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A Critical Review on Design and Development of New Generation Energy Storage Devices

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Abstract

A next-generation technology, the Supercapacitor, has emerged with the potential to enable significant advances in energy storage. The fundamental phenomenon and equations for conventional capacitors and supercapacitors are the same. But the improved efficacy of supercapacitors over conventional capacitors is due to the larger surface area of the electrode and thinner dielectrics. The existing review addresses a brief overview of the history, principles, and theory of operation of supercapacitors, along with various models, and significantly in current energy saving and storage. Here, a concise description of technologies and working principles of different materials utilized for supercapacitors has been provided. The main focus has been on materials like carbon-based nanomaterials, metal oxides, and conducting polymers. The performance of nanocomposites has been analyzed by parameters like energy, capacitance, power, cyclic performance, and rate capability. The use of supercapacitors in various applications is cited, and their advantages over alternative technologies are considered. Also, it comprises efficient techniques to minimize multi-response problems such as the fabrication of supercapacitors and storage capacity size, *etc.* This review embedded the current progress achieved in innovative materials for supercapacitor electrodes.

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1. Introduction

Human civilization has achieved very high development, which consistently requires an expenditure of a high amount of energy.^[1] The rising global population and the global energy crisis have led to electricity generation and consumption concerns. With the rapid development of modern science and technology, the application of electronic products is also expanding at a very high speed. In the modern period, we are

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flexible, and miniaturized electronic devices and components.^[2] These electronic devices are widely used in industries such as mobile phones, health trackers, and microsensors. At present portable devices mainly rely on micro-batteries and micro-supercapacitors as power sources.^[3] Typically, they can be integrated with miniaturized electronic devices and provide the necessary power. Owing to the rapid development of the global economy and the consumption of fossil fuels like coal and natural gas, the problem of global climate change and environmental pollution is increasing to a significant level.^[4] Traditional energy source is limited; therefore, there is always a search for renewable energy sources. Thus, the solar, wind, tidal, hydroelectric, geothermal, and gravitational energy are gaining importance day by day.^[5] Also, global pollution is an important issue that should never be ruled out. Today's world is running fast against time and depends on energy-based sources. Still, there is insufficient energy to do new experiments and fulfill essential needs. Therefore, attempts have been made to store electrical energy in different devices such as batteries, capacitors, and supercapacitors.

living worldly life with the help of standard, intelligent,

Supercapacitors have been described as a capacitor that offers high storage space, more significant than capacitors with low internal resistance, which viaducts the gap between rechargeable cells and conventional capacitors. In addition to high power capacity and longevity, low weight and extensive heat range of -40 °C to 70 °C, ease of packaging, and affordable maintenance are the main advantages supercapacitors have over other energy storage devices.[6] However, each of these devices has its advantages and disadvantages.^[7-9] Electrochemical supercapacitors and fuel cells are the most important inventions among energy storage systems and conversion. The electrochemical Supercapacitor is also called an ultracapacitor or electrochemical double-layer capacitor. The global economy is highly affected by energy, its production, utilization, and the environment, *i.e.*, the ecosystem. The scarcity of energy is a burning problem for developing nations. Technological innovations can provide a possible solution.^[10,11] Today's energy requirement is fulfilled mainly by using fossil fuels with limited deposition. Also, of the excess use of fossil fuels environment is seriously affected, such as stress on the environment, global warming due to the greenhouse effect, etc. As a result, the scientific community started worldwide activity to develop more sustainable energy conservation and use advanced technologies to reduce dependence on fossil fuels. To overcome this scenario, efficient electrical energy storage in various devices is becoming important day by day becoming important.[8,12,13]

As far as world development is concerned, the economy is entirely dependent upon imported crude oil, and a suitable example is INDIA, which imports 80% of its crude oil from other countries. Petroleum resources worldwide are depleting at a high rate due to the significant dependence of the transportation sector on petroleum as the primary fuel. Also, there is a vast greenhouse gas emission that is disturbing the quality of air and causing too many health problems to living things (life) and the environment. Therefore, it becomes essential to focus on unconventional sources of energy such as solar and wind energy, which are pure and renewable, easy to handle and store, and cost-effective too.^[14] Also, it is essential to store thermal and electrical energy for future uses. Every nation is seriously working on the burning energy issue and seeking something next-generation solutions through different research organizations. As far as India is concerned, the thermal conversion efficiency and utilization aspects are focused on government and non-government organizations like the Bureau of Energy (BE) and Petroleum Conversion Research Association, etc.[14,15] Current energy-saving concerns with electric vehicles are attracting more and more consideration because of their clean, cost-effective, and ecofriendly features. Meanwhile, the usage of electric vehicles is facing two significant problems: battery life and charging time. However, new resources have been employed to lengthen the battery life, and also exhibited the growth in storage density to 8) High power density due to high discharge currents. protect weight and space.

Some researchers are still working on forming hybrid energy storage systems to improve battery operation conditions using new kinds of simple or nanomaterials. Nevertheless, nowadays, some fast charging patterns and related devices are established to shorten the charging time. Associated with supercapacitors are energy-storing devices with the high power density and low energy density. Batteries have very low power density and high energy density compared to supercapacitors. The Supercapacitor is a nextgeneration technology that assurances to show an essential part in meeting the demands of electronic devices and schemes for both the present and future. The genuinely developed technology of Supercapacitors is creating a simple path for engineers to poise their use of both energy and power. Energy storage devices like supercapacitors are routinely employed along with batteries to compensate for the inadequate battery power capability.^[16] The proper control of the energy storage arrangements indicates both a challenge and an opportunity for the power and energy management system. To provide examples with which to outline practical implementation issues, systems incorporating supercapacitors as vital components. Because of the advantages of charging efficiency, long lifetime, fast response, and wide operating temperature range, it is tempting to try and apply super capacitors to any application that requires energy storage. The limitations of the current technology must be fully appreciated, however, and it is essential to realize that supercapacitors are only valid within a finite range of energy and power requirements. The most important thing to remember about supercapacitors technology is that it is a new and different technology in its right.[17,18]

On the other hand, electric vehicles need high power density during acceleration or starting and high energy density to travel more distance on a single charge. Electric vehicles have regained a solid global presence, and no single source can supply energy and power demands. Supercapacitors are the best and most affordable to tackle this problem because of their perfectly small size, weight, and space compared to ordinary batteries. Most recently, the supercapacitor unit can be employed in blending with the batteries in a storage system electric vehicle to of any achieve the following advantages:[19,20]

1) To improve vehicle acceleration.

2) To improve overall drive efficiency, thereby increasing the driving range.

3) To reduce life cycle costs by extending the battery life.

4) To reduce capital costs by direct replacement of some batteries.

5) Higher cycle life, making them suitable for automotive applications

6) Ability to operate at temperatures as low as -40 °C

7) low equivalent series resistance (ESR).

2. Energy storage devices

According to the first law of thermodynamics, energy is constant, *i.e.*, it is conserved that the energy can neither be created nor destroyed; it can be transformed from one form into another. Also, possible to store energy in a suitable form with minimum loss. Energy storage can be categorized in the following ways:

- 1. Thermally Storage of Energy (TSE).
- 2. Electrically Storage of Energy (EST).

Thermal energy storage is carried out with the support properties associated with the latent heat of various materials, while electrical energy is the majority resourceful form of energy. Depending upon the mechanism of electrical charge storage, it is classified as:

- 1. Capacitors (Storage employing Electrostatic)
- 2. Batteries and fuel cells (Storage employing Chemicals)
- 3. A supercapacitor (Storage employing Electrochemical)

Electricity is an enormous and flexible form of energy that is universally used. Storage of energy in chemicals is simple and long-lasting, but electrical energy storage is too crucial.^[21,22] The chronological development in energy storage devices is as batteries, capacitors, and supercapacitors. Batteries have a large energy density, but it requires more time for the charging process. The capacitors charge up instantly, but the charge storage capacity is smaller. The bridge between batteries and capacitors is nothing but Supercapacitor (SC), is electric power-driven in the future.^[23,24] which Supercapacitors can overcome the drawbacks described above and are available in a cost-effective too. Supercapacitors are high-energy electrochemical capacitors with ample higher capacitance than conventional capacitance of the same size. This emerging technology is also known by different titles such as ultra-capacitors, electric double-layer capacitors, gold capacitors, etc.[25-27] They are valuable alternatives to conventional battery storage systems as they offer a much higher power density. Compared to the battery, the storage of energy involves electrochemical reactions, the supercapacitor stores energy in electrostatic fields by ion polarization. One of the significant challenges that supercapacitors face is that their energy density is considerably low compared to batteries.^[28,29]

There are mainly energy storage systems such as conventional capacitors, supercapacitors, and batteries. The plot explaining the performance comparison of various energy-storing devices is called the Ragone plot, as shown in Fig. 1. In this plot, the power density is plotted along the Y-axis measured in Watt per kilogram (W kg⁻¹), and the energy density along the X-axis, measured in Watt-hours per kilogram (Wh kg⁻¹). Electrical energy can be stored in batteries or capacitors differently. In the case of batteries, there are two electrical terminals known as electrolytes separated by a chemical substance called an electrolyte. When potential is applied between the two terminals, a chemical reaction occurs between the electrodes and electrolyte solution. As a result, the chemical nature of the substance inside the battery is altered, releasing electrical energy. The Ragone plot illustrates storage

devices' specific power density and energy density.^[30] Also, the plot represents the power densities of various energy storage devices, measuring along the vertical axis versus their energy densities along the horizontal axis. Also, it was found that the supercapacitors occupied the region between conventional capacitors and batteries.^[31]



Fig. 1 Ragone plot-power density versus energy density for various electrical energy storage systems.

The specific energy density and power density are the most factors in determining the performance of critical electrochemical supercapacitors. The higher the densities, the better the device should perform. Research from around the globe employing their knowledge to increase the energy density of the supercapacitors while maintaining the power density is going on.^[31,32] Most of them focus on finding new electrode materials with a higher surface area, uniform porosity, and cost-effectiveness. Studies on pseudocapacitors, which utilize fast surface redox reactions, also gain momentum. Despite the wide variety of choices available for different materials and device architecture, electric doublelayer capacitors having activated carbon or aerogel-based electrodes are the most widely used technology for transient power applications. Additionally, printed supercapacitors based on graphene and carbon nanotube-based electrode materials are famous for low-power applications.^[33,34]

Moreover, as they reversibly store charge, the number of charging-discharging cycles of a supercapacitor will be much higher than that of batteries. Currently, supercapacitors having a capacitance of thousands of Farads with a Voltage limited to 3 V are available in the market. They offer low serial resistance and are best suited for applications that demand high instantaneous power levels. Other advantages of electrochemical capacitors include extended shelf life, high efficiency, and the ability to charge and discharge without affecting the performance and lifetime entirely.[35,36] In addition, they can work at shallow temperatures. Owing to these advantages, supercapacitors are widely employed for substituting/assisting batteries for various applications like electric vehicles, traction, microgrids, aeronautical systems, energy-harvesting systems in wireless nodes, and so on. While

appreciating all advantages of supercapacitors, the design of a Supercapacitor based system faces several challenges. Most of those challenges originate because of the porous structure of the supercapacitor electrodes, diffusion effects of the ions, and charge storage on the electrode-electrolyte double-layer interface.[37-39]

Furthermore, Fig. 2 addresses the basic construction system of supercapacitors, which are embedded in two conductive plates separated by a small distance, and the gap is filled with dielectric materials. The nature of dielectric materials may vary, such as mica, air, oiled papers, glass, porcelain, titanate, etc.[40-42] The conductive plates are generally metallic, and dielectric materials are always insulators. When an external potential difference is applied across the two plates, the charging of the capacitor takes place. Positive charges gradually accumulate on one plate during the charging process, while negative charges accumulate on another plate. When the external voltage difference is removed, both the positive and negative charges reside on their corresponding electrodes. Thus, the electrical charges are separated using capacitors. The capacitors are often better than batteries as they do not contain toxic chemicals. Their basic design prevents them from storing anything like the same amount of electrical energy as batteries^[42]



Fig. 2 General construction of Supercapacitor.

3. Construction of capacitance

The negative ions in the electrolyte experience a solid and attractive force from the positively charged electrode. As a result, negative ions move toward the positively charged electrode. Similarly, the positive ions in the electrolyte experience a solid and attractive force from the negatively charged electrode.^[43] As a result, positive ions move towards the negatively charged electrode, as shown in Fig. 2.

two current collectors, a Separator, and Electrolyte Solution. (a) Electrodes The electrodes of the Supercapacitor are made of Activated Carbon material. The electrodes have porous nature, which helps to store more charge carriers. Moreover,

we know that if the electrodes can store more charge carriers, the capacitance will be increased. There are twoelectrodes one is the positive electrode, and another is the negative electrode. (b) Current collectors The current collectors are used to connecting the electrodes and the terminals of the capacitor. The current collectors are generally made up of foil metals. Mainly aluminum is used. There are two current collectors in the Supercapacitor, one for the positive electrode and another is the negative electrode.

(c) Separator The separator provides insulation or separates the electrodes to prevent short-circuit. The separator is mainly made up of Kapton material. The separator is very thin, like paper. The separator provides insulation between the electrodes, but it allows the flow of the charge carrier through it.

(d) Electrolyte solution The Acetonitrile or propylene carbonate as solvents are mainly used as electrolytic in the Supercapacitor. The electrolyte solution consists of the charge carriers like positive cations and negative anions. The explanation above confirmed that the Supercapacitor has the construction same as a lead-acid battery. The theory of the Supercapacitor is nearly the same as a lead-acid battery; in fact, the Supercapacitor is the combination of battery and capacitor. The Supercapacitor uses the charging property of a standard capacitor and the discharging property of the battery.

3.1 Working principle of supercapacitor

Understand the charging and discharging concepts of the Supercapacitor.

3.2 Charging of process

We already know that the positive and negative Ions are present in the electrolyte solution mixed in. So at first, when we apply a voltage across the electrodes of the Supercapacitor, then it starts charging. After that, the electrodes start to attract the ions of opposite polarity. That means the positive electrode attracts the negative Ions or charges, and the negative electrode attracts the positive Ions or charges. As a result, the positive ions or charges create a layer near the negative electrode, and the negative ions create a layer near the positive electrode. As the electrical charge carriers form these two layers, it is called an Electrical Double Layer Capacitor (EDLC). The process is illustrated in Fig. 3a.

3.3 Discharging process When we connect a load across the Supercapacitor, the electrodes cannot attract the ions, and the ions start distributing through the electrolyte solutions and go to the mixed state. The discharging of the Supercapacitor is shown in Fig. 3b.

Generally, the Supercapacitor is distinguished from an The Supercapacitor has the following parts, two Electrodes, ordinary capacitor mainly in two ways: 1) Because of the porous nature of plates, SC has a much larger surface area, and 2) The distance between two plates is of the order in angstrom units which is much smaller, as compared to the separation between two electrodes in an ordinary capacitor.^[44] Due to the



Fig. 3 (a) The charge process of the Supercapacitor, (b) the Discharge process of the Supercapacitor.

the large surface area obtained by coating powders, activated The conventional capacitor C is directly proportional to the charcoal enhances the storage capacity. In an ordinary capacitor, the plates are separated by a comparatively thick insulator whose behavior can be modified in an electric field called a dielectric, e.g., mica (a ceramic), a thin plastic film, or even simply air. When we charge a capacitor, positive charges induce one plate and negative charges on the other, forming an electric field. Because of this, field polarization of the dielectric occurs, so its molecules align in the opposite direction in the applied field and reduce its strength which is responsible for the storage of charge on the plates in minimum Voltage.[43,44]

The energy density and power density of the energy storage device can be calculated by the following equations:

$$\mathbf{E} = \frac{1}{2} \mathbf{C} \mathbf{V}^2 \tag{1}$$

$$P = \frac{V^2}{4 \times ESR}$$
(2)

where, E - Energy density, P - Power density, C- Specific capacitance, V- Operating potential window, ESR-Equivalent series resistance. According to above Equations 1 and 2, it is seen that the energy density from the capacitor to the battery increases significantly, whereas the power density decreases (See Fig. 1). The conventional capacitor exhibits a high power density, while the battery and fuel cell shows a higher energy density. Supercapacitor bridges the gap between conventional capacitor and battery with intermediate power density and energy density.^[45,46]

4. Glimpses on the development of supercapacitors

The capacitor effect was discovered in 1745, consisting of two foil conductors separated by a dielectric region. Such a type of capacitor provides minimal energy, which is less than 360 joules per kilogram in energy density and with a unit of microfarad only. Conventional capacitors consist of two conducting electrodes separated by an insulating dielectric material. When a voltage is applied to a capacitor, an opposite charge accumulates on the surface of each electrode.^[47,48] The capacitance can be defined as below Equations 3:

$$C = A/t$$

(3)

surface area A of each electrode, and t is the thickness of the electrical double layer. The storage of electrical charge at the interface between a metal and an electrolytic solution has been studied by chemists since the nineteenth century. However, for the first time, the practical use of double-layer capacitors only began in 1957, when a patent was placed by General Electric (GE) for an electrolytic capacitor using porous carbon electrodes. This patent admits its limitations that 'it is not positively known precisely what takes place when the devices are used as energy-storing devices.[49] However, it was believed that carbon pores are responsible for energy storage, and the capacitor exhibited exceptionally high capacitance. In 1966, Standard Oil Company, Cleveland, Ohio, had patented a device that stored energy in the double-layer interface. Thus, it was assumed that the double layer at the interface behaves like a capacitor of relatively high specific capacity. Then, Standard Oil of Ohio (SOHIO) registered a patented device disc-shaped capacitor in which a carbon paste was soaked in an electrolyte.[50]

SOHIO handed over the technology to NEC in the subsequent year, and this company finally marketed the device as supercapacitors. Later on, NEC started developing doublelayer capacitors under the name of Supercapacitors. These devices could be operated at low Voltage and had high internal resistance and, therefore, could be used in memory backup applications.^[51] Later on, several companies developed an interest in fabricating supercapacitors, such as ELNA. ELNA had started to produce its Supercapacitor under the name of Dynacap. The standard oil company of Ohio or Sohio was an American oil company. Later on, this company was acquired by British Petroleum, founded by John D Rockefeller.^[50]

SOHIO acknowledged that "the 'double-layer' at the interface behaves like a relatively high specific capacity capacitor." SOHIO went on to patent a disc-shaped capacitor in 1970 utilizing a carbon paste soaked in an electrolyte. The capacitance of a device is mainly dependent on the characteristic of the electrode materials, particularly the surface area and pore size distribution. The electrolytic stability usually determines the operating Voltage of supercapacitors. The electrolytes can be of two types, viz aqueous and non-aqueous. The aqueous electrolytes have the advantage of high ionic conductivity and low manufacturing costs. However, they suffer from specific problems such as relatively low decomposition voltages. Non-aqueous electrolytes allow cell operating Voltage above 2.5 V.^[50,51]

4.1 Need for supercapacitor

There is an ever-increasing pollution threat and vanishing oil layer deposition, which requires searching for supercapacitors as an alternative high-power source. In addition, there is tremendous growth in portable electronic devices such as laptops, cameras, etc. Thus, for high-power applications, essentially supercapacitors are required. Therefore, supercapacitors are claimed as an emerging technology that promises to play an essential role in meeting the requirements of electronic devices and systems. The scientific community is aware that supercapacitors are becoming attractive energy storage devices. Supercapacitors fill the gap between batteries conventional capacitors. The superiority and of supercapacitors over other energy storage devices is that they have higher power density and longer life cycles than batteries. Energy storage for portable electronic devices, which is becoming increasingly important to the present society, forms the largest mobile energy storage market today and is experiencing innovation for future applications such as flexible/printed electronics and displays. Flexible energy storage is required to operate flexible devices. Electrochemical supercapacitors with high energy and power capabilities can power flexible devices. In order to be integrated with flexible electronics, supercapacitors should be made flexible with sheet-like structures, which are light weight.^[52] The various designs and power needs of soft portable electronic equipment, such as roll-up displays, electric paper, and wearable systems for personal multimedia, require the development of flexible energy devices. Flexible supercapacitors have played an increasingly important role in power source applications since they combine the advantages of the high power of conventional capacitors and the high specific energy of batteries.^[53]

4.2 Electrolytes

The use of electrolytes as dielectric was initially developed by Charles Pollak in 1886. However, electrolytic capacitors have faced numerous difficulties in applications due to their low reliability. The capacitance of an EDLC is greatly influenced by the choice of electrolytes. The ability to store charge is dependent on the accessibility of the ions to the porous surface area, so ion size and pore size must be optimized. Therefore, the pore size distribution of the electrode is an essential factor. The pore size distribution of the electrode depends upon the size of the ions in the electrolyte.^[52,53] Therefore, the proper choice of electrode and electrolyte both are essential factors.

The breakdown voltage of electrolytes governs the

attainable cell voltage of a supercapacitor. Therefore, the energy density will be limited by the electrolytes. The power density is dependent on ESR, which ultimately depends upon the nature of electrolytes. The common electrolytes used can be broadly classified into two types (1) aqueous electrolytes and (2) organic electrolytes. Organic electrolytes are more prevalent in commercial devices due to their higher dissociation voltages. The cells using an organic electrolyte can usually achieve Voltage in the range of 2-2.5 V.

