and an advanced operating system. [135]. Another application of polymers is the rapid detection of chemical or biological substances in portable sensors for security applications. Detecting and monitoring emerging or recurring infectious at an early stage is crucial for managing healthcare advancements and managing or creating efficient medical interventions. This is vital in mitigating the substantial global economic burden posed by diseases, especially considering the lack of awareness surrounding evolving health threats. [136].

Perovskite materials are also suitable for neuromorphic computing and real-time data analysis applications. Xiao et al. have explored $MAPbI_3$ based memristor for neuromorphic learning and remembering process [137]. The synapse shows promise in achieving low energy consumption at femto-joule per event per (100 nm)2, a level comparable to that of biological synapses. These devices exhibit several functions akin to those found in biological synapses, encompassing spike-timing-dependent plasticity (STDP), spike-rate-dependent plasticity (SRDP), short-term plasticity (STP), long- term potentiation (LTP), as well as learning-experience behavior. The device effectively showcases four types of learning rules, such as symmetric Hebbian learning, asymmetric Hebbian learning, symmetric anti-Hebbian learning, and asymmetric anti-Hebbian learning. These rules play different roles in information processing and storage. John et al. have explored a resistive switching device based on $CsPbBr_3$, demonstrating both volatile and non-volatile switching capabilities emerging due to the diffusion and drift of ions respectively [138]. This reconfigurable $CsPbBr_3$ memristor can also serve as a platform for neuromorphic implementation of synapses that demand both volatile and non-volatile switching properties simultaneously, allowing for a range of computational functions to be achieved using the same material/device. The reconfigurable memristors have also undergone testing in virtual reservoir neural network simulations. In this scenario, the perovskite memristors are arranged with a short-term diffusive configuration in the reservoir layer and a long-term stable drift configuration in the trainable readout layer. This network has been successfully applied to classify four common neural firing patterns observed in the human brain i.e. Bursting, Adaptation, Tonic, and Irregular. This makes it suitable for reservoir computing and real-time data analysis applications. Many perovskite-based memristors exhibit multiple resistance states, controllable either by the level of compliance current or the amplitude of the applied voltages [139, 140, 141]. The concept of multilevel storage within a single memristor has generated significant interest in boosting storage density without compromising scalability. This characteristic makes these materials well-suited for highly dense memory storage or information processing devices. Moreover, owing to the frequently observed photovoltaic behavior in perovskite materials, they possess the capability to detect light. Thus, the adjustment of a perovskite-based memristor isn't solely dependent on electrical synapse-driven switching; it can also be accomplished through photo synapses[137, 141]. This photovoltaic property of perovskite-based memristors holds promise for applications in visual information prostheses. Consequently, the detection of light by photoreceptors and the subsequent signal processing by synapses in the human visual system could potentially be integrated into a single perovskite-based synaptic device. The ability to tune perovskite memristors through photo-mediation presents opportunities for various visual sensors and detection systems. Wang et al. have developed vision chips inspired by a movement-sensitive and wide-field visual neuron located in the third visual neuropile of the lobula [142]. They utilized $CsPbBr_3$-based light-mediated memristors to detect real-time collisions. This progress could enhance robot navigation by enabling obstacle avoidance and facilitate biomimetic compound eyes with wide-field detection capabilities. Nowadays security is a critical concern for everyone. Currently, many technologies are under work for the development of surveillance without humans. [143]. Real-time image processing in surveillance systems where high-speed pattern recognition is crucial. Real- time surveillance is important because of immediate detection hence a memristor that shows promising characteristics and a high on/off ratio like perovskites is essential[144]. Environment monitoring is important to keep a check on the contaminants and pathogens in the air around us. Rapid environmental monitoring using sensors that require quick response to changing conditions. The continuous, on-site monitoring of air, water, and land quality holds huge importance across various fields. Utilizing low- cost and non-invasive chemical sensor arrays such as perovskites, emerges as a fitting approach for this purpose [145] . We can also look at fast decision-making in autonomous vehicles by analyzing real-time sensor data for navigation and obstacle detection as one of the applications of perovskite memristors[146].

In recent various proteins such as silk, ferritin, keratin egg albumen, gelatin, rDNA have been analyzed as a functional layer in memristors[147, 148, 149, 150, 151, 152, 153]. Synaptic devices based on bio-memristors can mimic brain-like functionality at extremely low voltages [154, 155]. The proteins-based bio-memristor can have specific applications such as detecting the protein matrix, which proves valuable in virus detection applications[156]. In recent times, research sciences have moved or shifted towards using cost-effective biosensors for various purposes such as testing food and water contaminants, regulating human biological processes, and facilitating precise health diagnostics [157]. There's a growing demand among researchers and medical professionals for safer and more economical methods to conduct their studies, uphold public safety, and provide specific and tailored healthcare options to patients. Biosensors offer a straightforward solution that aligns with these requirements [158]. There is also rapid detection of specific proteins in biosecurity applications for quick response to potential threats as one of the applications to consider. Despite significant advancements in understanding the pathogenicity of most biothreat agents and the availability of increased treatments over the past decades [159], they continue to pose a substantial public health risk in today's era marked by concerns of bioterrorism, indiscriminate warfare, pollution, climate change, unchecked population growth, and globalization [160]. Early detection stands out in nearly all aspects of prevention, protection, prophylaxis, post-exposure treatment, and mitigation against any bioagent.