On the other hand, non-aqueous electrolytes suffer from disadvantages such as high cost, low conductivity compared with aqueous electrolytes, and low dielectric constant, resulting in smaller capacitance and complex purification procedures. Therefore, a large number of non-aqueous electrolytes were tested. In the current scenario, ionic liquid has attracted scientists' attention. Ionic liquids are suitable electrolytes because of their excellent chemical and physical properties, such as high thermal stability and high electrochemical stability.^[54]

5. Classification of supercapacitor

Based on the charge storage mechanism concept, supercapacitors can be classified into three types: 1) Electrochemical double-layer capacitors (EDLCs), 2) Pseudocapacitors, and 3) Hybrid types formed by a combination of EDLC and pseudocapacitors. Each capacitor class is recognized by its unique mechanism of charge storage.^[55] In the early period, the concept of an electrochemical Supercapacitor was based on an electrical double layer existing at the interface between a condenser and containing electrolyte solution. Electrostatic and its electrolytic capacitors are considered first and secondgeneration capacitors. With the rapid development in materials, the third generation, known as Supercapacitor, is developed. Fig. 4 addresses the classification of Supercapacitors. SC is mainly classified into two types based on the charge storage mechanism: electric double-layer capacitors (EDLCs) and pseudocapacitors.^[56] The details information on different kinds of SC based on different storage mechanism are given below:

5.1 Electrochemical double-layer capacitors (EDLCs)

Von Helmholtz first introduced the concept of EDLCs in the 19th century. The Helmholtz double-layer model has two layers of opposite charge formed at the electrode-electrolyte interface separated by an atomic distance. This model is almost similar to that of the two-plate capacitor.^[57] The Helmholtz EDLCs model was further modified by Gouy and Chapman,^[58] considering a continuous distribution of electrolyte ions in the electrolyte solution, driven by the thermal motion, which was referred to as the diffuse layer (as shown in Fig. 5). Later, Stern combined the Helmholtz model with the Gouy-Chapman model to explicitly recognize two regions of ion distribution-the inner region and the diffuse layer. In the inner layer, ions are strongly adsorbed to the electrode. The specifically adsorbed ions and non-specifically



Fig. 4 Schematic representation of supercapacitor types: (a) EDLC type; (b) Pseudocapacitor type; (c) Hybrid capacitor type.

adsorbed counterions are distinguished as the inner Helmholtz between an electrode and an electrolyte. The charge storage proportional to the distance between the two electrodes.^[59] The capacitance calculation for an EDL supercapacitor is similar to that of a parallel-plate capacitor, which can be defined as 5.2 Pseudocapacitors below Equations 4:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{2} \tag{4}$$

where εr is the dielectric constant of the electrolyte, εo is the permittivity of vacuum, A is the surface area of the electrode accessible to the electrolyte ions, and d is the effective thickness of the EDL (*i.e.*, the Debye length). Furthermore, the energy storage and release mechanism are based on nanoscale charge separation at the electrochemical interface formed

plane (IHP) and the outer Helmholtz plane (OHP). The mechanism is nonfaradaic, and no chemical oxidationcapacitance of two separated arrays of charges is directly reduction (redox) reactions are involved. EDLCs have proportional to the surface area of the electrode and inversely relatively long cycle lives because only physical charge transferring occurs.^[60]

In the case of pseudocapacitors, the capacitance arises for thermodynamics reasons and mainly due to charge acceptance (ΔQ) and a change in potential (ΔV) .^[61] The derivative C = $d(\Delta Q)/(d\Delta V)$ corresponds to a capacitance called pseudocapacitance.^[62] The primary difference between pseudocapacitance and EDL capacitance is that pseudocapacitance is faradic, involving redox reactions between the active material on the electrode and the electrolyte.^[63] The electrochemical characteristics of



Fig. 5 Models of the electrical double layer at a positively charged surface: (a) the Helmholtz model, (b) the Gouy–Chapman model, and (c) the Stern model, showing the IHP and OHP.

pseudocapacitive materials are neither entirely capacitive nor bulk faradaic processes. Energy storage devices involving pseudocapacitive materials exist between EDLCs and batteries, which predominantly depend on the surface faradaic electron transfer by the intercalation or adsorption of chargecompensating ions.^[64] Pseudocapacitor can be considered a complementary form of EDLC since it is not purely electrostatic but exhibits similar electrochemical profiles (cyclic voltammetry and galvanostatic charge-discharge). The term "pseudo" is used to distinguish it from EDLCs. The surface or near-surface charge interactions leads to a surface faradaic reaction that exhibits swift reaction kinetics similar to EDLCs.^[65] As a result, pseudocapacitive electrodes have near rectangular cyclic voltammograms and almost linear chargedischarge curves. In recent years, the line between battery-like material and pseudocapacitive material has become very thin. To properly understand the charge storage mechanisms of the electrode material, *i.e.*, to accurately differentiate between the pseudocapacitive and battery materials, quantification of the kinetics is one of the most effective techniques.

5.3 Hybrid supercapacitors

Hybrid supercapacitors: are the third type of supercapacitors that consolidates the features of both EDLCs and pseudocapacitors. The electrodes of hybrid supercapacitors are made of composite materials that include EDLC materials and pseudocapacitive materials or can have asymmetric electrodes, one pseudocapacitive electrode, and another EDLC electrode.

On the other hand, the oxidation and reduction processes composites obtained by combining two or more constituent or

simultaneously occur in supercapacitors. The process is based on the Nernst equation. The term redox is formed by 'Red,' which signifies reduction, and 'oxi,' which signifies oxidation. The Nernst equation that can calculate the emf of the cell is given below Equations 5.

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[Red]}{[Oxi]}$$
(5)

where, E° = the standard potential; R = universal gas constant; T = absolute temperature;

F = Faraday constant; n = ion charge (moles of electrons)

Therefore, the amount of charge from the above equation is a function of potential E. The charge-discharge curve is the result of overlapping redox reactions.^[20] Adsorption of ions: The deposition of ions to form a monolayer on the electrode substrate is a reversible process that results in Faradic charge transfer and hence gives rise to pseudocapacitance in a similar manner as shown in redox reactions.^[66]

6. Materials for supercapacitor

For the construction of supercapacitors, mainly two types of materials are used such as (1) carbon-related materials such as carbon nanotubes (CNTs), graphene, and activated carbon, and (2) Based use of metal oxides such as Ruthenium, Manganese, and Copper, Cobalt, Nickel oxides and polymers like polyaniline (PANI) and polypyrrole (PPy), *etc.* The details of electrode materials related to their types are presented in Fig. 6.

The other categories of supercapacitor materials are



Fig. 6 Details of electrode materials based upon types of Supercapacitors.

nanomaterials. An example is a composite formed by mixing CNTs with conducting polymer or metal oxides. Combining CNTs with nanomaterials allows for a substantial increase in surface area and enhanced capacitive performance. As a result, the synthesis and engagement of nano-oriented resources are now recognized as a critical factor in developing the high performance of supercapacitor devices.^[67]

6.1 Carbon-based materials

Carbon is the 15th most abundant element in the earth's crust and fourth. It is a reactive non-metal. In nature, we observe several allotropes of carbon, such as diamond, graphite, lonsdaleite, Buckminsterfullerene, amorphous carbon, and carbon nanotubes. Carbon nanotubes are tube-shaped materials made up of carbon having a diameter measuring on the nanometer scale. Carbon nanotubes are formed from graphite sheets, and graphitic Nanotubes are a member of the fullerene structure family. Their name is derived from their long, hollow structure with the walls formed by one-atomthick sheets of carbon called graphene. Carbon nanotubes were discovered by Japanese scientist Iijima in 1991 and are now considered a top-class subject in academic research and various industrial areas.^[68] The chronological developments in carbon nanotubes can be summarized in Table 1.

 Table 1. Evolution of Carbon Nanotubes and their Applications in Supercapacitors.

Year	Discovery
	Rudushkevich and Lukyanovich published a paper
1052	in the Soviet Journal of Physical Chemistry
1932	showing hollow graphite carbon fibers 50 nm in
	diameter. ^[69]
	John Abrahamson presented evidence of carbon
1979	nanotubes at the 14th Biennial conference of carbon
	at Pennsylvania state university. ^[70]
	A group of Soviet scientists published the results of
1021	chemical and structural characterizations of carbon
1981	nanoparticles produced by a thermodynamical
	disproportionation of carbon monoxide.[71]
	Nanotubes were discovered in the soot of the
1991	discharge at NEC by Japanese researcher Sumio
	Iijima. ^[72]

These nanomaterials are allotropes of carbon, made of graphite, and constructed in cylindrical tubes with nanometerscale in diameter and several millimeters in length. The carbon nanotubes have been constructed with a length-to-diameter ratio of 132,000,000:1. A carbon nanotube structure is formed by a layer of carbon atoms bonded together in a hexagonal mesh. This one-atom thick layer of carbon is called graphene, and it is wrapped in the shape of a cylindrical structure. Their impressive structural, mechanical, and electronic properties are due to their small size and mass, incredible mechanical strength, and high electrical and thermal conductivity. The

strength of the carbon-carbon bond gives rise to extreme interest in the mechanical properties of carbon nanotubes. Theoretically, carbon nanotubes should be stiffer and more robust than any known substance. Thus, carbon nanotubes have a higher tensile strength than steel and Kevlar. The extra strength in carbon nanotube comes from sp² bonds between the individual carbon atoms. Here the bonds are even more potent than the bonds observed in diamonds. Carbon nanotubes are strong, but they are also elastic. It is possible to press on the tip of a nanotube and cause it to bend without damaging the nanotubes. Once the deforming force is removed, the nanotube will regain its original dimensions.

The strength of nanotubes can be weakened by creating a defect in them. The defects can be generated from atomic vacancies or the rearrangement of carbon bonds. On the other hand, all nanotubes are expected to be excellent thermal conductors. It is expected that carbon nanotubes will be able to transmit up to 6000 watts per meter per kelvin at room temperature. Furthermore, graphene and carbon nanotubes are carbon-derived nanomaterials that have received significant attention in their potential application as efficient electrode materials in the design of supercapacitors owing to their high mechanical properties with great specific surface area and, most importantly, competent electrical properties. Other forms of carbon-based nanomaterials like xerogel, carbon fibers, activated carbon, and templet carbon have been used to design and develop supercapacitors. They also serve as the Supercapacitor's electrode. The carbon-based materials are comparatively cheap, readily available, and very common with characteristic permeability, which enables easy penetration of electrolytes in the electrode to boost the capacitance of the supercapacitors.^[73]

In order to enhance the performance of the supercapacitors, different forms of carbon materials used as electrodes for electric double-layer capacitors (EDLCs) are activated carbons, carbon aerogels, carbon fibers, and carbon nanotubes. Maaximun-specific capacitance values of different materials are shown below in Fig. 7.^[74]

6.1.1 Carbon nanotubes (CNTs)

Carbon nanotubes have excellent nano porosity properties 1D form of carbon, permitting minute spaces for the polymer to stand in the tube and act as a dielectric. Carbon nanotubes can store about the same charge as charcoal (almost pure carbon) per unit of surface area. However, nanotubes can be arranged in a regular pattern that exposes a better suitable surface area. Carbon nanotubes can be considered cylinders made of graphite sheets, mostly closed at the end. Thus, one considers CNTs the folding of graphite sheets, just like one rolls a piece of paper into cylindrical forms. These nanostructured materials were accidentally discovered by Iijima while observing under Transmission Electron Microscopes.^[75]

Moreover, electrodes of CNTs have been made as an intertwined material of CNTs, with an open and obtainable



Fig. 7 Maximum specific capacitance values reported from the addition of different supercapacitive materials. Reproduced with permission from [74], Copyright 2016 American Chemical Society.

network of mesopores. The mesopores in CNTs are interconnected, forming a continuous distribution, thus developing the specific surface area more efficiently.^[76] CNT electrode has lower equivalent series resistance (ESR) than activated carbons, as the electrolyte ions can simply enter into the mesoporous network.[77] Carbon nanotubes act as pillars for the uniform distribution of metal oxides, creating high pseudocapacitance and electric double-layer capacitance. A similar electrode type accomplishes higher specific capacitance (Cs) than specific carbon, metal oxide, or conducting polymer electrodes.^[78,79] Recently, PEDOT/PSS and CNTs composite materials have been developed^[80] and that could reach Cs varying from 85 to 150 Fg⁻¹, while the energy density (Ed) could exceed 0.92 Whkg⁻¹ and Pd could range from 100 to 3000 Wkg⁻¹. Similarly, the same path has been approached to fabricate the Co₃O₄/CNTs, and Co₃O₄/CNFs with enhanced electrical conductivity and a substantial surface area.[81,82]

In addition, the carbon nare classified as (1) Single-walled carbon nanotubes (SWCNTs) and (2) Multiple walled carbon nanotubes (MWCNTs), respectively.

(a) Single-walled carbon nanotubes (SWCNTs)

Single-walled nanotubes are close to one nanometer and can be considerable enough. The structure of SWCNTs can be theorized by enfolding a one-atom-thick layer of graphite into a cylinder. SWCNTs are an essential variety of carbon nanotubes because most of the properties change significantly with the indices, and this dependence is non-monoatomic. Current research developments recommend growing attention to CNTs as an EDLC electrode material. Electrodes made from this material developed commonly as an entangled of CNTs, with an open and accessible network of mesopores. Unlike other carbon-based electrodes, the mesopores in CNT electrodes are interconnected, allowing a continuous charge distribution that uses almost all the available surface area.

capacitances comparable to those in activated-carbon-based SCs, even though CNT electrodes have a modest surface area than activated carbon electrodes. The surface area is utilized more effectively to achieve capacitance comparable with activated carbon-based super capacitance. Due to the porous nature of carbon, the electrolyte ions can diffuse into the mesoporous network.[83] Based on the nature of SWNTs, some work has been done like freestanding PEDOT-PSS/SWCNTs, which exhibit the C_s of 104 at 0.2 Ag⁻¹, energy density (E_d) of 7 Wh kg⁻¹, power density (P_d) of 825 W kg⁻¹ and 90% of the Cs retention after 1000 cycles^[84] shown C_s of 1715 Fg^{-1} for RuO₂ based SCs in which RuO₂ is electrodeposited on the SWCNTs film electrode. Also, they have fabricated superiorperformance, self-standing composite electrodes with SWCNTs.^[85] The 3-D mesoporous SWCNT-based electrodes allowed unimpaired ionic carriage in thick films and brought enhanced results in an ace line frequency of 120 Hz. Measurements of 601 µFcm⁻² with a -81° phase angle and a time constant of 199 µs were obtained. As-fabricated electrodes were capable of cycling at higher than 200 V s⁻¹ showing a parallelepiped cyclic voltammetry (CV) shape at one kV s⁻¹.

Thus, the surface area is utilized more efficiently to achieve

(b) Multiple walled carbon nanotubes (MWCNTs).

MWCNTs have mesopores in structure, which agree with the easy movement of ions across the electrode-electrolyte interface. Suppose the pore size becomes equivalent to the size of the ion, and the molecules of the solvent are moderately showing outcomes in the form of high ionic packing density. Nevertheless, their mechanical stability drops due to significant volume change because of repetitive intercalation and depletion.^[86] Some reported data shows that a Cs of 50 Fg⁻¹ for MWCNTs and HPNCTs with willow catkins made by an easy carbonization process and exhibit SSA of 1775.7 m² g⁻¹, Cs of 292 Fg⁻¹ at 1 Ag⁻¹ and better rate capability with 83.5%

of the Cs retention at 10 Ag-1 for HPNCT-800.^[87] Applying asymmetric polymer electrolyte with NaOH-treated polyethylene oxide (PEO-NaOH) was prepared to produce a thermally-induced voltage in SCs. They found that Au and MWCNTs deposited on Au electrodes showed the thermopotential of 10 mV K⁻¹, the Cs of 1.03 mFcm⁻², and E_d of 1.35 mJcm⁻² at the temperature difference of 4.5 K.^[86] PANI nanowires have been deposition within the MWCNTs employing in situ electro-polymerization. It was found that aligned MWCNTs supported the organic polymers with a pathway for charge transfer. The films made with conducting polymers encapsulated in MWCNTs showed a Cs of 296 F g ¹ at 1.6 A g⁻¹. Also, found that MWCNT channels bound the structural changes in PANI chains while charging-discharging and increased the lifespan of the structure.[88]

On the other hand, Different Π -conjugated sulfonate patterns and additional support of graphene and MWCNTs are used to investigate the polymerization activities of PEDOT.^[86] As fabricated PEDOT: MWCNT composite exposes an interconnected network due to the Π - Π interaction of PEDOT with non-covalent functionalized MWCNT and shows a specific capacitance (C_s) of 199 F g⁻¹ at 0.5 A g⁻¹. Meanwhile, the high-efficiency SCs with upgraded electrochemical characteristics can be made by chemical vapor deposition (CVD) and graphene hybridized with MWCNTs.^[89] Another work was done followed by CVD to prepare MWCNTs, and graphitic layers over MgO assisted metal catalyst, which designates that such materials are responsible for fast charge transport in the cell or SCs device.^[88]

6.1.2 Activated carbons

Due to its eco-friendly nature, less expensive, and high surface area, activated carbon (AC) has been the desired choice of electrode material for EDLC compared to other forms of carbon. Conventionally, AC was primarily obtained from coal, petroleum, and derived products.^[90] However, due to environmental pollution and the finite reserve of fossil fuels, academics are considering biomass waste as a possible resource for the fabrication of AC.[91] Activated charcoal is a powder made up of tiny and very "rough" particles and a lowdensity heap with many holes that looks like a sponge. The surface area of even a thin layer of such a material is many times greater than a material like aluminum, letting many more charge carriers be deposited in any given volume. However, charcoal is not a better insulator; it still replaces the excellent insulators used in conventional devices, so in general, EDLCs can only use low potentials on the order of 2 to 3 V. Concerning the surface area of AC, the capacitance is directly proportional to the surface area, and calculation reveals that not all the high surface area contributes to the capacitance of the device. This discrepancy may be due to electrolyte ions that are very big that they cannot diffuse into smaller micropores. Large pore size correlates with higher power densities, and smaller pore correlates with higher energy densities.^[92] The specific capacitance values are directly

proportional to the surface area and published articles^[93-95] confirmed similar capacitive behavior of activated carbon. As of 2010, virtually all commercial supercapacitors use powdered activated carbon developed from coconut shells, and higher-performance devices are made based on synthetic carbon precursors activated with potassium hydroxide.^[96]

Taking account of activated carbon fiber material (ACFM), the composite of (ACFM)-Ni(OH)2 has been reported and displayed the Cs of 370-380 Fg⁻¹. Also, the dependence of shape, structure, and volume of material on the composition and concentration of the solution was established.^[97] An asymmetric SC (with 1.9 V) was developed using AC as the ve electrode and a silicon carbide-MnO₂ (SiC-NMnO₂) composite as the + ve electrode in Na₂SO₄ electrolyte solution.^[98,99] Also, porous activated carbon was extracted from rotten carrots at different values of activating temperature under an inert atmosphere, employing a chemical activation method and ZnCl₂ as an activation agent. Further, the electrochemical performance of synthesized AC was studied as an electrode in the aqueous, organic, and ionic liquid-based electrolyte. It was confirmed that the prepared electrode showed the highest specific capacitance in the aqueous electrolyte and the highest specific energy along with specific power in the ionic liquid-based electrolyte.^[100]

6.1.3 Carbon aerogels

The complete artificial ultralight solid, extracted from gel substance by supercritical extraction without a need for binder material, is called aerogel-the supercritical extraction outcomes in the formation of enormously low-density materials and low thermal conductivity. The electrodes of aerogel supercapacitors are a composite material usually made of non-woven paper made from carbon fibers and coated with organic aerogel, which undergoes pyrolysis. The carbon fibers provide structural integrity, and the aerogel provides the required large surface area. Carbon aerogels are nanoporous carbon consisting of a weighty class of carbon nanomaterials and three-dimensional hierarchical morphology.[101] Due to these properties, carbon aerogels can be used as electrode material for EDLCs. Carbon aerogels are designed from the continuous net of carbon nanoparticles with a mesoporous structure with no binding agent. Usually, lower ESR was found in the binderless electrode of carbon aerogels. It was found that reduced ESR, which yields higher power, is of curiosity for investigators working in the SCs area.[102] The small aerogel SCs are being used as backup electricity storage in microelectronics. However, Aerogel capacitors can only work at a few volts. At higher voltages, ionize the carbon and damage the capacitor. According to a literature survey, carbon aerogel capacitors have achieved 325 J/g (90 Wh/kg) energy density and 20 W/g power density. Some aerogel electrodes manufactured by pyrolysis of resorcinol-formaldehyde aerogels are better conductors than activated carbons. They provide thin and firm electrodes representing mechanical and vibrational constancy for SCs for their application in a highvibration environment. Recently, Ultrahigh-specific capacitance for supercapacitors has been achieved by nickel cobaltite/carbon aerogel composites.^[103]

6.1.4 Graphene

Graphene is nothing but a single layer of graphite material or crystal. The graphite crystal has a stack of carbon layers lightly bound with each other, and each layer embedded а hexagonally arranged carbon atoms. As a sole isolated unit, these layers are self-standing materials identified as graphene and widely act as superconducting hybrid materials. The expansion in capacitance depends on the high surface area, lattice density, and interlayer spacing of graphene. Also, combining graphene with other materials can bring many property alternations in super capacitance. This state that graphene has great potential as a supercapacitor electrode.^[104] Graphene-based ac line-filters on a large scale have been developed by Wu et al.[105] Here, graphene oxide (GO) is reduced by patterned metal interdigitates and engaged as the electrode material. A quasi-solid state micro-SC with cellular graphene films as an active material with PVA/H₃PO₄ as the gel electrolyte shows as a new type of flexible energy storage device. Here 3D graphene films served as high-performance SC electrodes and an ion reservoir for the gel electrolyte. The 3D cellular graphene films are generally fabricated by a freeze-casting assisted filtration assembly method and show great mechanical strength and flexibility. The quasi-solid state device retained about 89% of its initial capacitance after 1000 cycles while tested under repeated bending from 0 to 120.[106] Furthermore, Furthermore, Photoswitchable micro-SC based on the diaryl ethene-graphene film was prepared by Liu et $al.^{[107]}$ to exhibit the Cs modulation up to 20% demonstrating photo switchable micro-supercapacitors. Meanwhile, Zhang et al.^[108] fabricated graphene-based Ni foam electrode, which shows a higher E_d and P_d and good cycling performance. Xu al.^[109] have synthesized a nanocomposite et of graphene/AC/PPy by vacuum filtration method.^[109] Gao^[110] developed a graphene/ polymer electrode on Ni foam using the vacuum pressure method. The distribution of graphene could not be tuned by applied vacuum pressure and its duration. In the end, Ramaprabhu has developed poly (phenylenediamine) (PpPD) and hydrogen exfoliated graphene (HEG) sheets which show a C_s of 248 F g⁻¹ at 2 A g⁻¹.^[111]

6.2 Conducting polymers (CPs)

The conducting polymers are pseudocapacitors with poor lifecycles compared with carbon-based materials. Conducting polymer has become a vital electrode material for pseudocapacitors due to the advantage of enormous capacity, good conductivity, facile synthesis, and cost-effectiveness. In recent years conducting polymers has attracted the attention of researchers due to their great potential in supercapacitors. Despite these properties, conducting polymers have not become so popular among researchers and industrialists due to drawbacks such as low stability and poor mechanical

properties, which restrict their applications in the fabrication of supercapacitor devices-conducting polymers, which are more correctly identified as intrinsically conducting polymers. CPs have attained considerable attention as they supply high specific capacitance (due to their redox behavior), rapid charge-discharge process, lesser cost than carbon-based material, and a low ESR value. Notably, the n/p type polymer configuration has enormous potential for high E_d and P_d .^[97] However, the dearth of proficient n-doped conducting material and less cycling stability has postponed the improvement of CPs pseudocapacitor. Conducting polymers are organic polymers that can conduct electricity. These compounds have metallic conductivity or may sometimes act as semiconductors, a desirable property for SCs electrode materials. Again, it was confirmed that the mechanical stress on the conducting polymers during the reduction-oxidation reaction bounds the stability of pseudocapacitors through many charge-discharge cycles. Basis of electrical conductivity: the conductivity of organic polymers is owed to many processes. Polymer-like polyethylene, the valence electrons are in sp³ hybridized, and sigma bonding electrons have low mobility and do not contribute to the electrical conductivity of the materials. The critical feature of bond structure available in conductive polymers can be easily calculated with the tight-binding model.[112]

On the other hand, conducting PANI polymer is lightweight, highly conductive, mechanically flexible, ecofriendly, and highly theoretical capacitance. The problem is that, because of ion doping/dedoping, PANI shrinks and swells during the charge/discharge process. To reduce this problem, the PANI is coated on metal oxides (MOs)/carbon materials forming PANI/MOs/ nanocarbon ternary hybrid, which holds good cyclic stability and specific capacitance.^[97] Also, PANI obtained a wide range of colors due to their many protonation and oxidation forms. These electrochromic characteristics can be utilized for the fabrication of electrochromic SCs.

Moreover, Polyacetylene is the most crystalline CP, but it is easily oxidized in air. On the other hand, Polypyrrole (PPy) and polythiophene can be produced directly in doped form and are very stable.[113] PPy has superior density and higher flexibility than other conducting polymers. It has high electrical conductivity (10-500 Scm⁻¹), and it undergoes a self-rapid redox reaction for charge storage.[113] Composite like Lignin-PPy is synthesized by coating lignin with PPy by the polymerization of PPy with and without the presence of methyl orange, which conceded to the formation of PPy films of globular and nanotubular morphology. Stable PPy films with a surprising doping degree have been achieved by the pulse polymerization process.^[114] Pulse on time controls the chain size along with chain defects, and pulse off time controls the direction and conjugation of the polymer chain. A C_s of 400 F g⁻¹ has been visualized in these films with E_d of 250 Wh kg⁻¹ at 5 mA cm⁻² current density and long cycle life.

Another conducting polymer of Polythiophenes (PTs) was obtained by a chemical oxidative method using FeCl₃ as an oxidant and the absence of numerous surfactants. It is found that surfactants change the PTs morphology, and PTs with TritronX-100 show a Cs of 117 F g⁻¹, whereas the Cs for surfactant-free PTs are 78 F g^{-1.[115]} Polyindole (Pind) has gathered attention due to the mixed properties of both poly (pphenylene) and PPy, such as high redox properties, good thermal stability, meager degradation, and better air stability compared to PPy and PANI.^[116] PANI-Solution (nanocrystal), PANI-emulsion (nano pedal), and PANI- interfacial (nanosphere) are reported.[117] Furthermore, symmetric SCs based on alternate layers of different CPs prepared to develop SCs have been studied.^[118] The capacitive properties of a prepared multilayered system are better than individual CP, which may be related to the better porosity of multilayered material. Flexible worm-like SC electrodes are fabricated using cellulose nanofibres (CNFs) and graphite nanoplatelets (GNP), doped with PANI by in situ polymerizations.^[119] Also, an all-solid-state symmetric SC has been fabricated using PANI/CNF (20% loading)/ GNP electrodes, which shows good C_s retention at various bending angles. There are numerous good properties of conducting polymers, such as flexibility, conductivity, ease of synthesis, financial viability, and high pseudocapacitance. Conducting polymer materials such as polythiophene, polypyrrole and polyaniline have received significant attention in the potential supercapacitor applications. Despite these promising properties, polymer-

based supercapacitors exhibit poor cycling stability and low power density and energy density.

6.3 Transition metal oxide

Transition metal oxides (TMOs) of ruthenium, iron, vanadium, manganese, tin, and copper are highly used in research and applications of pseudocapacitances. Transition metal oxides exhibit multiple oxidation states at specific potentials, and the selection of materials with multiple stable states within an electrolyte's potential window allows maximum capacitance to develop. Another essential advantage of crystalline metal oxide is that its high conductivities allow charge propagation along with the lattice structures of thin surface layers. However, considerably lower conductivity is observed for amorphous hydrous metal oxides. The conductivity can be increased by crystallization. The process of crystallization needs the removal of water which eliminates pore spaces.[120] For the super capacitance applications, firstly, ruthenium oxide was used. However, ruthenium is a rare earth mineral and a highly toxic metal. Also, ruthenium is very costly. Therefore, there was a need to search for alternative metal oxide that is less toxic and cost-effective. Thus, different transition metal oxides were tried, such as manages oxide, vanadium oxide, etc. Fig. 8 depicts how a double layer is developed on the CP chain.



Fig. 8 (a) and (b) Development of double layer at CPs chain.

Here an attempt has been made to synthesize copper oxide nanoparticles dopping with different materials. Copper oxides exist in two stable forms, cuprous oxide Cu₂O and cupric oxide CuO. These two oxides have very different colors, crystal structures, and physical properties. The differences in such properties are due to differences in the oxidation state of transition metal copper. For example, Cu₂O is reddish in color, a cubic semiconductor, and displays interesting excitonic properties.

iron-gray color, and crystallizes in a more complicated tenorite structure exhibiting monoclinic interesting antiferromagnetic ordering.^[121] CuO is an intrinsic p-type semiconductor as some of the oxygen ions are lost from the crystals, which impart a positive charge on the entire crystalline structure. The capacitance of copper oxide is controlled by the structure, composition, type, and density of charge carriers. Metal oxides have been explored as an electrode material for SC due to their high conductivity, various oxidation states, and the possibility of constructing high-energy, high-power SCs.[122] The majority of relevant research concerns ruthenium oxide. This is because other metal oxides have yet to obtain equivalent capacitances. The metal oxides like ruthenium oxide (RuO₂), nickel oxide (NiO), cobalt oxide (CO_3O_4) , iridium oxide (IrO_2) , and manganese oxide (MnO₂) have been extensively studied as electrodes for pseudocapacitors. The specific capacitance of RuO2 is achieved through the insertion and extraction, or intercalation, of protons into its amorphous structure. In its hydrous form, the capacitance exceeds that of carbon-based and conducting polymer materials. Furthermore, the ESR of hydrous RuO₂ is lower than other electrode materials. As a result, ruthenium oxide pseudocapacitors may achieve higher energy and power densities than similar EDLCs and conducting polymer pseudocapacitors. Thus, a significant area of research is the development of fabrication methods and composite materials to replace an alternative electrode material to reduce its cost without reducing its performance. However, the prohibitive cost of ruthenium oxide makes it impractical.^[123]

Transition metal oxides/hydroxides are considered the best candidates as electrode materials for energy conversion and storage applications. In recent years, nanostructured materials have achieved great interest due to their large surface-tovolume ratio and exceptional mechanical, electrical, and optical properties endowed by confining the material dimensions. Some materials that are not stable in the bulk form and do not exist in the ambient atmosphere may exist in a more stable state at the nanoscale. Specially transition metal oxide (TMO) nanoparticles have received wide attention for energy applications.^[124] The extensive benefits of TMO nanoparticles are: (i) structural changes that allow the altering of lattice symmetry and cell parameters, (ii) a change in electrochemical behavior due to the quantum confinement effect, and (iii) a change in surface properties leading to a drastic increase in the bandgap that influences the conductivity and the chemical

activity of the nanoparticles (Immanuel *et al.*, 2019). Fabrication of desired quality of PDPU 38/180. Higher pseudocapacitance than the EDLC carbon electrode materials. It is well established that properties of nanomaterials, like composition, crystalline phase, structural and morphological properties, and the surface and interface properties between the electrode and electrolyte, greatly influence the electrochemical performance in device applications.^[125]

Different nanostructured metal oxides and hydroxides On the other hand, CuO is having different color-it is a dark, include RuO₂, IrO₂, MnO₂, Co₃O₄, NiO, Co(OH)₂, and Ni(OH)₂.^[126] TiO₂, ZnO, WO₃, SnO₂, CuO, Cu₂O, Fe₂O₃, and RuO₂.H₂O show excellent electrochemical performance not only in electrochemical energy conversion, storage, sensors, and detector applications but also in terms of good electrical conductivity, UV absorption, photo-oxidizing capacity against chemical and biological species and antimicrobial/selfsterilization^[127]. Not restricted to energy applications, many metal oxide nanoparticles have been successfully employed in different biomedical applications such as efficient electrochemical detectors of biomolecules, including NiO, ZnO, MnO₂, Fe₂O₃, TiO₂, and Co₃O₄^[128] Metal oxide nanoparticles such as MgO,^[129] Al₂O₃,^[130] and ZnO^[131] are also employed to decontaminate various nerve agents.^[132]

> Copper oxide is one such transition metal oxide with exciting properties, which was also one of the first substances known to behave as a semiconductor. The study started in the 1920s and '30s. However, the interest in copper oxides was received after the 1970s. Man has used copper since prehistoric times; in fact, one of the significant stages of human history is named after a copper alloy, *i.e.*, Bronze Age. Humans have used it for about 10,000 years.^[133] As per records worldwide, copper resources are around 5.8 trillion pounds (out of which only 12% have been mined), and also, it is highly recyclable.^[133] It is a soft, flexible, ductile, and pliable metal that conducts heat and electricity very effectively, commonly making it suitable for electrical wiring. It is in group 11 of the periodic table; has one s-orbital electron on top of a filled dshell. Copper oxide is a binary compound and has two PDPU 40/180 stable forms Copper(I) oxide (Cu₂O) and Copper(II) oxide (CuO). The physical properties, i.e., color, crystal structure, and electrical and optical properties of Cu₂O and CuO, vary significantly. Intrinsically, CuO and Cu₂O are ptype semiconductors having band gap energies in the visible and near-infrared regions of 1.2 to 1.5 eV and 2.1 to 2.6 eV, respectively.^[134] Both are non-toxic and have abundant source material on earth. They have favorable bandgap and band edge positions for solar energy conversion applications, and the bandgap could be easily adjusted by altering the composition. They have a high absorption coefficient in the visible range and can be prepared at a low cost by adopting simple methods. There are several reasons for choosing Cu₂O and CuO as the absorber layers for solar cells, gas sensors, biosensors, magnetic media, enzyme-free glucose sensors, photodetectors, nanofluids for enhanced thermal conductivity, junction devices such as a p-n diode,^[135] the catalyst for water gas shift

reactions, cathode material in photoelectrochemical water splitting applications, heterogeneous catalysis in the complete conversion of hydrocarbons into carbon dioxide, nanoenergetic materials, and as active materials in lithium-ion batteries (LIBs) owing to its peculiar properties.^[136,137] Copper oxide nanostructures also exhibit some exclusive magnetic and superhydrophobic properties. Along with the specific optical, electrical, and electrochemical properties, copper oxides have some general advantages, as environment friendly and abundantly available. However, copper oxides had not gained enough attention from researchers until recent years.^[138]

Thus, developing a reliable and cost-effective method for the large-scale production of Cu₂O and CuO is highly desirable.^[139] Manifold vacuum and non-vacuum techniques have been explored so far for the synthesis of copper oxides, including different nanostructures such as activated reactive evaporation, electrodeposition, spay pyrolysis, radical oxidation with nitrogen plasma treatment, sol-gel dip technique, reactive magnetron sputtering, oxidation of metallic Cu sheets, photochemical deposition, and thermal oxidation, wet chemical method, anodization, thermal solvothermal process, transformation, electrospinning, chemical bath deposition, and electrodeposition.^[136] Several studies on copper oxide-based systems have explored their efficacy in various applications. Based on the literature survey (few mentioned and some not mentioned due to scope of limitation), attempts have been made to develop copper oxide photocathodes and electrodes for photoelectrochemical cell (PEC) and supercapacitor applications, respectively, since nanostructured materials have a distinct feature compared to their bulk counterparts exhibiting enhanced properties which can be efficiently utilized for the PEC and supercapacitors.

Mahendra et al.^[140] have reported that the CuO thin films can be formed of 3 different thicknesses, i.e., 20nm, 100nm, and 200 nm were deposited on glass substrates by magnetron sputtering techniques. They studied their structural, optical, and electrical properties. The study of nanostructured CuO thin film on stainless steel substrate is successfully done by Dubal et al. Here; they have synthesized the nanomaterials by simply changing the complexing agent. The result reveals maximum specific capacitance at 5mV s⁻¹. They also studied the long-term cycling performance of CuO is examined at different scan rates. Prasad et al.[141] reported that the Cuo thin film was synthesized by sol-gel route with carbon embedded. The specific capacitance of 300 Fg⁻¹ was reported. Shaikh et al.[142] reported that they synthesized the hybrid CuO-PAA thin films using a facile spin coating technique at room temperature for supercapacitor application.

The coated films are annealed at different temperatures to study the annealing effect on Csp. They found that the Csp increases from 41 to 136 F g⁻¹ with an increase in annealing temperature. They also revealed that as annealed temperature increases with an increase in porosity. Patake *et al.*^[143] reported that the amorphous and porous copper oxide thin film electrodes were prepared by cathodic electrodeposition for

supercapacitor application. The cyclic voltammogram was obtained at 20 mV s⁻¹ scan rate of Csp is 36F g⁻¹ in 1M Na₂SO₄ electrolyte. The amorphous nature of oxide plays a vital role in improving Supercapacitors. The capacitance of the copper oxide electrode increases with an increase in film thickness. Dubal *et al.*^[144] reported that the chemical bath deposition (CBD) method prepared the complex hierarchical CuO nanostructures. The structures of Cuo thin films are of woolen clumps, stacked nanosheets, and nanobuds fabricated on a stainless steel substrate. They also found high specific capacitance of nanobuds CuO sample is 396 F g⁻¹.

Shinde et al.^[145] synthesized nanoflowers-like CuO/Cu(OH)₂ hybrid thin films on stainless steel substrate by using simple and inexpensive successive ionic laver adsorption and reaction (SILAR) method. The CuO/Cu(OH)2 nanoflower with diameters of about 4-5µm exhibits the maximum specific capacitance of 459 F g⁻¹. Hsu et al.^[146] prepared CuO/Cu(OH)₂hybrid material using a liquid-solid reaction route, and Csp is found to be 278 Fg⁻¹. Shaikh et al.^[147] reported that nanostructured Ru-doped CuO thin films by colloidal solution method via a simple and cost-effective spin coating technique. They observed the highest Csp of 406 F g ¹. Wang et al.^[148] reported that CuO nanosheets with nearvertical orientation on nickel foam substrate are composed of interconnected nanoparticles by a template-free growth method. As a result, the CuO exhibits the highest Csp of 569 F g⁻¹. Dar et al.^[149] reported that Graphene nanosheets (GN) disseminate with macroporous copper oxide (macroCuO).

This was investigated on a glassy carbon electrode (GCE) as an electrode material synthesized by a modified Sol-Gel route for supercapacitor application. They reported a maximum specific capacitance of 417 F g⁻¹. Pendashteh et al.^[150] stated that the CuO nanoparticles had been synthesized on graphene oxide (GO) nanosheets by the electrostatic coprecipitation method. The composite CuO-GO material shows a better specific capacitance of 245 F g⁻¹ at a current density of 0.1 A g⁻¹. Dubal et al.^[144] reported that the different nanostructures of CuO thin films were directly grown onto stainless steel substrates with the help of surfactants such as Triton X-100 and polyvinyl alcohol (PVA) prepared by CBD. It shows the maximum specific capacitance of 411 F g⁻¹. Finally, Huang et al.[151] reported that the electrode of Agdoped CuO. Table 2 depicts the various types of materials used in the development of supercapacitors and their morphology and Csp.

 Table 2. List of materials with their morphologies and Csp.

Material	Morphology	Csp
(in Fg-1)		
CuO		
CuO	micro-woolen	346
CuO	rodlike morphology	300
hybrid CuO–PAA	Island like structure	136
CuO	well-adherent and	
Cuo	porous	

cauliflower structure	36			202 as-deposited		
CuO	Nanobuds	396	MnO2/ 2M KCl/ Pt	charge-discharge		
CuO/Cu(OH)2 hybrid	Nano flower			method		
(diameters-				Thickness 1.0-1.2		
4-5 μm)	459			mg cm-2 240 for		
. /	nanobuds with a		MnO2/ 2M KCl/ Pt	MnO2 deposited at		
CuO in [HPMIM][Cl] IL	bunch of nano			0.5V/SCE		
	pedals-like			45 Mf charge-		
Structure	60		MnO2/0.5LiCl/Pt	discharge high		
	Lotus like			stability		
CuO/Cu(OH)2hybrid	morphology	278		Area 1 cm2 with		
	Nanocrystal		MnO2/1.0 M Na2SO4/Pt	loading 0.5 mg		
Ru doped CuO	structure	406		Thickness of 0.94		
CuO	Hierarchical		MnO2 / 1.0M Na2SO4/Pt	micrometer		
multilayer nanosheets	43		RuO2 hydrothermal	meremeter	400 Fg-1	
	Circle-like			Atomic laver	100 1 8 1	
Hybride Cu-PAA	structures	65	ZnO nanomembrane	deposition	846 Fg-1	
	Circle-like			deposition		
CuO-PAA/CNT films	structures	258	Nanosheet arrays wer	e prepared by doping (uO nanosheet	
CuO	Nanachaota	560	arrows using A g by the	cilver mirror reaction	The specific	
CuO	manosheets	309	anays using Ag by the	at 1 A g 1 and 200 E g	$1 \text{ at } 10 \text{ A } \alpha 1$	
GN/macroCuO	macro-structured	417	respectively. Vurby Lie	at TAg-1 and 299 Γ g-	an at 10 A g-1,	
	porous		CuO nonouving and no	<i>i al.</i> ⁽¹⁾ revealed that h	liliza different	
CuO-GO	globular snaped	245	CuO hanowires and ha	anosheets and nower-	like different	
	nanoparticles		morphology grown on c	opper toam substrate v	vere prepared	
	Nanosheets arrays		by thermal treatments for	or supercapacitors app $\frac{1}{2}$	lication. CuO	
CuO	as well as flower-		nanosneets exhibited	nigher specific capa	c_{12} contains c_{12} co	
C1	like		nanowires, with a flower	-like nanostructure of	212 F g ·. Yu-	
Cluster	411	(00)	Kuei Hsu <i>et al.</i> ^[133] reveale	ed that hierarchical stru	ctures of wire-	
NSA–Ag/CuO	Nanosheets	689	like CuS deposited on co	opper foil substrate using	ng simple and	
	nanowires and		cost-effective liquid-so	lid reactions. The l	high specific	
CuO	nanosheets and		capacitance of CuS and N	W nanoelectrodes is 30	5 F g^{-1} . Wang	
	flower-like		et al ^[154] reported that C	u2O/CuO/RGO nanoc	omposite was	
Structure	212		synthesized using the	hydrothermal metho	od on RGO	
CuS	Nanowire	305	nanosheets for supercapa	citor application. The n	anocomposite	
Cu2O/CuO/RGO	Nanoporous	136.3	exhibited supercapacitor	performance of 173.4	$F g^{-1}$ at the	
	particles		current density of 1 Ag ⁻¹ and remained at 136.3 F g ⁻¹ at 10 A g ⁻¹			
CuO/N-RGO	unique particle-	340	¹ with a retention of 78.6	%.	1 .	
	nanosheet structured	0.0	Moreover, the capa	city remains 133.8 I	$f g^{-1}$, almost	
MnO2/NaCl/Pt	Thickness		unchanged (98.2%) after	100,000 cycles at 10 A	g ⁻¹ . Li <i>et al</i> . ^[155]	
	0.02mg/cm-2		revealed that the CuO/nit	rogen-doped reduced g	raphene oxide	
	Specific		(CuO/N-RGO) composi	ites are prepared by	refluxing in	
MnO2/2KCl/Pt	conductance 212,		ammonia solution and	low-temperature an	nealing. The	
	21%		CuO/N-RGO composite	shows a high specific of	capacitance of	
21% higher than plain Mn			340 F g^{-1} .			
oxide						
MnO2-MWCNT/3M	Specific capacitance		7. Applications of super	capacitors ^[156-161]		
KCl/Pt	160, Sc decreased		Supercapacitors have sev	veral applications, inclu	ding:	
from 160 to 80 Fg			1) Transportation: The tr	ansportation system re	quires the use	
MnO2/0.1M Na2SO4/Pt			of supercapacitors. The	automobiles require su	percapacitors	
	230, potential		with a compilation of oth	er devices such as batte	eries. The fuel	
	window: 1V (for		efficiency can be increase	sed by storing the ener	gy at braking	
	galvanostatic		and releasing the en	ergy at acceleration	n. Also, the	
	methods)		supercapacitors can per-	form well in a cold a	atmosphere at	
MnO2/0 1M Na2204/D4	Thickness 0.4-0.5		shallow temperatures of	about – 40 °C temperat	ure.	
1v11102/0.11v1 1va2504/Pt	mg cm-2					

2) Consumer electronics: Supercapacitors are widely used in various electronic devices as backup energy sources for system memories, microcomputers, system boards, clocks, and toys. These are ideal for devices that require a quick charge. In addition, supercapacitors are cost-effective as they have an incredibly long life, and usually, their replacement is not required during the lifetime of the device they are used.

3) Uninterrupted power supply: UPS requires a continuous power supply. It is possible to maintain the continuous power supply of UPS by using supercapacitors. Also, supercapacitors are best suited to provide power for startup and peak-up buffering.