The memristor is widely regarded as one of the most promising contenders for the advancement of next-generation computing systems. However, it's important to note that the choice of materials also depends on factors like scalability, fabrication complexity, compatibility with existing technologies. Like for example, The utilization of biocomposites-based memristors, particularly in simulating artificial synapses known as bio-memristors, has significantly accelerated the development of environmentally friendly bioelectronics [161]. Hence, specific application requirements should be considered when selecting materials for real-time data processing. Several applications of the memristor are highlighted in Table 2.

Table 2. Some explored applications for memristors-based devices.

Sr. No.	Application	Reference
1	Compute-in-memory	[162]
2	Edge computing	[163]
3	Image processing	[164]
4	Thermal sensors and artificial nociceptors	[165]
5	Neuromodulation Device for real-time monitoring and adaptive control of neuronal population	[166]
6	Sparse coding for data processing and natural image processing	[167]
7	Vision chips for real-time collision detector	[160]
8	Thermoreceptor system	[168]
9	Artificial photonic receptor	[169]
10	Artificial injury response system for mimicking a sense of pain, signs of injury, and healing	[150]

11	Artificial spiking warm receptor	[170]
12	Analog-encoded image recognition	[171]
13	Protein detection	[170]

4. Challenges and prospects

The review delves into the possibilities of utilizing memristors as a hardware solution for reservoir computing, particularly in the realm of real-time data analysis applications. The review systematically discussed various functional layer materials in the context of memristors, encompassing metal oxides, polymers, perovskites, and protein-based compositions. It rigorously explores the distinctive characteristics of each and assesses their potential applications within the realm of memristive devices. Each functional layer material in memristors possesses distinct characteristics, enabling their behavior to be tailored for specific applications. Metal oxide-based memristors, for instance, have been widely explored in areas such as in-memory computing, image processing, edge computing, pattern recognition, temporal information processing, artificial nerve sensory systems, artificial nociceptors, and real-time obstacle detection and avoidance in robotics. These materials are known for their high environmental stability and compatibility with existing CMOS technology. However, their fabrication demands highly controlled environmental conditions to achieve consistent and reproducible performance, and the high temperatures required during processing make them unsuitable for next-generation flexible sensors and devices. On the other hand, polymeric materials are well-suited for flexible and wearable devices due to their low-temperature processing. Polymers have demonstrated excellent switching characteristics and the ability to mimic synaptic functions. Despite these advantages, polymer- based materials also have drawbacks, including the formation of weak and unstable conduction filaments, which can lead to poor performance and reduced efficiency. Furthermore, for synapse and biosensor applications, protein-based memristors hold promise due to their non-toxicity and low-voltage switching characteristics. Additionally, perovskites have gained attention for their remarkable analog switching behavior and the added ability to be tuned via optical signals, making them promising candidates for optical sensors, such as artificial bionic eyes for robots. However, they undergo degradation in ambient environmental conditions over time. This impedes their application in commercialized technologies. Hence, from a materials perspective, extensive research is imperative to attain optimized characteristics and enhance the stability of memristors. Each functional layer material exhibits unique characteristics in memristive behavior, and their utilization for specific applications can be tailored based on these distinctive behaviours. However, the obstacle to achieving controlled and optimized behaviour poses a hindrance to the commercialization of technologies built upon memristors. One such obstacle is the variability in both spatial (device-to-device) and temporal (cycle- to-cycle) characteristics, which deviate from the desired uniformity and consistency in the developed devices. Ensuring high reproducibility of the functional layer, along with optimized parameters, can effectively mitigate this challenge. However, achieving reproducibility of the functional layer presents a significant challenge. In the case of metal oxides, which are predominantly explored for memristive applications, maintaining highly controlled environmental conditions is crucial to ensure consistent and reproducible characteristics. Additionally, the temporal stability of materials is a critical concern. For instance, perovskites, known for their remarkable analogue switching behaviour, undergo degradation in ambient environmental conditions over time. These limitations impede their application in commercialized technologies. Hence, from a materials perspective, extensive research is imperative to attain optimized characteristics and enhance the stability of memristors. In addition to the aforementioned challenges, the realization of memristor-based brain-like chips necessitates significant technological advancements. To fully exploit the capabilities of memristors in brain-like computing, it is crucial to address various complexities associated with dedicated algorithms, peripheral circuits, and the interface of the computing system. Therefore, the memristor holds promise as a candidate for futuristic high-speed real-time data processing applications; however, substantial research is needed on both the hardware and software fronts to achieve the commercialization of memristors-based high-speed real-time data processing units.

Author Contributions

SG conducted the literature survey and drafted the manuscript. HS and NS did the supervision, and review of the work, and they also edited the manuscript. NS oversaw overall panning.

Disclosure of interest

It is stated that there is no interest to declare.

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Data availability statement

All data analyzed during the current study are included in the manuscript or available from the corresponding author.

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