4) Other Application: Supercapacitors can be used in hospitals, cell phone towers, banking centers, transmission lines, in 4. system frequency and stability control; supercapacitors are suited as an energy storage system for hardening sensitive equipment against voltage sag, in wind turbine systems 5. supercapacitors can provide a simple, highly reliable solution, 6. airport control towers. They are also used in many portable gadgets and devices.

5) Medical Applications of Supercapacitors: The internal organ of a human sometimes do not function properly, and even with the use of medicine, they can not be cured; in such a situation, transplantation is one possibility. However, transplantation of every organ is not possible, and even it is very costly. Therefore, some suitable devices are often planted into living organisms to perform the function of dysfunctional body parts. However, most of these devices require a power supply to function appropriately. The batteries can be used as a power supply source, but they have a life span that will never be long enough, especially if they are implanted. Thus, the device needs to be brought out whenever the batteries discharge, and the batteries need to be changed. Here, introducing a supercapacitor to the batteries or replacing the power is possible.

Biosupercapacitor comprises graphene layered with modified human protein as an electrode, a conductor through which electricity from the energy harvester can leave. The platform could eventually also be used to develop nextgeneration implantable devices to speed up bone growth, promotes healing, or stimulates the brain.



Fig. 9 Applications of Supercapacitors.

The biological Supercapacitor that the researchers invented uses charged particles of ions from bodily fluids to produce power. It uses electrolytes or ions present in body fluids such as blood, urine, and other extracellular biological fluids. It is possible that the supercapacitors can work with other devices known as energy harvesters. The biomedical and other types of applications of supercapacitors are depicted in Fig. 9.

8. Advantages of a supercapacitor:

- 1. Very high efficiency.
- 2. Fast-charging property
- 3. A supercapacitor has a longer life than a 10 to 15 years battery
- The Supercapacitor can withstand temperatures between -30 to 65 degrees centigrade, whereas a battery can withstand -10 to 40 degrees centigrade.
- 5. The Supercapacitor is very light in weight.
- 6. Supercapacitors can be installed in a short area as they are significantly smaller.
- 7. The Supercapacitor has a swift transient response.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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Review article

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Cooperative catalysis: Condensation-aromatization for synthesis of 2-(4-nitrophenyl)-1H-benzimidazole by silica immobilized Brønsted-Lewis acidic ionic liquid (Si-BLAIL)

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ARTICLE INFO	A B S T R A C T
Keywords: Cooperative catalysis Heterogeneous catalyst SEM BLAIL Equivalence point etc	Herein, pleasing the advantageous of both Brønsted and Lewis acidic site of Si-BLAIL the condensation- aromatization reaction has been carried out. The striking distinctiveness of work is optimum reaction condi- tion, easy work-up, high yield, catalyst recyclability, non-inertness of reaction flask, simple catalyst loading method. The decreases in the amount of catalyst and reaction time shows good to high (71%–93%) yield suggests about the involvement of some interesting mechanism such as cooperative catalysis. The mechanism has been hypothesizes as, the Si-BLAIL increase the efficiency of condensation reaction possibly by providing the proton in 2-position of cationic imidazolium ring of BLAIL through the hydrogen bond interaction with carbonyl group and nucleophilic activation during aromatization by hydrogen bond acceptor ability of Lewis adduct anion of BLAIL. The catalyst Si-BLAIL shows massive affirm for industrial applications. The Si-BLAIL has identified as the best

1. Introduction

The acid catalyzed synthesis are generally preferred for production of various chemical, pharmacologically important synthetic derivatives etc. [1-5] For bulk production, from the academic laboratory to a chemical industry large number of acid catalyst has been used [1]. The conventional mineral acids provides effectual surface area hence it shows privileged catalytic activity but its use allied with several downsides such as, difficulty in product isolation, corrosion of equipments, acidic waste that hazardous to the environment. Solid acids catalysts are environmental and non-volatile but they have an inadequacy such as high molecular weight to active site ratio, severe reaction condition, matrix coupled acidic sites, longer reaction time and fast deactivation [1,2]. Hence, the researcher takes huge efforts for development of new acidic catalyst. From, the last several decayed the Ionic liquids (ILs) has attracted much attention of researchers due to their unique physical and chemical properties such as favorable solvating power, low vapor pressure, wide liquid range, good conductivity, thermal stability, structural designability etc. [3] Moreover, acidic ionic liquids are well known green solvents and catalysts such as- IL has been used for efficient and reusable green catalyst for biodiesel production [4], Synthesis of 4-phenacylideneflavene [5], tetrahydropyranylation of alcohols [6], benzoxanthenones derivetives [7], benzoxazoles, benzthiazoles, benzimidazoles [8], The Brønsted acidic ionic liquid was used for one pot reductive amination of aromatic aldehydes [9]. Such, efficient synthetic utility of acidic IL motivates to its use as heterogeneous catalysis. The ILs is also referred as versatile materials used in chemical manufacture plants [10]. The ILs as a solvent or homogeneous catalyst shows good catalytic activity and high selectivity but the use of ILs as a homogeneous catalyst or solvent has several shortcomings such as extremely difficult disposal of waste materials, expensive disposal operations, due to high viscosity of ILs as Homogeneous catalyst for industrial bulk scale production is not recommended [11].

acid catalyst for 2-(4-nitrophenyl) benzimidazole synthesis with additional benefits of cooperative catalysis.

The Heterogeneous catalysis gets hold of great attention for large scale production in various chemical industries due to its recyclability, easy separation ability, practical convenience, lower corrosion effect etc. The heterogeneous catalysis has been widely used in the organic synthesis [12] by taking advantageous of cooperative effect of catalyst and solid support [13]. Such synergetic effect increases the catalytic efficiency of the catalyst [14] by the surface modification of the active site in the catalyst [15]. The solid supported ionic liquid take the

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Received 28 March 2022; Received in revised form 19 May 2022; Accepted 26 May 2022 Available online 2 June 2022 0019-4522/© 2022 Indian Chemical Society. Published by Elsevier B.V. All rights reserved. combine advantage of catalytic activity of ILs and solid supports. Hence, immobilization of ILs on solid support with or without covalent bond is more desirable [10]. Supported ILs has been effectively used for several organic reactions such as selective oxidation of alcohols [16], esterification [17], synthesis of methyl caprylate [18], one pot synthesis of 1-amidoalkyl 2-naphthols [19], Heterocyclic synthesis, CO₂ dissolution and fixation [20], polycyclic phenolic compound [21], polyoxymethylene dimethyl ethers [3], Chemoseletive synthesis of dicoumarols and substituted xanthene derivetives [22], hydrolysis of cellulose [23], synthesis of biodiesel, alkylation and oligomerisation [2], fuel oil desulfurization [24] etc. The supported Brønsted and Lewis acidic ionic liquid attracted much attention due to their exceptionally strong acidic characters.

Cooperative catalysis is emerging and most powerful strategy in many organic syntheses. During activation of starting material, Cooperative catalysis significantly increases the selectivity and catalytic activity. The catalyst involves hydrogen bond donor and acceptor moiety that activates both elecrophilic and nucleophilic sites of the reaction system. The concept of such cooperative catalysis has been used for several reaction such as Michael addition, Povarov reaction [25], Mannich reaction [26], Biginelli reaction [27] etc. During such catalysis the catalytic efficiency is mainly under control of hydrogen bond interaction between catalyst and reactants. For the reactions involving carbonyl activation, the cation and anion of the ILs can cooperatively activate the reaction centre and 1-butyl-3-methy-imidazolium based ILs shows prominent activity due to 2-position proton of imidazolium ring with same anion. Furthermore, for imidazolium based ILs, the anion Cl shows high catalytic activity very similar to strong hydrogen bond acceptor ability [25]. Hence the dual acidic ionic liquids with Cl containing anion can be more desirable.

2-nitrophenyl substituted benzimidazole is compounds with tremendous biological importance as it shows antimicrobial, antiinflammatroy, anti-histaminic, antiviral, antitumor, anticancer [28] etc activities. Hence, it is well thought-out that compounds are of multipurpose materials such as sensitive fluorescence sensor for the biomolecules sensing [29]. Furthermore, its derivatives can be possibly used for understanding of structural modification of the biomolecules like julolidine [30] and other fluorophores [31,32]. 2-aryl substituted benzimidazoles are synthesized either alkylation of benzimidazole or by condensation followed by aromatization of Orthophenylenediamne (OPD) with aldehydes. The number of conventional Brønsted and Lewis acid catalysts were used however the synthesis methods have short-comings such as low yield, expensive and unrecyclable catalyst, cruel reaction conditions etc. Those limitations can be overcomes by using Brønsted and Lewis acidic ILs on the solid supports.

Recently, Thai Nguyen et all has been reported first time the benzimidazole synthesis by BAIL gel [8]. Lewis acid catalyst were reported to be superior for benzimidazole synthesis [33]. The benzimidazoles were effectively synthesized by polymer supported pyridinium chloroaluminate as a heterogeneous Lewis acid catalyst [34]. liu et al. shown that the Lewis acid site are active centers for dehydrogenation and aromatization of isobutane [35]. Hence, by enchanting an advantageous of cooperative catalysis and efficiency of Lewis acidic site we report herein the use of silica supported Brønsted - Lewis acidic ionic liquid (Si-BLAIL) as a heterogeneous catalyst for benzimidazole synthesis. Interestingly, good to excellent yield, easy product separation, catalyst recovery, optimum reaction condition has been achieved. Herein, we employed the idea of cooperative catalysis of Silica immobilized BLAIL obtained by treating BLAIL with silica gel. The adsorption of BLAIL on the surface of silica gel enhances the catalytic activity. Lewis and Brønsted acidic catalysts are well known for benzimidazole synthesis and the Lewis acidic catalysts are considered as effective catalyst for aromatization. We have identified the cooperative catalytic effect of silica supported Brønsted - Lewis dual acidic ionic liquid for benzimidazole synthesis. The Si-BLAIL shows, the simple catalyst loading method, optimum reaction condition especially- room temperature, free air medium, minimum reaction time, easy work-up, high yield of the product minimum catalyst leaching with respect to other reported silica supported IL catalyst [8,36,37].

2. Experimental section

2.1. Materials and method

1-Methyl imidazole, 1, 4-Butane sultone, aluminum trichloride, Orthophenylenediamne (OPD), 4-nitrobenzaldehyde, 4-chlorobenzaldehyde, 2-chlorobenzaldehyde, 4-N,N-dimethyl aminobenzaldehyde, anisaldehyde were purchased from Molychem, India all has purity 98-99% and used without any further purification. Silica gel (100-200 mesh) was purchased from lobachemia and 4-methylbenzaldehyde (99%) was purchased from spectrochem and used as received. 0.1g of a Si-BLAIL was dissolved in 25 ml distilled water and stirred for 2h at room temperature and kept in dark for 24 h to settle down the solid residue. After decantation the solution was titrated with 0.025 M NaOH and the conductance was recorded after each addition by using Equiptronics conductivity meter (Model EQ 665 EQ 665). FTIR spectra were recorded on FTIR spectrometer- 4600, Jasco, Japan. Morphology was characterized by Termogravimetric analysis (TGA) using Perkin Elmer STA6000 Instrument and by using SEM analysis. The XRD was recorded on Rigaku miniflex-600 equipment using Cu K α radiation ($\lambda = 0.1540$ nm) operated at 30 kV.

2.2. Synthesis of Brønsted -Lewis acidic ionic liquid (BLAIL)

To a vigorously stirred solution of 1-Methyl imidazole (1) (10 mmol) in acetone (25 ml), 1, 4-Butane sultone (2) (11 mmol) was slowly added at room temperature and stirred for 12h. After completion of reaction acetone was decanted and the remaining white solid was separated and was repeatedly washed with diethyl ether to yield pure ionic liquid and dried in vacuum. In the second step ionic liquid (3) was taken in round bottom flask and added equivalent amount of concentrated HCl, then reaction was heated for 24 h at 80 °C. The viscous liquid obtained was dried in oven at 60 °C to give IL (4). This IL (4) was then dissolved in toluene and followed by addition of aluminum trichloride (11 mmol) and stirred it for 24 h at room temperature. Then the solvent was evaporated under vacuum to give the desired BLAIL (5). see the Scheme 1.

2.3. Synthesis of silica supported dual acidic ionic liquid (Si-BLAIL)

Silica gel (100–200 mesh, 10 g) was activated by heating at 100 °C in an oven for 24h. In 50 ml round bottom flask BLA IL (5) (2 g. 41.06 mmol) was dissolved in 10 ml distilled water and heated at 70 °C. The activated silica were added slowly with constant stirring in the hot water and obtained mass (\sim 16.6 wt %) is dried in an oven at100 °C for 48h. The white free flow powder of Si-BLAIL **(6)** is stored in glass bottle and used without any further activation.

2.4. Procedure for synthesis of 2-aryl benzimidazole

In a 25 ml round bottom flask equipped with magnetic stirrer, Orthophenylenediamne (OPD) (7), (0.200g, 1.85 mmol) and 4-nitrobenzaldehyde (8) (0.279g, 1.85 mmol) was taken with 10 ml absolute ethanol and Si-BLAIL (0.0042g) was added with constant stirring at room temperature. The progress of reaction was monitored periodically by TLC. After completion of a reaction catalyst was separated by adding more ethanol followed by centrifugation and the crude product was precipitated by adding distilled water in ethanol. The crude product was collected by filtration and recrystallized in ethanol to get pure product (9) (0.455g, 1.90 mmol) and formation of product was confirmed by M. P., FT-IR and ¹H-NMR.



Scheme 1. Synthesis of silica gel immobilized dual acidic ionic liquid (Si-BLAIL).

3. Result and discussion

3.1. Characterization of catalyst

Reza et al. has been reported that the structure of silica supported catalyst can be analyzed by different techniques IR, Conductometry, TGA, SEM etc. [17] Hence, the prepared Si-BLAIL was characterized by conductivity measurement, IR, SEM, EDS, DSC, XRD and TGA analysis. The prepared Si-BLAIL catalyst was analyzed for determination of density of acidic group by titrating it with NaOH. The concentration of acid center of the Si-BLAIL has been determined by conductometric titration method. The conductometric titration cure is recorded and shown in Fig. 1. It is quite evident from Fig. 1, that the titration curve is chair shaped which are characteristics of the conductometric titration curve



Fig. 1. Conductometric titration Curve of 0.1g of Si-BLAIL with 0.025 M NaOH at room temperature.

for weak acid with strong base. Due to presence of heavy ions in the suspension of Si-BLAIL catalyst, the small change in conductance was observed up to equivalent point. Once the equivalence point is reached then hydroxonium ion goes to increase in the suspension solution and hence conductance increases [38]. The concentration of acid group on the surface of catalyst was found to be ~1.5±0.05 mmol/g Such reasonable loading of acid on the surface of silica suggest the adsorption of BLAIL (5) on the surface of Si. The XRD pattern of Si-BLAIL show peak at $2\theta = 22^{\circ}$ as supported silica only. The XRD data shows that, the nature of the silica support preserves after immobilization of BLAIL [39,40]. (cf. *Fig. S3*).

3.1.1. Infra-red spectral characterization

The FT-IR spectra of BLAIL, Si and Si-BLAIL have been recorded and the results are shown in Fig. 2. The FTIR spectrum of silica gel has characteristics absorption band in at 3454 cm⁻¹ (O-H, SiO-H stretching), 1633 cm^{-1} (bending vibration of adsorbed water), 1090 cm^{-1} 800 cm⁻¹(Si–O stretching), Reza et. all has been reported that on immobilization of IL on Si-gel surface the spectral characteristics of Si-gel change [17]. Due to immobilization of BLAIL on Si the absorption bands of silica are shifted. It is evident from Fig. 2 that, the Si-IL shows strong absorbance at 3465 cm⁻¹ due to Si–OH bond stretching vibration and the water absorbed by the silica gel. The peak at 1563 cm^{-1} and 1644 cm⁻¹ correspond to C=N and C=C vibrations of imidazole ring. The band centered at 2958 $\rm cm^{-1}$ and 1455 $\rm cm^{-1}$ are due to C–H stretching and ring deformation of imidazole and long hydrocarbon chain. The strong absorption peak at 1092 cm^{-1} is because of stretching mode of vibration of Si–O–Si bond in the silica. The band at 1168 cm⁻¹ is assigned to Si=O stretching vibration. Such spectral changes in the FTIR of Si-BLIL further confirm immobilization of BLAIL on the surface of Si. The presence of two strong peaks at 1092 cm^{-1} & 1168 cm^{-1} further assigned to S = O stretching vibration of SO₃H group of Brønsted acidic site. [41-43]. The S = O stretching vibration in Si-BLAIL suggest the existence of Brønsted acidic site in the catalyst.



Fig. 2. Fourier Transform Infra-red (FT-IR) spectra of BLAIL neat (solid), silica gel (dashed) and Si-BLAIL (dotted) with KBr pellet. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.1.2. Scanning electron microscopy (SEM)

The SEM images of Si, Si-BLAIL and four times reused Si-BLAIL has been recorded, compiled as reported in literature [44,45] and shown in Fig. 3. Fig. 3A and B, 3C demonstrate that, the dimension of silica is approximately unchanged after immobilization of BLAIL and reused four times. The unaffected particle size of Si indicates the mechanical permanence of Si during the immobilization processes. The inset of Fig. 3B shows that, the surface morphology of Si-BLAIL has small aggregate type shell. These aggregates type layer is not observed for Si only (inset of Fig. 3A) hence, the aggregate type shell formation is due to immobilization of BLAIL. Such changes in the surface morphology of silica due to immobilization of IL was reported earlier [3]. The formation of such aggregates type shell in Si-BLAIL confirms the immobilization of BLAIL on the surface of silica. Fig. 3C show the particle size and surface morphology of Si-BLAIL recycled four times almost remains constant. The EDS spectrum of Si-BLAIL and four times reused Si-BLAIL shows the presence of S, Cl, Al and O elements further suggest the presence of both Brønsted and Lewis acidic sites. (cf. Fig. S2).

3.1.3. Termogravimetric analysis (TGA)

The thermogravimetric analysis of Si and Si-BLAIL has been carried out and presented in Fig. 4. Fig. 4 reveals that, the activated silica dose not shows any significant peak in the TGA. Additionally, the silica shows approximately 8% of weight loss as the nature of Si is hygroscopic that is responsible for such peak in TG curve and such weight loss has been reported for silica [46]. The observed weight loss is expected due to removal of absorbed water with dehydroxylation of silica surface.



Fig. 4. The TG curve of Silica gel (solid line) and Si-BLAIL (dotted line). Samples were dried in a hot air oven at 80 $^\circ C$ for 30 min before recording the spectra.



Fig. 3. The SEM images of Silica (A), Si-BLAIL (B), and (C) after four times reused Si-BLAIL catalyst.

Furthermore, it is also evident from Fig. 4 that the Si-BLIL shows weight loss in two stages, the first stage of weight loss over the range of 52 °C–148 °C, slightly higher than Si can be due to desorption of absorbed water which remains associated with Si after immobilization of BLAIL with silica by using water as a solvent. The thermal decomposition of Si-BLAIL shows the second step weight loss of approximately 16.2% over the temperature range 148 °C to 700 °C which can be due to degradation of bounded BLAIL. The removal of BLAIL from the surface of Si was further supported by the DSC curve (cf. Fig. S1). At a temperature higher than 700 °C the constancy in the weight indicates the presence of only Si. The loading of BLAIL on the surface of silica in weight percent can also be determined by analyzing the TG curve [17]. The detail analysis of TG curve shows that loading of BLAIL on Si is 16.18%.that matches very well with the weight percent determined by the calculations.

3.2. Application to synthesis of 2-aryl substituted benzimidazole

The Thai Nguyen et al. reported the synthesis of benzimidazole using BAIL gel as a catalyst [8]. They were not getting any product formation below 100 °C under solvent free condition and time required for completion of reaction was minimum of 5 h. The Lewis or Brønsted acid centers are known for the condensation and formation of Schiff base of acetaldehyde [47]. P. Sarma et al. and A. Khazaei et al. has been reported that, synthesis of benzimidazole at room temperature is also feasible by the use of high-valent oxidoiorn (IV) as an intermediate in presence of FeCl₃ and air [48,49]. The dehydrogenation and aromatization of isobutene by Lewis acid as active centers were reported by liu et al. [35]. The presence of H- bonds in ILs as a catalyst reduce the energy barrier of the reaction with stabilization of transition state [50] Furthermore, Hong Bo Wang et al. shown that the Mannich reaction can be catalyzed by mesoporous silica supported Brønsted-Lewis dual acidic ionic liquid with mild reaction condition, excellent yield and good reusability of the catalyst by the cooperative catalysis methodology [26]. Hence, our expectation is that it is possible to synthesize the benzimidazole derivatives at ambient temperature in suitable solvent with minimizing the reaction time. To check the possibility of such synthesis we have tested catalytic efficiency of Si-BLAIL for synthesis of benzimidazole.

The BLAIL was synthesized by the method as described earlier, characterized by the various techniques and tested for their catalytic efficiency as a heterogeneous catalyst for the synthesis of 2-aryl benzimidazole. Firstly, we have compared the catalytic activity of number of traditional Brønsted and Lewis acid catalyst towards synthesis of 2-aryl benzimidazole that reported in the literature and presented in Table 1. It has been observed from Table 1 that, the velocity of a reaction enhances drastically with maximizing the greener approach towards the synthesis of 2-aryl substituted benzimidazole with moving from traditional catalyst to supported heterogeneous catalyst. Nowadays, lot of researchers

Table 1

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Brønsted and Lewis acid	catalyst used	for synthesis	of 2-aryl	benzimidazole.

Sr. No.	Catalyst	Reaction condition	% Yield / Time (h)	[Ref.]
1	No catalyst	Reflux in Ethanol	27 / 6	[33]
2	0.3 wt% ZrO(NO3)2	Reflux in Ethanol	58 / 3	[33]
3	1 wt% ZrO(NO3)2	Reflux in DCM	70 / 4	[33]
4	0.05 mmol Yb(OTf)3	R.T., Solvent free	66 / -	[51]
5	5 wt% FeCl ₃ /PANI	R.T., in Ethanol	50 / 1.5	[52]
6	19 wt% FeCl ₃ /PANI	R.T., in Ethanol	70 / 3	[52]
7	5 wt% H3BO3	R.T., in water	60 / 1	[53]
8	BLAIL	R.T., in Ethanol	20 / 12	This
				work
9	0.1 mmol PS-PyCl-	R.T. in Ethanol	83-95 / 6–30	[54]
	xAlCl ₃		min.	
10	BAIL gel	130 °C, Solvent	88 / 5	[8]
		free		

focused on the solid supported heterogeneous catalyst for efficient synthesis hence we have plan for such benzimidazole synthesis and to the best of our knowledge this is the second report for such synthesis using dual acidic ionic liquid immobilized on silica. The Thai Nguyen et all have been used only Brønsted acidic ionic liquid [8] but we have employed Brønsted and Lewis dual acidic ionic liquid for such synthesis. Because of both acidic sites in the catalyst the reaction condition such as temperature, time decreases drastically.

3.2.1. optimization of reaction condition

The condensation and aromatization reaction between OPD and 4nitrobenzaldehyde to form 2-(4-nitrophenyl)-1-H-benzimidazole has been considered as a model reaction to study the catalytic activity of the Si-BLAIL. The silica gel does not show any product formation after 48h for condensation reaction between OPD and 4-nitrobenzaldehyde. Then we have tested the efficiency of Si-BLAIL towards product formation by changing the quantity of catalyst and it was observed that 4.2 mg (see table- 2) of catalyst is good enough to form benzimidazole in possibly minimum time with good yield. The most effective catalytic activity involves the less energy consumption with respect to mild reaction condition and amount of catalyst [55]. Hence the amount of Si-BLAIL of 4.2 mg is considered as effective for the formation of product. Moreover, the effect of solvents on the reaction condition has been carried out. The solvent mixture Ethanol-Water takes longer time to complete the reaction with minimum yield of the product. Also Table 2 reveals that, the ethanol is good solvent for this reaction as it shows good yield (87.04%) only in 60 min Also the ethanol is referred as good and relatively less volatile solvent in organic synthesis. Hence, the ethanol is selected as best fit solvent for this synthesis. The formation of 2-(4-nitrophenyl)-1H-benzimidazole (9) has been confirmed by FTIR and ¹H-NMR as representative example (cf. Fig. S4).

3.2.1.1. Typical reaction mechanism. The detailed mechanism was not clearly understood hence by considering the Thai Nguyen et al. proposed reaction mechanism; possible route for the formation of benzimidazole has been discussed by considering the concept of cooperative catalysis. During the aromatization, the participation of Si-BLAIL is also expected. The interaction of aldehydes with acidic site of the catalyst leads to protonation of carbonyl oxygen of aldehyde. The protonated aromatic aldehyde reacts with –NH₂ group of OPD gives an intermediate (X). The intermediate (X) on dehydration leads to formation of imine (Y) and another –NH₂ group of (Y) attacks imine to generate intermediate (Z) [8]. It has been mentioned earlier that the Lewis acid sites are responsible for aromatization of isobutane [35] and acidic site of the catalyst in presence of oxidizing agent is liable for the catalytic oxidation of the

Table 2

The optimization of solvents, time and amount of catalyst for the synthesis of benzimidazole by using Si-BLAIL as a catalyst.



Entry	Solvent	Cat. / (mg)	Time / min.	% Yield
1	EtOH	SiO ₂ -only	-	-
2	EtOH	4.200	60	87.00
3	EtOH	8.400	60	81.04
4	EtOH	16.800	70	97.84
5	EtOH	40.000	115	93.33
6	EtOH:H ₂ O (9:1)	4.200	120	72.98

reaction site [56,57]. Hence, it is considered that the intermediate (Z) either in presence of Si-BLAIL and air oxygen (O₂) undergoes partial oxidation to form the benzimidazole or in presence of Lewis acid site of the Si-BLAIL in the reaction mixture undergoes aromatization and leads to formation of benzimidazole by dehydrogenation. The enhancement in the yield with reduction in the amount of catalyst and changing the reaction medium suggest the special kind of reaction mechanism. Hence, the formation of benzimidazole was considered by the fact that cooperative catalysis effect of Brønsted and Lewis acidic sites of the Si-BLAIL (see the Scheme 2) and such Cooperative catalysis was reported by for Mannich reaction [26], Biginelli reaction [27].

3.2.2. Entry

To estimate the substrate scope of the Si-BLAIL, the Si-BLAIL has been tested for the synthesis of other substituted benzimidazole and the product formation was confirmed by comparing the melting point (MP), characterization of synthesized compound with that reported in the literature. The result is presented in Table 3, it is evident from Table 3 that the yield and time required to complete the reaction depends on the position and electronic character of the substituent on the benzaldehyde. The catalyst shows medium to good product formation capability in 15–240 min. Hence, it can be interpreted that the Si-BLAIL has good catalytic activity as a heterogeneous catalyst over the selected range of substituent on benzaldehydes.

3.3. Reusability study

The efficiency of catalyst is largely determined by their ability to show the catalytic activity after number of runs. Hence, the reusability of the Si-BLAIL was monitored for the model reaction OPD, 4-nitrobenzaldehyde in ethanol at room temperature. After completion of a reaction monitored by TLC, the product was isolated by the dilution of reaction mixture with ethanol and catalyst was recovered by centrifugation followed by washing with hexane and dried in oven at 100 °C for 2h. And the white free flow powder is used for next run. The recoverability of the catalyst was recorded and presented in Fig. 5. Fig. 5 reveals that Si-BLAIL can be used at least four successive runs without considerable loss in its catalytic activity. The present results clearly indicate the sustainability and reusability of the Si-BLAIL under the given reaction condition. The catalyst leaching has been investigated by hot filtration type test [36,60]. In the hot filtration test, continuous monitoring of the TLC for reaction between OPD and 4-chlorobenzalde-hyde has been carried out. The TLC of a reaction mixture at after 70 min (50% completion of reaction) shows the unreacted aldehyde in the reaction mass. The same reaction mixture was then centrifuged and filtered to separate the Si-BLAIL and filtrate continue to stirring for next 240 min After 150 min The TLC shows again unreacted starting aldehyde. Further, after 240 min monitoring of TLC shows unreacted starting material. In presence of catalyst the starting was completely consumed in 150 min but on removing the catalyst after 70 min The reaction was not complete after 310 min suggest that, the possibility of leaching of Si-BLAIL is minimum.

4. Conclusion

In conclusion, The Si-BLAIL contains both the hydrogen bond donor and acceptor moiety that activates both elecrophilic and nucleophilic sites of the reaction system. Further, the reduction in the amount of catalyst and the large decreases in the reaction time with optimal reaction condition recommend the participation of both the cations as well anions of Si-BLAIL. The presence of hydrogen bonding ability and both cations and anions increases the efficiency of Si-BLAIL as a heterogeneous catalyst. Hence, we have prepared heterogeneous, green, and efficient silica immobilized 1-methyl-3-(4-sulphobutyl)-1H-imidazolium tetrachloroaluminate (Si-BLAIL) as a cooperative catalyst for synthesis of 2(4-nitrophenyl)-1H-benzimidazole. The Si-BLAIL catalyzes the condensation-aromatization reaction compliantly. Moreover, the optimum reaction condition with respect to reaction time, temperature and solvent system were achieved using only 4.2 mg of Si-BLAIL. The ideal reaction condition, simplicity of catalyst preparation and characterization method and reusability makes the Si-BLAIL as an effective cooperative catalyst.



Scheme 2. Proposed reaction mechanism of the synthesis of benzimidazole.

Table 3

Substrate scope of Si-BLAIL toward synthesis of more benzimidazoles derivatives.

Substrate	Aldehyde	Time / min.	Product	% Yield	M.P. / ⁰ C [Ref.]
NH2 NH2	CI	150		86.02	292–295 °C [54]
NH ₂ NH ₂	O H	60		87.00	236–239 °C [58]
NH2 NH2	O H	240		71.14	217–220 °C [58]
NH ₂ NH ₂	O H Cl	60		79.00	230–232 °C [54]
NH2 NH2	N H	15		93.00	236–240 °C [59]



Fig. 5. Reusability study of Si-BLAIL for a model reaction of Orthophenylenediamine (OPD) (7), (0.200g, 1.85 mmol) and 4-nitrobenzaldehyde (8) (0.279g, 1.85 mmol) in 10 ml absolute ethanol and Si-BLAIL (0.0042g) was added with constant stirring at room temperature.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

No any financial interest / personal relationship are considered as potential competing interest.

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Appendix A. Supplementary data

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SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF PROCESSABLE POLYAZOMETHINES FOR HIGH TEMPERATURE APPLICATIONS

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ABSTRACT

New dithiazole-diamine monomer containing cyclohexylidene ring and pendant methyl group i.e. 1,1-bis [4-(2-aminothiazole)-3-methyl phenyl] cyclohexane (BATMPC) was synthesized through various steps. The structure of new dithiazole amine monomer was confirmed by FT-IR, ¹H NMR and ¹³CNMR Spectrometry. A series of polyazomethines containing cardo cyclohexane-thiazole unit have been incorporated by the polycondensation of a new diamine i.e. (BATMPC), with proportionate of aromatic dialdehydes. The impact of insertion of cardo cyclohexane, pendant methyl group and thiazole entity in the polyazomethine matrix with the dialdehydes [isophthalaldehyde (1,3 IPA) and terephthalaldehyde (1,4 TPA)], on solubility and thermal stability has been studied. All polyazomethines shown Tg in the range of 220-241°C and T₁₀% value of all thermally stable polyazomethines in nitrogen atmosphere was in between of 395-415°C These polyazomethines exhibited solubility in various polar aprotic solvents such as NMP, DMSO, DMAc, DMF etc. However, these polyazomethines were insoluble in common solvents such as DCM and CHCl₃. X-ray diffraction study confirms that all the polyazomethines are amorphous in nature having broad peak in the range of $2\theta=20^\circ$. The UV absorption at 360 nm shows that there is a formation of imine (-C=N-) linkages in the polymer matrix which is helpful for the conduction of electron throughout. The structure-property correlation among these polyazomethines was studied, in view of their potential applications for high temperature applications.

Keywords: 1,1-bis[4-(2-aminothiazole)-3-methyl phenyl] cyclohexane, Pendant methyl group, Cyclohexane, Polyazomethines.

1. INTRODUCTION

Aromatic polyazomethines (polyimines) shows excellent thermal stability, good mechanical and conducting properties, which makes them favourable members for high temperature applications in the engineering [1]. In addition, polyazomethines exhibit desirable useful properties such as electronic, optoelectronic [2-5] and liquid crystalline [6-8], fiber forming and ability to form metal chelates [9-11]. These polymers also show leading role in gas sensing applications [12-16]. However, the main drawback of polyazomethines is their limited solubility in most common organic solvents [17-20], high molecular weight polymers are problematic to obtain, because the growing macromolecular chains precipitate the solution during out of polycondensation. Furthermore, their high melting temperature and

insolubility makes them inflexible for processing by conventional techniques. Efforts devoted towards obtaining soluble and fusible polyazomethines include: insertion of flexible spacer between main chain aromatic rings [21, 22]; introduction of pendant groups, i.e. aromatic or alkyl substituents, insertion of methyl group into the polymer chain [23-25], introduction of structural irregularities such as kinks, bents, crankshaft-shaped units, etc. [26-28]. It is generally recognized that the presence of an alkyl group and ether linkage in the polymer backbone imparts segmental mobility to the polymer which enhances thesolubility and lowers the glass transition temperature.

The present study describes a successful synthesis of new semi-conjugated and processable aromatic polyazomethines for high temperature semiconducting applications by incorporation of thiazole unit, pendant methyl group and cardo cyclohexane moiety in the backbone. For this, a new aromatic diamine monomer havingthiazole unit, cardo cyclohexane moiety with ether linkage as well aspendant methyl group was designed and synthesized, which was subjected to high temperature polycondensation with isophthalaldehyde and terephthalaldehyde.

2. MATERIAL AND MEASUREMENTS 2.1. Material

Isophthalaldehyde (IPA), terephthalaldehyde (TPA) were supplied by Sigma-Aldrich and used as received. Thiourea, 4-fluro acetophenone, O-cresol, 3-mercaptopropanoic acid (3-MPA) were purchased from spectrochem, S.D. fine and used as received. N,N'dimethyl acetamide(DMAc) purchased from spectrochem and were dried over P_2O_5 ,distilled under reduced pressure and keptover 4Å molecular sieves. Solvents such as THF, DCM, methanol, ethanol and glacial acetic acid, were used as collected. K_2CO_3 and LiCl were dehydrated at 150°C in vacuum oven for 10 h.

2.2. Measurements

Fourier transform infrared (FTIR) spectrometry (Thermo Nicolet iS-10Mid Fourier transform infrared between wave numbers of 650-4000 cm⁻¹) was engaged to classify the functional groups of precursor and polymers. The ¹H-NMR scan was operated on 400 MHz Bruker spectrometer in dimethyl sulfoxide-d⁶.Ultravioletvisible(UV-Vis) spectra were recorded on a Shimadzu spectrophotometer in diluted DMAc solutions of 10⁻⁵M concentration, using 10 mm quartz cells, at room temperature. The XRD analysis was drifting out by using X-ray diffractometer (ULTIMA IV Goniometer).Inherent viscosities of the PAMs were determined by an Ubbelohde suspended-level viscometer. Thermal behaviour of the CHPAMs was studied by TA SDT Q600 at a heating degree of 10°C/min under nitrogen atmosphere.

2.3. Experimental

2.3.1. Monomer Synthesis

2.3.1.1. Synthesis of 1, 1-bis(4-hydroxy-3-methyl phenyl) cyclohexane (I)

This bisphenol was synthesized as per reported procedure [29]. In 250 mL three necked flask equipped with HCl gas deep tube, reflux condenser and magnetic stirrer were placed 58.84g (0.6mol) of O-cresol and 9.8 g (0.1

mol) of cyclohexanone and 0.2 mL3-mercaptopropanoic acid. To this reaction mixture dry HCl gas was bubbled at room temperature. The reaction mixture became solid within 2 h. The solid reaction mixture was dissolved in ethyl acetate (600 mL) and neutralized by washing with aq. NaHCO₃ solution 3 X 200 mL, followed by washing with distilled water 2 X 200 mL. The organic layer was dried over magnesium sulfate, filtered and distilled off to obtain viscous liquid. Then upon addition of pet ether in viscous liquid, solid product was separated out. The product was washed with water then dried under vaccum. Finally the bisphenol was reprecipitated through methanol-water mixture; Yield: 20.72g (70 %), M.P.:130°C.

2.3.1.2. Synthesis of 1,1-bis[4-(4-acetyl phenoxy)-3-methyl phenyl] cyclohexane (II)

This diketone intermediate was synthesized as per the reported procedure [30]. In a 500mL three neck round bottom flask equipped with calcium chloride guard tube, thermowell, N2 gas inlet and magnetic stirrer, placed 14.8 g 1,1-bis(4-hydroxy-3-methyl were phenyl) cyclopentane (I) (0.05 mol) and 13.81g 4fluoroacetophenone(0.1 mol) in 125 mL DMAc, then 13.82 g (0.1mol) of anhydrous K₂CO₃ was added. The resulting reaction mixture was refluxed for 12 h, allowed to cool at room temperature and precipitated the product from solution by addition of water. The product was isolated by filtration, washed with water and then methanol, and finally dried under vacuum. Recrystallized product in methanol; Yield: 24.18 g (93%), M.P.: 90°C.

2.3.1.3. Synthesisof 1,1-bis[4-(2-aminothiazole)-3-methyl phenyl] cyclohexane (III) (BATMPC)

Into 100-mL single-neck round-bottom flask, diketone (II) (15.96 g, 0.03mol), thiourea (13.68 g, 0.18 mmol) and iodine (7.62 g, 0.09 mol) were dissolved in 125 mL THF. The mixture was stirred and refluxed for 48 h. Cooled the clear solution, transferred to another beaker containing cold sodium acetate solution and stirred for 3 h. The crude product was filtered, washed with THF and finally with pet ether-ethyl acetate (8:2) mixture. Dried the product under vaccum for 10h; Yield: 17.38 (90%), MP: 225°C. IR: 3350 cm⁻¹ (-NH₂ stretching), 3108, 2932, 2855, 1617, 1246, 835 cm⁻¹ H NMR (400MHz, CDCl₃), δ (ppm): 6.9-7.8 (Aromatic Protons), 6.8 (thiazole ring proton), 2.5(Methyl protons), 1.5, 2.0 (Cyclohexane ring protons). ¹³C NMR (100MHz,

CDCl3), δ (ppm):169.87 (NH₂ attached C), 157.86, 150.91, 144.46, 130.37, 129.88, 128.70, 127.68, 126.05, 119.46, 117.03, 116.18, 101.31, 44.68, 36.40, 25.70, 22.54 and 16.10.

2.4. Polyazomethines Synthesis

In a 100-mL three-neck round-bottom flask, a mixture of diamine (BATMPC) (0.644g 1 mmol) and 3 mL of dry DMAc containing 5% lithium chloride (0.150 g) was stirred under nitrogen gas to get transparent solution of diamine. Then, 0.134 g of dialdehyde was added (TPA/IPA/(TPA+ IPA) and stirred at room temperature for overnight in N₂ atmosphere. Finally, the polymerization mixture was heated at 140°C for 4 h. On cooling, the polymer mixture was gradually poured into water while stirring was continued, and precipitate of the resulting polymer was filtered off. Rinsed with water and resulting brown product was obtained in high yield, dried under vacuum at 80°C for 8 h to produce CHPAMs. The polyazomethines CHPAM-1 to CHPAM-4 were synthesized with various diamines by a similar procedure. All the polyazomethines gave better yield between 97-99%.

IR Spectrum

CHPAM 1: 3025, 2910, 1640, 1590, 1497, 1230, 1155, 830 cm⁻¹

CHPAM-2: 3030, 2905, 1641, 1595, 1492, 1235, 1155, 835 cm⁻¹

CHPAM-3: 3040, 2915, 1645, 1600, 1492, 1240, 1157, 832 cm⁻¹

CHPAM-4: 3045, 2913, 1642, 1585, 1480, 1240, 1156, 831 cm⁻¹

3. RESULTS AND DISCUSSION

3.1. Monomer Synthesis and Characterization

In the presented work, dithiazole amine monomer containing cyclohexylidene moiety, viz. BATMPC has been synthesized and used as building blocks for preparation of thiazole containing polyazomethines. The new dithiazole amine, 1,1-bis[4-(2-aminothiazole)-3methyl phenyl] cyclohexane (III) was synthesized starting from O-cresol and cyclohexanonein three steps as shown in Scheme 1.

The 1,1-bis(4-hydroxy-3-methylphenyl) cyclohexane(I) was synthesized by reacting *o*-cresol with cyclohexanone in the presence of 3-MPA as catalyst. The 1,1-bis[4-(4-acetyl phenoxy)-3-methylphenyl]cyclohexane(II) was obtained by reaction of (I) with 4-fluoroacetophenone and potassium carbonate in DMAc. Structure of (II) was confirmed by IR spectroscopy.

In the third step, diketone (II) undergoes ring closure with thiourea to give 1,1-bis[4-(2-aminothiazole)-3-methylphenyl] cyclohexane (III)(BATMPC). Chemical elucidation of new diamine precursor BATMPC was confirmed by ¹HNMR, ¹³C NMR and FTIR spectroscopy.



Scheme 1: Synthesis of 1,1-bis[4-(2-aminothiazole)-3-methylphenyl] cyclohexane

The FTIR spectrum of the corresponding diamine monomer BATMPC supported the evidences of the successful achievement of complete ring cyclization of thiazole monomer, as shown in Fig.1. The infrared spectrum showed characteristic absorption bands at 3350 cm⁻¹ ($-NH_2$ stretch), 1617 cm⁻¹ (>C=C< stretch), 1246cm⁻¹ (>C-O-C< stretch), 3108cm⁻¹ (aromatic -CH stretch), 2932, 2855 cm⁻¹ (aliphatic -CH stretch). The proton-NMR spectra of BATMPC is shown in Fig. 2. The resonance peak were observed at 6.9-7.8 ppm (Aromatic Protons), 6.8 ppm (thiazole ring proton), 2.5 (Methyl protons), 1.5 ppm, 2.0 ppm (Cyclohexane ring protons). ¹H NMR analysis clearly indicated that diketone structure is completely transformed into diamine structure by cyclization.

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Further ¹³C NMR spectrum of BATMPC showed eighteen NMR signals to 18 types of different carbons atoms shown in Fig. 3. The NMR signals appeared at 169.87 ppm (NH₂ attached C), 157.86, 150.91, 130.37, 129.88, 128.70, 127.68, 126.05, 119.46, 117.03,

116.18 ppm (aromatic carbons), 144.46, 101.31ppm (thiazole C). The signal at 44.68, 36.40, 25.70, 22.54 ppm confirms presence of cyclohexane ring and signal at 16.10 ppm confirms presence of pendant methyl group in the monomer.



Fig. 1: FT-IR spectrum of 1,1-bis[4-(2-aminothiazole)-3-methylphenyl] cyclohexane



Fig. 2: ¹H NMR spectrum of 1,1-bis[4-(2-aminothiazole)-3-methylphenyl] cyclohexane 3.2. Polymer Synthesis and Characterization

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As presented in Scheme 2, a series of four new CHPAMs were synthesized from new diamine precursor, i.e.1,1-bis[4-(2-aminothiazole)-3-methylphenyl] cyclohexane (BATMPC) with varying mole ratios of IPA + TPA by a high-temperature solution polycondensation method [29]. Yields and inherent viscosities are shown in Table 1. The synthesised CHPAMs were proved by FTIR spectra.

The vibrational assignments of various cyclohexanethiazole-based polymers are reported in Fig. 4. The stretching vibrations of -C=N- (azo linkages) absorption bands are typically located at 1640 cm⁻¹. The loss of stretching vibrations at 1700 and 3400-3150 cm⁻¹ specified that total dialdehyde and diamine functionality had proceeded to produce with great molecular framework of CHPAMs. The stretching absorption at 1590 cm⁻¹ is attributed to aromatic -C=C- stretching frequency of aromatic and thiazole unit which is well-constructed in polyazomethine. The stretching at 3025 cm⁻¹ explains the aromatic C-H stretch of the polyazomethines chain.

Dolumor ^a		Monomers		Inhouse	
Code	Diamine (III) mol %	TPC (X) mol%	IPC (100-X) mol %	Yield %	Viscosity dL/g ^b
CHPAM-01	100	100	0	99	0.35
CHPAM-02	100	75	25	99	0.33
CHPAM-03	100	25	75	98	0.29
CHPAM-04	100	0	100	97	0.27

Table 1: Yield and Viscosity of Polyazomethines (CHPAM-1 to CHPAM-4)

^aPolymerization was carried out with 1 mmol each of diamine and dialdehyde, ^bInherent viscosity was measured at a concentration of 50 mg/10 ml in **DMAc** at 30° C



Fig. 3:¹³C NMR spectrum of 1,1-bis[4-(2-aminothiazole)-3-methylphenyl] cyclohexane

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Scheme 2: Synthesis of Polyazomethines (CHPAM-1 to CHPAM-4)





3.2.1. Solubility and inherent viscosity

As shown in Table 2, solubility of CHPAMs was proved qualitatively in numerous organic solvents. All CHPAMs were dissolved at room temperature in DMAc and conc. H_2SO_4 . These polymers are partly soluble in DMSO, NMP, pyridine and DMF. Moreover, they were totally insoluble in fewer active solvents such as DCM and chloroform.

As shown in Table 1, the resulting CHPAMs showed inherent viscosities in the range 0.27-0.35 dL/g,

measured in DMAc at concentration of 0.50 dL/g at 30° C.

3.2.2. XRD analysis

The X-ray diffraction (XRD) technique has been used to check the crystallinity/amorphous nature of series of polyazomethines (Fig. 5) over in the 2θ range of 5°-90° [29]. Broad diffraction peaks at ~ 12° and ~ 20° (2θ) were detected which support the amorphous nature of CHPAMs. No more sharp peaks are detected which specifies amorphous nature of CHPAMs.



Fig. 5: XRD of Polyazomethines (CHPAM-1 to CHPAM-4)

From the observed arrangements, it is granted to confirm that considered material had an amorphous

nature which was predicted and also in good compliance with the reported literature [31, 32].

Polymor Codo				Solubility	behaviou	r		
1 orymer Code	DMF	DMAc	DMSO	NMP	DCM	CHCl ₃	Pyridine	Conc. H ₂ SO ₄
CHPAM-01	±	+	<u>±</u>	<u>±</u>	-	-	-	+
CHPAM-02	±	+	<u>±</u>	±	-	-	<u>+</u>	+
CHPAM-03	+	+	+	+	-	-	+	+
CHPAM-04	+	+	+	+	-	-	+	+

Table 2: Solubility behaviour of Polyazomethines (CHPAM-1 to CHPAM-4)

+: Soluble; -: Insoluble on heating; \pm : Sparingly soluble

3.2.3. Thermal analysis

The thermal properties of the cyclohexane-thiazolebased CHPAMs were estimated by TGA and DSC in nitrogen atmospheres. The outcomes are outlined in table 3, and the representative TGA curves of the polyazomethines are displayed in Fig. 6. As presented in table 3, the strategy of polyazomethines with the merger of 1,4 and 1,3 linkages and cardocyclohexanethiazole structure provides high thermal stability. Polymers CHPAM-01 to CHPAM-04 were in the range 380-415°C in nitrogen atmosphere. In addition, these polymers remained 31-49 % of original weight at 900°C in nitrogen atmosphere. Amongst these polyazomethines, the CHPAM-01 presented uppermost thermal stability with T10% at 415°C in compliance with the previous reports [31, 32]. Polyazomethines composed of more percentage of rigid backbone, i.e. para orientated (1,4 linkages, TPA) shows higher thermal stability than the meta oriented (1,3 linkages, IPA). This varying composition of polyazomethines (CHPAM-01 to CHPAM-04) is also clearly seen in the residual weight at 900°C.

These polyazomethines gave the glass transition temperature (T_g) in between 220-241°C and are displayed in Fig. 7.

Table 3: Physical properties of Polyazomethines(CHPAM-1 to CHPAM-4)

Polymer	Thermal behaviour ^b						
Code	T _d °C in N ₂	T _g °C	Residual Wt % at 900°C				
CHPAM-01	415	241	31				
CHPAM-02	405	229	49				
CHPAM-03	380	220	43				
CHPAM-04	395	221	48				

^b Temperature at which onset of decomposition was recorded by TG at aheating rate of $10^{\circ}C/min$. T_g -Glass transition temperature determined by DSC at a heating rate of $10^{\circ}C/min$, T_d -Temperature of $10^{\circ}\%$ decomposition



Fig. 6: TGAof Polyazomethines (CHPAM-1 to CHPAM-4)



Fig. 7: DSC of Polyazomethines (CHPAM-1 to CHPAM-4)

The polymers CHPAM-1 and CHPAM-2 show the uppermost T_g value because of the presence of more

percentage of rigid 1,4-benzene linkage (TPA) and a lower percentage of 1,3 benzene linkage (IPA), whereas the polymer CHPAM-4 gave the lowest Tg value due to the existence of cardo cyclohexane, pendant methyl group andmore percentage of 1,3 linkages.

3.2.4. Photophysical properties

The photophysical properties of the polyazomethines were investigated by UV-vis absorption spectroscopy in DMAC solutions (10^{-5} M) . In solution, all polyazomethines presented at least two absorption bands (Fig. 8). The first absorption band in the range 352-360 nm is attributed to $\pi-\pi^*$ progression of aromaticring conjugations. The next most important absorption area is sighted around 463-471 nm owing to $n-\pi^*$ transition of imine conjugations. From this, it was confirmed that all the precursors or starting material totally vanished and increased electron shifting in the polymer backbone. These results are in good compliance with reported literature [33-37].



Fig. 8: UV-Visible spectrum of Polyazomethines (CHPAM-1 to CHPAM-4)

4. CONCLUSIONS

A series of CHPAMs were prepared by the hightemperature solution polycondensation of a novel diamine precursor 1,1-bis[4-(2-aminothiazole)-3-methyl phenyl] cyclohexane (BATMPC), with varying proportion of aromatic dialdehydes comonomer [1,3 linkage isophthalaldehyde (IPA) and 1,4 linkage terephthalaldehyde(TPA)]. Inherent viscosities of these CHPAMs were in between the 0.27 and0.35 dL/g indicating built-up of moderate molecular weights. These CHPAMs revealed solubility in many polar aprotic solvents without appreciable loss in thermal stability, so it is possible to process these polyazomethines in polar aprotic solvents. The existence of -CH=N- (azo linkage) in the CHPAMs framework was committed by UV-Vis spectra. The 10% weight loss in nitrogen range from 380°C to 415°C indicates that these polyazomethines are suitable for high temperature applications. The glass transition temperature of polyazomethines (220°C to 241°C) can allow processing of polymers above 220°C. X-ray diffraction study shows amorphous nature of these polymers.

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Conflict of interest

None declared

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Synthesis and characterization of organosoluble thermally stable polyamides containing spacer methylene linkage and bulky tetraphenylfuran moiety

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Synthesis and characterization of organosoluble thermally stable polyamides containing spacer methylene linkage and bulky tetraphenylfuran moiety

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ABSTRACT

Thermally stable and organo-soluble polyamides synthesized by polycondensation reaction of diacid monomer, 2, 5-bis (4-carboxymethylene phenyl) 3, 4-diphenyl furan (BCMPDF) with various commercially available aromatic diamines such as 4,4'-Oxydianiline, 4,4'-methylenedianiline, 4,4'sulphonyldianiline, 4,4'-Diaminobenzophenone and 4,4'-(hexafluoroisopropylidene)dianiline by using Yamazaki's direct phosphorylation method. A 2, 5-bis (4-carboxymethylene phenyl) 3, 4-diphenyl furan (BCMPDF) as a new compound containing methylene linkage and bulky moiety of tetraphenylfuran was successfully prepared by a four step reaction. The resulted polymers show excellent thermal stability, good solubility in aprotic polar solvent and inherent viscosities between 0.50 and 0.58 dl/g. Wide angle Xray diffraction of all these PAs show amorphous nature. Polyamides showed glass-transition temperatures in the range of 169-213°C indicate that polymers are easily processable. Thermogravimetric analysis of the polyamides indicated a 10% weight loss (T_{10}) in the temperature range of 449-510°C and char yields at 900°C under nitrogen atmosphere in the range of 49-58% depending on the diamine monomer used for the synthesis polyamides. The structure -property correlation among these polyamides were discussed. The limiting oxygen indexes of all polyamides are more than 37.1, thus such type polymers of can act as flame retardant materials. These polyamides will be useful for high performance applications.

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Introduction

Aromatic-aliphatic polyamides are superior high performance class of polymeric material. Aromatic polyamides, or aramids, comprised >90% by amide groups (-CO-NH-) attached directly to two aromatic rings.^[1,2] Outstanding mechanical strength and superior high thermal resistance are the speciality of these aromatic polyamides. Among all the heat resistant materials aromatic polyamides have received particular attention. Some of them are available for use as flame-resistant, high-strength, high-modulus fibers, and high-efficiency semipermeable

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membranes as well as high-performance plastics.^[3–7] Such brand of outstanding properties of these materials was built-up by the aramids framework which is based on the rigid aromatic amide linkage. These rigid Polyamides (PAs) are difficult to process because they show limited solubility in organic solvents and high melting temperature and glass-transition temperature (Tg). The renowned thermally stable aromatic polyamides have the solemn disadvantage of being unwell soluble in organic aprotic solvents. To condense these polymers processable, there is a requirement to boost their solubility. The usual style of refining the solubility of a polymer comprises the introduction of flexible units into the backbone.^[8–20] Polyamides containing bulky moieties i.e. tetraphenylthiophene tetraphenylfuran and tetraphenylpyrrole units have been reported.^[5,6] They were found to have good thermal stabilities but very poor solubilities. Yamazaki's "phosphorylation" reaction was used for the direct synthesis of polyamides from diacids and diamines.^[18]

The present research deals with the synthesis and characterization of polyamides derived from aromatic-aliphatic diacids, viz. 2, 5-bis (4-carboxymethylene phenyl) 3, 4-diphenyl furan (BCMPDF) and various commercial available aromatic diamines such as 4,4'-oxydianiline (ODA), 4,4'-methylenedianiline (MDA), 4,4'-sulphonyldianiline (SDA), 4,4'-Diaminobenzophenone (BDA) and 4,4'-(hexafluoroisopropylidene)dianiline (6FDA) by Yamazaki's phosphorylation. The alteration of the polymer backbone by the integration of aliphatic units into the double-strand heterocyclic units improved better-quality of the solubility.

Experimental

Materials

4,4'-Oxydianiline (ODA), 4,4'-methylenedianiline (MDA), 4,4'-sulphonyldianiline (SDA), 4,4'-Diaminobenzophenone (BDA) and 4,4'-(hexafluoroisopropylidene)dianiline (6FDA) were purchased from Sigma Aldrich Company without further purification. Potassium tertabutoxide, 1, 2-diarylethanone (deoxybenzoin), thiourea, iodine (I₂), aluminum chloride (AlCl₃) acetyl chloride of s d fine chemical were used as received. LiCl (Sigma Aldrich) was dried for 24 h at 180 °C under vacuum before use. Solvents such as ethyl acetate, dimethyl sulfoxide (DMSO, s d fine), N, N'-dimethyl acetamide (DMAc, s d fine), triphenyl phosphine (TPP, Sigma Aldrich) and toluene (s d fine), N-methyl-2-pyrrolidone (NMP, s d fine), N, N'-dimethyl foramide (DMF, s d fine), Pyridine (Py, Sigma Aldrich) THF (s d fine) and DCM (s d fine) were used as received.

Measurements

The FTIR spectra were measured by Thermo Nicolet iS-10 Mid Fourier Transform Infrared spectrometer (FTIR) in the $650-4000 \text{ cm}^{-1}$ frequency range. The spectra of monomer were obtained using KBr pellets, recorded at 4 cm^{-1} resolution with 16 scans and the vibrational transition frequencies were reported in wavenumbers (cm⁻¹). The ¹H NMR (400 MHz) spectra were measured with a Brucker Spectrometer (Switzerland) using dimethyl sulfoxide (DMSO)-d6 as solvent. The Mass spectrum was recorded on MASS Model AB Sciex API 5500 using Methanol-Acetonitrile as solvent. 200 nanogram/ml sample concentration is prepared. Electrospray ionization method is used for this analysis. XRD was recorded on X-Ray Diffraction system Ultima IV with ULTIMA IV Goniometer (Japan). Inherent viscosities were measured using an Ubbelohde suspended Level Viscometer with a 0.5 g/dL in NMP solution at 30 °C. Molecular weight of polyamide (PA-1) was measured on Thermo-Finnigan make gel permeation chromatograph (GPC) using N-methyl pyrrolidone (NMP) as an eluent at a flow rate of 0.5 mL.min^{-1} at $30 \,^{\circ}\text{C}$ temperature. Sample concentration was 2 mg.mL^{-1} and Polystyrene was used as calibration standards. The thermogravimetric analysis was recorded

using a TGA instrument (Mettler-Toledo, Switzerland) in the temperature range of 30-900 °C. Samples having mass of ca. 5 mg were placed in 100 mL alumina crucibles. Thermal decomposition experiments were carried out using a heating rate of 10 °C/min in nitrogen atmosphere with a gas flow rate of 50 mL.min⁻¹. The DSC measurements were performed using a Mettler-Toledo DSC-1 STARe system in nitrogen atmosphere (flow rate of 50 mL.min⁻¹). Samples of ca. 5 mg were weighed, sealed in aluminum pans, heated to their respective final temperatures that was used for each sample, kept isothermally at that final temperature for 5 min, and then cooled. Tg values were read at the middle of the transition in heat capacity and were taken from the second heating scan after cooling from 350 °C at a cooling rate of 20 °C/min.

Monomer synthesis

2, 3, 4, 5-Tetraphenylfuran (TPF) and intermediates (Scheme 1) were synthesized in our laboratory according to previous literature reports.^[21,22] All the synthetic details of monomer are discussed below and the reaction scheme for monomer synthesis is shown in Scheme 1. The monomer (BCMPDF) was characterized by FT-IR, ¹H-NMR, ¹³C-NMR and MASS spectroscopy to confirm their structures.

2, 5-Bis (4-acetyl phenyl)-3, 4-diphenyl furan (BAPDF)

In three-neck flask, TPF (6.678 g, 18.05 mmol), anhydrous DCM (50 mL), and AlCl₃ (4.783 g, 36.10 mmol) were added under nitrogen atmosphere. The whole mixtures were then cooled to 0° C using ice-water bath. Acetyl chloride (2.833 g, 36 mmol) was then added drop wise to the stirred reaction mixture at 0° C. The reaction was allowed to warm to room temperature and stirring was continued for overnight. The resulting mixture was poured into ice cold water (300 mL), and the organic layer was collected, evaporated to give crude product BAPDF, recrystallized from toluene to get pure yellow crystals of BAPDF.

Yield 3.2g (70%) M.P: 252–254°C.

2, 5-Bis (4-thioacetomorpholide phenyl)-3, 4-diphenyl furan (BTMPDF)

4.42 g (10 mmol) of BAPDF, 0.640 g (20 mmol) sulfur and 1.741 g (1.75 mL, 20 mmol) morpholine added in a 100-mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer. This reaction mixture was stirred, gentle reflux to remove complete evolution of hydrogen sulfide and then continued stirred more vigorously for 16 h. Cool, the reaction mixture to room temperature. 200 mL of ethanol was added to obtain a brown buff-color product that was filtered, washed with excess ethanol, and dried.

Yield 5.90 g (88%), M.P.: 140–142°C.

The IR spectrum exhibited absorption at 1240 cm^{-1} (C=S).

2, 5-Bis (4-carboxy methylene phenyl)-3, 4-Diphenyl furan (BCMPDF)

A 100 mL round-bottom flask contains a reaction mixture of 6.58 g (BTMPDF, 10 mmol) and 65 mL of 10% ethanolic sodium hydroxide solution. Reaction mixture was refluxed for 12 h with stirring. After the completion of reaction excess ethanol was distilled out under reduced pressure. To these residual product with stirring 150 mL of hot water was added and filtered. The filtrate was acidified by 1:1 hydrochloric acid. The precipitated product was stirred and then filtered,



Scheme 1. Synthetic route for the synthesis of 2, 5-bis (4-carboxy methylene phenyl)-3, 4-diphenyl furan (BCMPDF) diacid monomer.

washed thoroughly with hot water, and dried. The product was recrystallized from ethanol to get (BCMPDF)

Yield: 3 g (67%), M.P.:
$$242-240^{\circ}$$
C.

The IR spectrum of (BCMPDF) exhibited absorption at $2500-3300 \text{ cm}^{-1}$ (-COOH), 1704 cm^{-1} (C=O), and $2857-2918 \text{ cm}^{-1}$ (C-H aliphatic).

Polymer synthesis

By using the precursor 2, 5-bis (4-carboxymethylene phenyl) 3, 4-diphenyl furan (BCMPDF) a novel series of five polyamides were synthesized by using Yamazaki's phosphorylation method.

Polymer ^a code	Diacid BCMPDF	Diamines	Yield (%)	Viscosity ^b η _{inh} (dL/g)	Film formation	Color
PA-1	BCMPDF	ODA	99	0.54	Yes	Yellow
PA-2	BCMPDF	MDA	96	0.50	Yes	Faint yellow
PA-3	BCMPDF	SDA	98	0.58	Yes	Yellow
PA-4	BCMPDF	BDA	97	0.56	Yes	Dark yellow
PA-5	BCMPDF	6FDA	96	0.52	Yes	Yellow

Table 1. Synthesis of polyamides (PA-1 to PA-5).

^aPolymerization was carried out with 1 mmol each of diacid and diamines.

^bMeasured at a concentration of 0.5 g/dL in NMP at 30 $^{\circ}$ C.

Synthesis of polyamides (PA-1 to PA-5)

In a 100-mL three-neck round-bottom flask equipped with magnetic stirrer, reflux condenser, calcium chloride guard tube, and nitrogen gas inlet were placed 0.504 g (1 mmol) 2,5-bis(4-carboxy methylene phenyl)-3,4-diphenyl furan (BCMPDF), 0.200 g (1 mmol) 4,4'-diamino diphenyl ether (ODA), 0.200 g lithium chloride [8 wt % based on solvent *N*-methyl pyrrolidone (NMP) and pyridine mixture], 0.744 g (0.63 mL, 2.4 mmol) triphenyl phosphite (TPP), 0.5 mL pyridine, and 2 mL NMP. The mixture was stirred well and temperature was slowly raised to 100 °C. The mixture was heated at 100 °C for 3 h under nitrogen. After cooling, the resulting viscous polymer solution was poured into rapidly stirred 200 mL of methanol. The precipitated polymer was filtered, washed with methanol, and air-dried. The polymer was purified by dissolving in N, N'-dimethyl acetamide (DMAc) and reprecipitating in methanol. It was filtered, washed with methanol, and dried under vacuum at 100 °C for 8 h. The yield was 99%, and the inherent viscosity (η_{inh} .) of polymer in NMP was 0.54 dL/g. All other polyamides (PA-2 to PA-5), were prepared by similar procedure as mentioned in Table 1 and Scheme 2.

Results and discussion

Synthesis of monomer

The novel spacer methylene containing diacid 2, 5-bis (4-carboxy methylene phenyl)-3, 4-diphenyl furan (BCMPDF) was synthesized in several steps (Scheme 1).

Carbon-carbon coupling of deoxybenzoin catalyzed by sodium tertabutoxide followed by subsequently addition of iodine to yield 1, 2, 3, 4-tetraphenylbutane-1, 4-dione, further cyclization gave 2, 3, 4, 5 tetraphenylfuran (TPF). Acylation of TPF yields 2, 5-bis (4-acetyl phenyl)-3, 4diphenyl furan (BAPDF). Finally BAPDF undergoes Conrad Willgerodt reaction with Kindler variation give 2, 5-bis (4-carboxy methylene phenyl)-3, 4-diphenyl furan (BCMPDF). The structure of new diacid precursor was confirmed by FT-IR, ¹H and ¹³C NMR and mass spectroscopy.

Synthesis of polymers

Bulky tetraphenyl furan and spacer methylene containing aromatic-aliphatic polyamides were synthesized by reacting 2, 5-bis (4-carboxy methylene phenyl)-3, 4-diphenyl furan (BCMPDF) with various commercial aromatic diamines (PA-1 to PA-5). The high temperature solution polymerization, shown in Scheme 2, involves polymerization forming soluble polyamides by using Yamazaki's phosphorylation method.

All the polymers are in yield with inherent viscosities in the range of 0.50-0.58 dL/g (Table 1) giving as faint yellow to dark yellow polyamides(PA-1 to PA-5). The overall yield is 99%. The formation of the polyamides from the diacid monomer was confirmed by means of FT-IR and ¹H NMR spectroscopy.



Scheme 2. Synthetic route of polyamides (PA-1 to PA-5).

Structural characterization

The 2, 5-bis (4-carboxy methylene phenyl)-3, 4-diphenyl furan (BCMPDF) monomer characterized by FT-IR, ¹H and ¹³C NMR spectroscopy.

In the synthesis of compound BCMPDF, the appearance of the characteristic carbonyl band at 1704 cm^{-1} was observed on the FT-IR spectrum as shown Figure 1. Compound BCMPDF showed IR absorption at $2500-3300 \text{ cm}^{-1}$ characteristic of hydroxyl group of diacid together with the appearance of resonances at 3.50δ (4H) due to protons sandwich between carbonyl group and tetraphenylfuran unit on the ¹H NMR spectrum as shown Figure 2. The signals in the range of 7.12–7.65 δ of (18H) are attributed to the aromatic protons of phenylene rings whereas signal most downfield at 11.42 are assigned to carboxylic acid proton (2H). The ¹³C-NMR spectrum of BCMPDF exhibited twelve peaks due to symmetry, indicating the formation of the postulated diacid (Figure 3).

Polyamide (PA-1) is characterized by FT-IR spectroscopy. The Figure 1 shows polymer synthesis (PA-1), which confirms diacid monomers (BCMPDF) converted into polyamides by using Yamazaki's phosphorylation method. This Spectrum shows strong absorption vibrational peak at around 1658 cm^{-1} for amide carbonyl group. Polyamide linkage contains –NH group in main framework core which shows vibration peak at around 3302 cm^{-1} . The formation of polyamides



Figure 1. Comparative FT-IR spectrum of BCMPDF with PA-1.



Figure 2. ¹H-NMR spectrum of BCMPDF.

(PA-1) is also characterized by ¹H-NMR. As shown in Figure 4 there was a strong separation of the resonance signals of all aromatic and aliphatic protons in the range of 7.14–7.79 δ and 3.9 δ , respectively. Polyamides containing amide linkages –CONH, –NH group of polyamides shows signal at around 10.34 δ . From the ¹H NMR of PA-1 it clear that, there is a total conversion of novel diacid (BCMPDF) in to corresponding polyamide. The ¹H NMR spectra are in good agreement with the proposed assembly of the repeating unit of polymer PA-1.

The GPC data of polyamide (PA-1) are outlined in Table 2. The results showed that the number-average (Mn) and Weight-average (Mw) values were 39900 and $134800 \text{ g.mol}^{-1}$ respectively, with respect to polystyrene standards and the ratio Mw/Mn dispersity was 3.38.



Figure 3. ¹³C-NMR spectrum of BCMPDF.



Figure 4. ¹H-NMR Spectrum of PA-1.

Table 2.	Weight averag	e moleculai	r weights	(Mw),	number	average	molecular	r weights	(Mn)	and	dispersity	index	(Mw/Mn)	of
polyamid	e (PA-1).													

Sr. No.	Polymer code	Mn (g.mol⁻¹)	Mw (g.mol⁻¹)	PDIª (Mw/Mn)
1	PA-1	39900	134800	3.38

^aThe dispersity index (PDI) of the polyamide (PA-1) samples measured at 30 °C using N-methylpyrrolidone (NMP) as eluent at a flow rate of 0.5 mL.min⁻¹ by GPC.

Table 3.	Solubility	of po	lyamides	(PA-1	to PA-5)
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Solvents									
$$ \downarrow Polymers	DMAc	NMP	DMF	DMSO	Pyridine	Conc. H ₂ SO ₄	m-Cresol	CHCl₃	THF
PA-1	++	++	++	++	++	++	+ -	_	+
PA-2	++	++	++	++	++	++	+	_	+
PA-3	++	++	+	++	+-	++	+-	_	-
PA-4	++	++	+	++	++	++	++	_	+
PA-5	++	++	+	++	++	++	++	-	+

++: Soluble +: soluble on heating; + -: partly soluble; --: insoluble.

Solubility and inherent viscosity

Table 3 gave qualitative solubility of the bulky tetraphenylfuran and spacer methylene unit covering polyamides (PA-1 to PA-5). The concentration for the solubility tests was 3 wt %. Almost all polyamides (PA-1 to PA-5) were soluble in polar aprotic solvents such as DMAc, NMP, DMF (on heating), DMSO, in pyridine, m-cresol, THF (except PA-3) and Conc. H₂SO₄. While they are insoluble in chlorinated solvent chloroform, etc.

On other hand polyamides PA-1, PA-2, PA-4 and PA-5 having readily more soluble due to the more coordinating polar ether linkages (-O-), flexible methylene linkages ($-CH_2-$) sandwiched group (C=0) and two-CF₃ unit respectively. PA-3 shows less solubility due to the sandwiched less coordinating insoluble sulfur content sulfonyl group. As compare to bulky structures, the solubility of these bulky tetraphenylfuran and spacer methylene constructed polyamides were advanced than that of aromatic polyamides by taking analogous huge structures such as tetraphenylfuran, tetraphenylthiophene, tetraphenylpyrrole described.^[23]

Inherent viscosity measurements were used to establish an order of constructing molecules or building up of molecules and size of the polyamides chain in the series (PA-1 to PA-5). All these polyamides show excellent solubility in aprotic organic solvents at room temperature except DMF (on heating). Thus, the inherent viscosity of polyamides was recorded at 30 °C in NMP and values in between 0.50 and 0.58 dL/g were obtained as shown in Table 1.

Thermal analysis

The Figure 5 shows the TGA thermograms of PA-1 to PA-5 measured at a heating rate of 10^{0} C/min. 10% weight loss temperature of polyamides are summarized in Table 4.

The high thermal stability, chemical and mechanical stiffness for polyamides arises from the aromatic rings (bulky tetraphenylfuran) as well as the amide linkage. The mode elaborate in the degradation of PA-1 to PA-5, smaller units by the cleavage of hetero atom bonds such as C–O, C–N and C–O, homo atomic bond C–C bond. All polyamides (PA-1 to PA-5) show T_{10} value in the range of 449–510 °C in Nitrogen atmosphere. Amongst these polyamides, the PA-3 and PA-4 exhibits the highest thermal stability with a decomposition temperature of ca. 487 and 510 °C, respectively, this is for the reason that the polymer backbone contains more sandwiched rigid framework of carbonyl center (C=S) and (C=0).^[24] This could be credited to the molecular



Figure 5. TGA of Polyamides (PA-1 to PA-5).

Table 4. Thermal properties of polyamides (PA-1 to PA-5).

			Thermal behaviour	Residual W/t %		
Sr. No.	Polymers	Tg	T _i	T _d	at 900 °C	LOI
1	PA-1	180	338	462	58	40.7
2	PA-2	183	325	449	57	40.3
3	PA-3	200	343	487	54	39.1
4	PA-4	182	315	510	52	38.3
5	PA-5	178	320	473	49	37.1

^aTemperature at which onset of decomposition was recorded by TG at a heating rate of 10 °C/min.

T_g: glass transition temperature; T_i: initial decomposition temperature; T_d: temperature of 10% decomposition; LOI: limiting oxygen index.

repeating unit of PA-3 and PA-4 which involves stiff rigid polymeric chain framework and hence enhancing its strength and thermal stability. On other hand polyamides such as PA-1, PA-2 and PA-5 with its polymeric framework arrangements containing polar connecting group such as oxy (–O), methylene (–CH₂–) and flexible polar substituted group such as two –CF₃ group which due to which they are slightly lesser strength and thermal stability than PA-3 and PA-4.^[25] In addition, all these polyamides (PA-1 to PA-5) show greater thermal stability without sacrificing other physical properties. Also, all polyamides retained more than 49% weight in nitrogen even at 900 °C.

Here we are comparing the thermal stability of polyamides from tetraphenylfuran with earlier reported polyamide from tetraphenylthiophene^[18] as shown in Figure 6. The thermal stability of bulky tetraphenylfuran with spacer methylene unit based polyamides (PA-1 to PA-5) have greater thermal stability (449–510 °C) with respect to T_{10} of the structurally related polyamides containing spacer methylene and bulky tetraphenylthiophene components (580–600 °C). These results indicate that high thermal stability of the present polyamides (PA-1 to PA-5). On the basis of T_{10} , these tetraphenyl-furan unit had as higher thermal stability as in order tetraphenylfuran > tetraphenylthiophene. Outcome of synthesized bulky tetraphenylfuran with spacer methylene containing polyimides are very superior in thermal stability with other early reported polyamides. This effect also indicates that the difference in position of substitutions in the aromatic diamines also introduces significant dissimilarities not only in their decomposition temperatures but also in the final char yield.



Figure 6. Comparative $T_{10\%}$ weight loss of polyamides containing tetraphenylfuran (PA 01 to PA-05) with tetraphenylthiophene unit.

Flame-retardant property of polyamides (PA-1 to PA-5)

According to Van Krevelen and Hoftyzer's equation,^[26] the char yield can be useful as a conclusive factor for valuing the limited oxygen index (LOI) of polymers using equation,

$$LOI = 17.5 + 0.4CR$$
,

Where, CR is the percentage of polymer remaining at 900 °C.

In general, the material constituents showing LOI values higher than 26 shows self-extinguishing behavior and reflecting as flame retardant. On the basis of the LOI values the resulting polymers can be classified as self-extinguishing materials.

All polyamides have LOI more than 37.1 and such polymers can act as flame-retardant materials are summarized in Table 4. The LOI of all polyamides (PA-1 to PA-5) estimated in the range of 40.7 to 37.1.

DSC results

The DSC plots for PA-1 to PA-5 are presented in Figure 7. The glass transition temperature (T_g) and are summarized in Table 4. The present polyamides had relatively moderate T_g in the range of 169–213 °C. Polyamides PA-1 and PA-2 covered polar and flexible connecting group structures respectively. Among all polyamide PA-3 shows highest T_g values than other polyamides. This is due to the stiff rigid sulfonyl group ($-SO_2$). On other PA-2 shows excellent Tg curve pattern. This credited to the more spacer methylene groups in polymer frameworks and showing a smooth curve of Tg.^[27] The whole result consideration of bulky tetraphenyl-furan unit with other bulky tetraphenyl unit, the T_g values of the structurally related polyamides decreased as order: tetraphenylthiophene-bearing polyamides (226–273 °C) >the tetraphenylfuran unit centered polyamides (178–200 °C).



Figure 7. DSC of Polyamides (PA-1 to PA-5).



Figure 8. WAXD of Polyamides (PA-1 to PA-5).

WAXD analysis

The WAXD patterns of all polyamides are verified in Figure 8. All the polyamides (PA-1 to PA-5) derived from Polar flexible (–O– and –CH₂–), Sandwiched more polar (C=O), less polar (C=S) and sandwiched polar substituted two –CF₃ group showed broad diffraction peaks at $\sim 20^{\circ}$ (2 θ) was observed which confirms the formation of amorphous nature polymers. This amorphous nature of all these polyamides support to solubility and inherent viscosity of polymers.^[27,28] The polymers show no hint for crystallinity.

Conclusions

The new series of aromatic-aliphatic polyamides covering spacer methylene and bulky pendant tetraphenylfuran groups were introduced into the molecular framework of Polyamides via the newly designed diamine monomer and synthesized by the polycondensation of a novel diacid precursor 2, 5-bis (4-carboxymethylene phenyl) 3, 4-diphenyl furan (BCMPDF) and various aromatic diamines by using Yamazaki's phosphorylation method. The structure-property relationships of these polyamides due to the enterprise of bulky substituents and aliphatic spacer methylene were also studied. From the experimental results, it can be concluded that the synergic insertion effects of bulky phenyl substituents such as tetraphenylfuran and aliphatic unit such as methylene, into the polymer backbone was greatly operative for the synthesis of soluble polyamides inventing great $T_{10\%}$ values and adequate T_g analogous to the aromatic-aliphatic polyamides. All the synthesized polyamides have inherent viscosities in range of 0.50 and 0.58 dL/g. Almost all of polyamides were soluble in polar aprotic solvents at room temperature except DMF (on heating). The GPC data of polyamide (PA-1) showed that the number-average (Mn) and Weight-average (Mw) values were 39,900 g.mol⁻¹ and 134,800 g.mol⁻¹ respectively, with respect to polystyrene standards and the ratio Mw/Mn dispersity was 3.38. Synthesized aromatic polyamides (PA-1 to PA-5) are characterized by WAXD; it appraises the insertion effect of precursor on polymer backbone and showing the amorphous nature. They were characterized as high T_g in the range of 178-200 °C and great thermal stability (449-510 °C). It was agreed that the insertion of spacer methylene linkage and bulky pendant tetraphenyl unit is effective for developing novel thermally stable and highly organosoluble polyamides. By consideration of their properties are desired for advanced applications, such as the constituents for superior high thermal resistance.

Disclosure statement

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Image based anthracnose and red-rust leaf disease detection using deep learning

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Article InfoABSTRACTArticle history:
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Accepted Sep 19, 2022Deep residual learning frameworks have achieved great success in image
classification. This article presents the use of transfer learning which is
applied on mango leaf image dataset for its disease's detection. New
methodology and training have been used to facilitate the easy and rapid
implementation of the mango leaf disease detection system in practice.

Keywords:

Convolutional networks Deep neural network Image classification Mango leaf diseases Transfer learning Deep residual learning frameworks have achieved great success in image classification. This article presents the use of transfer learning which is applied on mango leaf image dataset for its disease's detection. New methodology and training have been used to facilitate the easy and rapid implementation of the mango leaf disease detection system in practice. Proposed system can be used to identify the mango leaf for whether it is healthy or infected with the diseases like anthracnose or red rust. This paper describes all the steps which are considered during the experimentation and design. These steps include leaf image data collection, its preparation, data assessment by agricultural experts, and selection and tranning of deep neural network architectures. A deep residual framework, residual neural network (ResNET), was used to perform deep convolutional neural network training. ResNETs are easy to optimize and can achieve better accuracies. The experimental results obtained from "ResNET architectures, such as ResNet18, ResNet34, ResNet50, and ResNet101" show the accuracies from 94% to 98%. ResNET18 architecture selected from above for system design as it gives 98% accuracy for mango leaf disease's detection. System will help farmers to identify leaf diseases in quick and efficient manner and facilitate decision-making in this front.

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1. INTRODUCTION

India is among the largest producers of crops world wide. Many people in India specially from the Maharashtra region are farmers, and they are dependent on crop production. However, the country is still lagging far behind the global market for field production export due to its poor yield and quality grading of production specifically different fruits due to bacterial growth in crops. This growth of bacteria in plants presents in different parts of the plant, that is, fruit, stem, and leaves, which are major factors for the rapid decline in nurturing growth in the production year for the farms [1]-[3]. There are various diseases that greatly affect crops [4]-[8]. On the other hand, these types of patches begin with smaller shape while soon they occupied the overall area within the leaf or the fruit and then finally it resulted within the rotten fruit or the rotten leaves. Apart from that it is much more necessary for controlling and detecting these types of disease within a specific duration and it is in their own initial state. Therefore, it is much more necessary in preventing the disease within the early stages of affecting the most basic operation regarding the overall plant body and it includes the process of photosynthesis, astranspiratuin, germination, fertilisation and pollination. On the other hand, these diseases generally occur because of several pathogens like viruses, bacteria and fungi.

Therefore, for this the farmers require the continuous monitoring of the overall plant body, and it is a process of time consuming [9]. Hence, there is a requirement of the method for detecting the diseases in the plant at the very early stages therefore, the proposed research work is presented which will be helpful for mango fruit farmers and research centres.

MANGO LEAF DISEASES 2.

Disease categories: there are two common diseases in plant leaves: anthracnose and red rust, as shown in Figure 1. As far as India and Indian subcontinent is considered, the study shows that, mango trees are mostly suspected for getting affected with anthracnose and red rust diseases on mango leaves. These diseases start growing from one part of tree to whole or emerging from leaves or fruits. Each leaf disease has unique symptoms and features, which can help to categorize and differentiate infected plants using deep learning algorithms, and deep neural networks have led to a number of progresses in the classification of images.

Anthracnose the disease that causes the serious losses for the young fruits and flowers. It affects fruits during storage [10]. It produces blossom blight, leaf spot, twig blight, wither tip, and fruit rot symptoms. Foliage and tender shoots are affected, causing the death of branches in earlier stages. Black spots develop on the panicles and fruits. Severe infection destroys the entire inflorescence, resulting in no fruit setting. Young leaves those are infected develop shrivel, black spot and drop off. Leaves and fruits infected at mature stage carry the fungus into storage and cause considerable loss during storage, transit and marketing.



Figure 1. Leaf disease

Red rust it is due to the alga that is being observed within the growing areas. Due to the attack of algal the overall reduction within the photosynthetic activity and also the defoliation of several leaves that occurred there is by lowering the overall validity within the host plant. On the other hand, the disease can be easily identified through the overall rusty red spots which is basically on the leaves and sometimes it is on the petioles and also on the bark of the young twigs which are mostly epiphytic. Therefore, the slightly and circular elevated spots sometimes coalesce in forming the irregular and larger spots.

3. DATESET

To determine the presence and incidence of leaf disease, a total of 1876 samples from 20 fields were systematically collected from production areas across Konkan (1876 samples; 20 fields). Using expert diagnostics, we identified infected plants from these fields. Infected fields were geographically searched in two provinces of the Konkan area, Ratnagiri and Sindhudurg, in West Maharashtra, where production of mango is on a large scale. Table 1 shows the field wise and location wise total mango leaf image data instances which have been collected for the study.

	Table 1. The leaf dataset collected from field	
Field	Localization (city)	Number of plants
Field 1	Regional fruit research station vengurle, District-Sindhudurg	400
Field 2	Research sub centre rameshwar (girye), Taluka-Devgad, District-Sindhudurg	885
Field 3 to Field 20	Orchids in Sindhudurg, Ratnagiri	460

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When we use the "deep neural networks", separate three of the databases are required for developing the overall model. Data has been splitted in to three sets: trainig, testing and validation and shown in the Table 2. The first set is the training set, and it is the collection of the several images that is to be fully used through the overall network for automatically learning the hidden parameters like biases and weights. Therefore, the actual set of validation which is the second set is also used for adjusting the overall hyperparameters manually and these are much essential settings that are not to be automatically learned during the time of training [11]-[13]. The photos collected by the camera of both healthy and non-healthy leaves were split into three categories: healthy, anthracnose, and rust under the supervision of experts from agriculture representing each class rather than splitting it into binary.

Data augmentation: the process of data augmentation is the strategy which enables the overall practitioners for significantly increase the overall diversity regarding the data that is available for the training models by not collecting the overall data. The techniques of data augmentation like padding, horizontal flipping and cropping are the most commonly used methods for training the larger neural networks. To increase size of mango leaf dataset, researchers have used certain data augmentation factors and these are shown in Table 3 with there factor values.

To build useful deep learning models, the validation error must continue to decrease with the training error. Data augmentation is a powerful method to achieve this. The augmented data presents a comprehensive set of all possible data points, and reduces the gap between the training andvalidation sets, as well as any future testing sets [14]-[16]. Table 4 shows the images in the training dataset, validation dataset, and testing dataset after data augmentation.

Table 2. The leaf dataset devided into training set, validation set, testing dataset

	6	/		0
Class	Number of images captured by camera	Training	Testing	Validation
Healthy images	566	396	85	85
Anthracnose	747	492	117	138
Red rust	608	426	91	91

Table 3. Augmentation factor used on training dataset



	Ľ.	l'able 4.	Training	dataset a	after	augmentation
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		0		
Class	Number of original + augmented images	Training	Testing	Validation
Healthy imagee	1939	1769	85	85
Anthracnose	2489	2213	117	138
Red rust	2390	2208	91	91

4. TRANSFER LEARNING

The process of transfer learning actually allows us for using the convolutional neural networks (CNNs) that is when the adequate amount of the training data is small within the overall context of identification regarding the crop disease. On the other hand, this technique generally helps in achieving the greater generalizability and the overall network has been learned previously in dealing with several larger numbers of examples. Apart from that, it is also a way of saving the capacity and the computing time. Transfer learning can be performed in two ways that is fine tuning and feature extraction [17]-[19]. In the process of feature extraction, the overall weights regarding the models that are pre-trained remain intact while it uses the embeddings and also produces for training the new classifier within the target datasets. On the other hand, the process of fine-tuning uses the overall weights regarding the model that is pre-trained for initialising the overall model and after that train the parts or these weights are within the target datasets [20]. A training strategy to be selected depends on technical and thematic considerations such as the number of computing capacity, images, architecture availability and also the compatible weights that are pre-trained with the used data. We used transfer learning to improve generalizability and computation time. After fixing all of the hyperparameters, the model is retrained by integrating the used images during the validation of the global training set and alsop during training, and we used four different CNN architectures (ResNet18, ResNet34, ResNet50, and ResNet101). We used a dataset augmented by a background class.

The ResNet18 and ResNet34 are two layers deep, while ResNet50 and ResNet101 are 3 layers deep [21]. The18-layernetworks are the subspace of34-layer network but it still performs better. If the network is deeper, residual neural network (ResNet) performs significantly.

5. TRAINING AND EVALUATION PHASE

Within the overall paper we simply present a simpler and more flexible architecture that uses ResNets' learning, utilizing the split-transform-merge approach for layers. The important challenge is for obtaining the trained model which is capable of analysing the unseen and new in machine learning. The overfitting doesn't allow the learning of the main characteristics regarding the overall classes, and it also captures the overall noise regarding the overall training set; when we try to run the model on this input data, the accuracy is high, and "deep learning neural networks are trained using the stochastic gradient descent optimization algorithm. The learning rate, which is a hyperparameter, controls the extent to which the model is changed in response to the estimated error each time the model weights are updated". The learning rates for all four architectures, ResNet18, ResNet34, ResNet50, and ResNet101 are discussed here. The learning rate of models ResNet18, ResNet34, ResNet50, ResNet101 is shown graphically in the Figure 2(a), Figure 2(b), Figure 2(c), and Figure 2(d).



Figure 2. Learning rate for (a) ResNet18, (b) ResNet34, (c) ResNet50, and (d) ResNet101

Therefore, when CNN was trained, the model was trained with hyper-parameters. The best values of the hyperparameters were found through tuning techniques to improve the model [22]-[25]. This tuning was performed using the learning rate finder (LRF), which compared these settings until it found the optimal learning rate for the model shown in Figure 2(a), Figure 2(b), Figure 2(c), and Figure 2(d). Figure 3 shows the model training information with train loss, error rate and model evaluation with accuracies found while checking the performance of model designed with ResNet18, ResNet34, ResNet50 and ResNet101 architectures. Figure 3(c) shows accuracy for ResNet18, ResNet34, ResNet50 and ResNet101 architecture.

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The confusion matrix is used to evaluate the performance of the model [26]. Researchers have used to the same for the model evaluation. The confusion matrix for validation set is given by all four architectures ResNet18, ResNet34, ResNet50, and ResNet101and shown in Figure 4.



Figure 3. Model training and evaluation of ResNet18, ResNet34, ResNet50, ResNet101 architectures with (a) train loss, (b) error rate loss, and (c) accuracy



Figure 4. Confusion matrix for ResNet18, ResNet34, ResNet50, ResNet101

6. **RESULT AND DISCUSSION**

From Figure 3, we can see that our network model was able to start model learning at near 1e-1, from 1e-6 to around 1e-1, the learning rate was too low, and the network was unable to learn. The minimum loss was observed at 1e-1, after which loss started to increase sharply up to1e-0 then decreased from which it finally exploded, meaning the learning rate was too large for the network to learn anymore. The CNN model, confusion matrix acuracy for the testing set is given in Figure 5.

Precision, recall, F1-measure and supportare shown in Table 5. Precision is the measure of accurately predicted true-positive values relative to the total number of positive predicted observations. Recall is a measure of the number of positive class predictions made with all positive predictions. The F-measure is a measure that balances both precision and recall.

Table 5. Accuracy for testing dataset							
Dieases	Precision	Recall	F1-score	Support			
Anthracnose	0.83	0.92	0.87	117			
Healthy	0.93	0.73	0.82	85			
Redrust	0.94	0.99	0.96	91			
Accuracy			0.89	293			
Macro avg	0.90	0.88	0.88	293			
Weighted avg	0.89	0.89	0.88	293			



Figure 5. Confusion matrix for testing dataset

7. CONCLUSION

Presented performance of model shown the promising results for the classification of mango fruit and leaf diseases such as anthracnose and redrust detection that is by training CNNs by using the imbalanced dataset. We applied focal loss, different imaging techniques and also the class weights to obtain the best performance. The ResNet18 model shows the best accuracy for the testing dataset. Therefore, while integrating this proposed model into a mobile application, researcher considered both the results for the validation set as well as the testing dataset. This mobile application will be useful for farmers and agricultural extension workers. Farmers can use smartphones for real-time monitoring of mango fruits, leaves andearlywarnings of several infections for applying the most important prevention methods.

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ANALISIS OF LAND-USE PATTERN IN SINDHUDURG DISTRICT : A GEOGRAPHICAL ANALYSIS

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Abstract

Land is the basic and limited natural resource. Land plays the key role in the determination of man's economic activities as well as social and cultural progress. All agricultural, animal and forestry production depend on the quality and productivity of the land. The terrestrial ecosystem which comprise of food, energy needs of livelihood. Land use is a special context is essential to understand a regional zonation of the area of optimum land use degraded areas etc. Land use of region is a combiner easel of the natural setup and human dynamism within social economic setup and technological development. In this research paper an attempt has been made to analyse the general land use pattern in Sindhudurg district. Study of land is pattern important for the development of agriculture sector, industrial sector as well as keep balance in environmental condition. This study plays vital role in the point of view the planning and development of the region.

Keywords: Land use pattern, Human Dynamism, National Planning, Underdeveloped.

Introduction

Land use is the surface utilization format of all developed and vacant land on a specific point, at a given time and region. Day to day the importance of the land use land cover study is increasing with continuous increase in population as well as urbanization also. After the industrial revolution, the world population is increasing at a progressively faster rate affecting the nature of earth surface. Human use of land resources gives rise to land use which varies with the many purposes it serves (*Briassoulis, 2000*). Land cover is the biophysical state or the natural state of the earth's surface particularly immediate surface (*Terner et al., 1995*). In this contest most, previous natural resources have used better life resulted, most changes in land use land cover pattern on the earth surface. There is observed, agricultural area being converted in to urban uses, forested land convert into agricultural practice in all over the world. In this situation most of the positive and negative changes occurred on the earth surface. That does why there is necessary to planning and regulation for minimize negative impact on natural environment. Land resource is very important for human being because direct and indirect many types of processes as like economical processes depend upon it. Land resources are natural wealth and property of a country. So, there are proper utilization of natural resources such as land resources is most important because of near about 70% population depend upon directly and indirectly on land for livelihood.

In Sindhudurg district utilisation of land increasing with increase in population, increasing in agriculture, increasing in industrialisation and mining also. It shows varies is from tahsil to tehsil. The utilisation of land is need to have a general framework of strategic and effective management and analysis of their characteristics and also used for developmental planning in the study area.

Study Area

Sindhudurg district is the southern part of coastal area that is known as the Konkan. Sindhudurg district situated between $15^0 17$ ' north latitude to $16^0 40$ ' North latitude and $73^0 19$ ' longitude to $74^0 13$ ' East longitude. It is bordered by Ratnagiri district on the north, Arabian sea on the west, Goa state on the south, Belgaum district of Karnataka state and Kolhapur district on the east also. The total area of the district is 5087 sq. km. Physiographically Sindhudurg district has divided into three section that is Khalati, Valati and Sahyadri hills region respectively. The coastal strip is called Khalati and its adjacent area called Valati. Sindhudurg district has 8,48,868 (Male-4,16,695, Female-4,32,173) population as per 2011 census. Mean monthly minimum temperature near about 16^0 C. and maximum temperature near about 33^0 C. Annual rainfall range is 2000 to 3000 mm.

Objectives

- 1. To study the general land use pattern in the study area
- 2. To study the impact of physical setting and social economic factors on the land use pattern in the study region
- 3. To study the utilisation of land use in the study area.

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Data Base

The present study based on secondary data which is obtained from social economic abstract of Sindhudurg district 2012 and gazetteer of the Sindhudurg district. For the calculation used the simple statistical techniques and calculated the proportion of every and each type are land use category.

Explanation

General land use pattern in Sindhudurg district is shown in chart with tehsil wise utilisation of land.

I) Area under Forest

The total geographical area of the Sindhudurg district is 503950 sq. ha. Out of this area 38643 sq. ha. is under the forest during the year 2012. It is the lowest proportion in the study region. The area under the forest presented with a varies from tehsil to tehsil the highest area under forest is found in Kudal tehsil (25.4%), where the lowest forest area is found in Malvan tahsil (0.7%) due to the physical condition and existence of the Arabian sea. Below 10% area of forest is found in Devgad (7.7%), Vaibhavwadi (7.7%) and Dodamarg (7.7%) tahsil general we have to experience the area under forest is a very less in Sindhudurg district.

(Area under hectares)										
Sr.no	Tahsil	Total	Area under	Area not available for	Uncultivable	Follow	Net sown			
		Geographical area	Forest	cultivation	Land	Land	Area			
1	Devgarh	78127	3004	35077	211	20810	16193			
2	Vaibhavwadi	41612	2744	8838	730	14635	10847			
3	Kankavli	77339	8997	12837	10203	541	28351			
4	Malvan	61829	298	22347	8896	5388	21329			
5	Vengurla + Sawantwadi	113573	11358	25236	933	6540	40457			
6	Kudal	81897	9843	20562	13786	4611	31145			
7	Dodamarg	49573	2399	18371	408	5465	14315			
	Total	503950	38643	143268	35167	57990	162637			

Tahsil-wise General land use pattern in Sindhudurg District (2012)

Source – Socio-Economic Abstract of Sindhudurg District (2012)

II) Area Not Available for Cultivation

Total 143268 sq. ha. area is under not available for cultivation in Sindhudurg district. The highest area under this category is presented in Devgadh district is 35077(24.4%) the lowest area of not available for cultivation is found in Vaibhavwadi tehsil (6.1%) and Kankavli (8.9%). Above 10% area under the not available for cultivation are found in Malvan (15.5%) tahsil Sawantwadi (17.6%), Kudal (14.3%) and Dodamarg (12.8%).

Tahsil-wise General land use pattern in Sindhudurg District (2012) (Area in %)

Sr.	Tahsil	Total Geographical	Area under Forest in %	Area not available	Uncultivable	Follow Land in %	Net sown
110.		area in 70	T OTEST III 70		Land III 70	Eana III 70	7 Med III 70
1	Devgarh	15.5	7.7	24.4	0.5	35.8	9.9
2	Vaibhavwadi	8.2	7.1	6.1	2.0	25.2	6.6
3	Kankavli	15.3	23.2	8.9	29.0	0.9	17.4
4	Malvan	12.2	0.7	15.5	25.2	9.2	13.1
5	Vengurla + Sawantwadi	22.5	29.3	17.6	2.6	11.2	24.8
6	Kudal	16.5	25.4	14.3	39.2	7.9	19.1
7	Dodamarg	9.8	6.2	12.8	1.1	9.4	8.8

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Source – *Compiled by Authors*

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II) Other Uncultivable Land (Excluding Fallow Land)

In Sidhudurg district, reveals that, 35167 sq. ha. (6.9%) area under the uncultivated land. The highest area under the category is found in Kudal tahsil (39.2%) whereas the lowest area found in Devgad tahsil (0.5%). Below 5% area of this category is found in Dodamarg (1.1%), Vaibhavwadi (2%), Sawantwadi (2.6%).



Source – Socio-Economic Abstract of Sindhudurg District (2012)

IV) Fallow Land

There is 57990 sq. ha. (11.5%) land is under fallow land. The proportion of fallow land is varies from tehsil to tehsil. The area under this category, below 10% area is found in Kudal (7.9%), Malvan (9.2%), Dodamarg (9.4%). The highest area under this category is found in Devgad tahsil (35.8%) whereas the lowest area under this category are found in Kankavli (0.9%). Above 10% area under the fallowing land is noticed in Vaibhavwadi (25.2%) Sawantwadi (11.2%).

V) Net Sown Area

There is noticed that, 62637 sq. ha. (33.2%) area is under the net sown area. The highest area under the net sown area found in Vengurla and Sawantwadi (24.8%). The lowest area under this category noticed in Vaibhavwadi tahsil (6.6%). It is observed that, below 10% area under this category is found in Dodamarg (8.8%), Devgad tahsil (9.9%). Above 10% area under net sown area presented in Malwani (13.1%), Kudal (19.1%), Kankavli (17.4%).

Conclusion

It is observed that, general land use pattern is varying from tehsil to tehsil due to the physiographic structure, climatic condition and economic activities. There is noticed, the highest proportion of the area under the net sown area 33.1% whereas lowest area found in under the uncultivated land 6.9%. The highest area under the forest is presented in Kudal tehsil (25.4%). There is lowest area under the forest found in Malvan tehsil (0.7%). It is also need and important for a better management of natural resources and development in study region. There are most potentiality for the precious utilisation of land and natural resources.

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Analysis of tehsil wise agriculture land distribution in Kolhapur District

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Abstract---Agriculture is the main primary activity of human being. In Kolhapur district is known as agricultural district, presented most of the agricultural production by cash crop like sugar cane. With cash crop there is most of the food crops also cultivated like jawar, rice, ground nut, soya bean etc. Agricultural land highlighted with variable tehsil to tehsil due to the physiographic condition and water availability. Most of the area under agriculture having in Chandgad tehsil, its need to proper cropping management. At least area under agriculture presented in Gaganbawada tehsil due to the unfavourable physical condition and heavy rainfall.

Keywords---agriculture land, distribution, agricultural production, analysis.

Introduction

Agriculture is one of the oldest economy activities of man demand for food for the increase in the 21st century which can only be made through increase in production area or in the amount of production per unit land area and crop productivity how your limited available and expansion of other land use type. In India about 70% of the total population is directly or indirectly engaged in agriculture sector. As per population is increasing the pressure of agriculture is also increasing eventually human is taking step towards increasing the crop production. The attempt is made to increase agricultural production as well as the improving the traditional method and using HIV, chemical fertilizer and advance method of irrigation. The land use is also changing from single crop to multi crops in Kolhapur district. It is not only having close relation with physio-agro- climatic conditions but also social-economic condition. Attempt is made to understand the condition of agriculture land use of Kolhapur district.

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Agriculture is considered as the most important of the all economic activities of man agriculture is related to domesticated plants and animal as activity to satisfy man's need. Nowadays agriculture has become the world's most important industry agriculture means response to it have become cardinal points of research.

Study Area

The Kolhapur district is a part of Deccan plateau, western Maharashtra and extremely southern part of Maharashtra state is Kolhapur district lies between 15 43' north to 17 17' north latitude and 72 40' east to 74 42' east longitude. The Kolhapur district comprises 7620 sq. km area which is 2.5 % of the state. The general height of the district is 1000 mtrs and administratively divided into 12 tahsils supports 38,76,001 population (2011). In general, the physiographic arrangement of the district has Sahyadri hills in a north-south direction, plateau area situated to the east of the Sahyadri hills and eastern plain area and Belgum district of Karnataka state in the south. The climate of Kolhapur is generally temperate. Minimum temperature of the district is 14° c and maximum is 36.9° c. The average annual rainfall is 2063.67 mm. The decadal growth rate (1991-2001) of population is 17.85 per cent. From the Kolhapur district around 70% of total population lives in rural area. The middle rivers and tributariesi. e. Warna, Panchganga. Kumbhi. Kasari. Bhogavati, Tulasi. Dhamani. Jambhali. Hiranyakeshi, Dudhganga, Vedhganga and Ghatprabha all these river flows from the west to east towards the Bay of Bengal. In the study area also found variety of utilization of land due to the physical setting of the district and socio-economic aspects also.

Aims and Objectives

The objective of this study is to analyse tehsil wise agricultural land use pattern in study area.

Data Base

For the study both primary and secondary data are used. Kolhapur gazetteer, toposheet, satellite images, GPS readings are used for the base mapping of the study region. The agricultural land-use study of Kolhapur district has conducted with the help of secondary data which is satellite imageries of 2018. Along with this, some primary data are used for analysis.

Methodology

A detailed study of agricultural land-use is conducted to understand the transformations in surface area in the study region. The collected tehsil wise agricultural data is tabulated, arranged in proper format and statistical methods, map are applied to obtain the specific results.

Discussion

Table :	Kolhapur	District:	Tehsil	wise	Agricultural	Land	Distribution-20	18
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Rank	Tehsil	Total Area	Percentage
1	Chandgad	53999.84	11.97
2	Hatkanangle	49917.95	11.06
3	Shahuwadi	48941.59	10.85
4	Karvir	46260.76	10.25
5	Kagal	44249.13	9.81
6	Gadhinglaj	39674.57	8.79
7	Shirol	39208.08	8.69
8	Radhanagri	32931.51	7.3
9	Ajara	31092.36	6.89
10	Panhala	28520.51	6.32
11	Bhudargad	25177.59	5.58
12	Gaganbawada	11077.33	2.45
	Total Area	451051.22	100%

Source- Satellite Image 2018

For agricultural land distribution we have created five categories for understanding the real condition and status of Agricultural land cover in tehsils.

1. Very Low proportional region (11077-19662 sq. hector): In this category included the very lowest proportions tehsils. In this region

included only one tehsil i.e. Gaganbawada tehsil (9552 hect.) due to hilly and forested land the formation of drainage is very low.

- 2. Low proportion region(19662-28246 sq. hector): In this category included the lowest proportions tehsils. In this region included only one tehsil i.e. Bhudargad (20822.60 hect.) tehsil due to hilly and forested land.
- 3. Medium Proportion Region (28246-36831 sq. hector): In this category there is high proportion is included. Ajara, Radhanagri and Shahuwadi tehsil are included in this region. There are medium type of Agricultural land is found. In this region there are agricultural region is between 45 % to 55 %.
- 4. High proportion region (36831-44415 sq. hector): In this category there is high proportion of agricultural land is included. Gadhinglaj, Kagal and Shirol tehsil are included in this region. There are medium type of agricultural land is found. There are region under agricultural land is above 80 percent.

Map: Kolhapur District: Tehsil wise Agricultural Land Distribution-2018



Source- Satellite Image 2018

- 5. Very high proportion region (45415-54000 sq. hector):
 - In this category there is very high proportion of agricultural land is included. Chandgad, Karvir, Hatkanagle and Shahuwadi tehsil are included in this region. There are very high region under agricultural land is found due to fertile soil, flat terrain, heavy rainfall and water availability.

Conclusion

It can be observed that there is agricultural area is maximum found in Shahuwadi, Chandgad, Karvir and Hatkanagle tehsils. Highest proportion of agricultural land presented in these tehsils due to suitable physiographic condition and sufficient rain fall. Gadhinglaj, Kagal and Shirol tehsils highlighted with high proportion of agricultural land due to plain region and water availability for over year. Gaganbawada and Bhudargad tehsils presented with very less area of agricultural land due to the unfavourable physiographic condition (Most of the area covered by hills), heavy rainfall. There is need of proper utilization, management for agricultural land resources. There is a need of super facility market for agricultural production in the high and very high proportional region. For the food security, it will be need protect agricultural land from settlements area and road network development in this area.

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गोषनारा -

शिवण कौशल्य हे रोजगार उपलब्ध करून देणारे एक महत्वाचे साधन आहे. या कौशल्यामध्ये व्यक्ती जेवढ्या प्रमाणात पारंगत असेल त्यानुसार त्याला प्रसिध्दी, प्रतिष्ठा तरोच जास्तीतजास्त उत्पन्न मिळण्यास मदत होते. स्त्रीयांना हे कौशल्य संपादन करण्यास सध्या वेगवेगळ्या खाजगी संस्था, एन.जी.ओ. तरोच सरकारी संस्थांमधून गृहविज्ञानाच्या अभ्यासक्रमातून शिवण कौशल्याचे प्रशिक्षण दिले जाते. अशा प्रशिक्षण घेतलेल्या महिलांमध्ये प्रशिक्षणाने झालेल्या बदलाचा अभ्यास करण्यासाठी अनुसूची पध्दत वापरून महिलांमध्ये होणाऱ्या आर्थिक, सामाजिक तसेच त्यांची निर्णय क्षमता आणि आत्मविश्वास यामध्ये झालेल्या यदलाचा अभ्यास केला असता शिवणकला कौशल्य संपादनाने त्यांच्या उत्पन्नात वाढ झालेली दिसून आली तसेच त्यांच्या आत्मविश्वासात आणि निर्णय क्षमतेत सकारात्मक वदल दिसून आला.

मुख्य शब्द - शिवणकला, कौशल्य, महिला.

प्रस्तावना -

शिवण कौशल्य हे सध्याच्या युगातील किंबहुना अगदी अनादी काळापासून आवश्यक असलेले एक कौशल्य आहे. याचे महत्व वदलत्या काळानुसार, गरजा फॅशननुसार खूपच वाढत आहे. व्यक्तीच्या दैनंदिन आवश्यक गरजांमधील अन्न, वस्त्र, निवारा मधील वस्त्राची गरज पूर्ण करण्याकरिता ज्याप्रमाणे कापड निर्मिती आवश्यक आहे त्याचप्रमाणे त्या कापडापासून व्यक्तीच्या गरजांना अनुसरून योग्य प्रकारचे कपडे बनविणे आवश्यक आहे. पूर्वीच्या काळी वारा बलुतेदार पध्दती होती आणि शिंपी कपडे शिवण्याचे काम करीत असे. वंशपरंपरागत त्यांची मुले आपल्या कुटुंवातील व्यक्तींकडून कपडे शिवण्याचे ज्ञान अवगत करीत आणि परंपरागत व्यवसाय पुढे जात होता. सध्याच्या युगात शिवणशास्त्राकडे सौंदर्य, अर्थ, आरोग्य या दृष्टीने पाहिले जाते. [1] फक्त लज्जारक्षण, शरीर संरक्षण इतपतच वस्त्राचे महत्व न राहता वस्त्रपरीधानातून व्यक्तीचे व्यक्तीमत्व खुलून दिसण्याकरीता सौंदर्य वाढीकरीता ते योग्य प्रकारे तयार केलेले असणे आवश्यक असून त्याकरीता शिवणाऱ्या व्यक्तीने आवश्यक प्रशिक्षण घेऊन योग्य पध्दतीने व्यक्तीच्या आवडीनुसार शिवल्यास, शिवणाऱ्या व्यक्तीची प्रसिध्दी मिळण्याबरोबरच त्याला रोजगार मिळण्यास मदत होते. ६४ कला प्रकारांपैकी एक असलेल्या या कलेच्या शास्त्रीय अभ्यासाद्वारे योग्य आणि पध्दतशीरपणे कपडे शिवता येतात. स्वयंरोजगार निर्माण करण्याकरीता शिवणकला अवगत करणे सहाय्यभूत ठरत आहे. अगदी प्राथमिक शिक्षण घेतलेल्या व्यक्तींनासुध्दा हे प्रशिक्षण घेऊन स्वावलंबी बनण्यास मदत होते.

सध्याच्या युगात शिवण कौशल्य हे रोजगार उपलब्ध करून देणारे एक महत्वाचे साधन आहे. या कौशल्यामध्ये व्यक्ती जेवढ्या प्रमाणात पारंगत असेल त्यानुसार त्याला प्रसिध्दी, प्रतिष्ठा तसेच जास्तीतजास्त उत्पन्न • मिळण्यास मदत होते. स्त्रीयांना हे कौशल्य संपादन करण्यास सध्या वेगवेगळ्या खाजगी संस्था, एन.जी.ओ., सरकारी संस्थांमधून तसेच गृहविज्ञानाच्या अभ्यासक्रमातून शिवण कौशल्याचे प्रशिक्षण दिले जाते. अगदी पेटीकोट पासून वेगवेगळ्या प्रकारचे कमीज, ड्रेस, टॉप, शर्टस्, ब्लाऊजचे फॅशननुसार वेगवेगळे प्रकार तसेच बाळंतविडा ते लहान मुलांचे कपडे इत्यादीचे एकत्रित तसेच प्रत्येकाचे स्वतंत्र प्रशिक्षण मिळण्याकरीता वेगवेगळे प्रशिक्षण वर्ग सुरू असून आपल्या आवडीनुसार प्रशिक्षण घेऊन व्यक्तीला स्वतःचे कपडे शिवूण तसेच इतरांचे कपडे शिवूण देऊन अर्थाजन

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करता येते. शिवणकला कौशल्याद्वारे व्यक्तीला घरवसल्या आपल्या दैनिक कामातून ठराविक वेळ काढला तरीही ही कला जोपासण्यात, त्यात विविधता आणण्यात, कापडानूरूप त्यामध्ये बदल करून नवीन फॅन्नन तयार करण्यास मदत होते.

National skill Development कार्पोरेशन नुसार Human Resource and Skill Requirements in Textiles and Clothing Sector च्या अहवालानुसार वदलते राहणीमान आणि उत्पन्नानुसार सर्व प्रकारच्या कपड्यांच्या मागणीत वाढ झाली असून भविष्य काळात ती आणखी वाढणार आहे. २०१३ मध्ये १५.२३ दशलक्ष इतके लोक या व्यवसायात होते तर २०२२ पर्यंत २१.२५ दशलक्ष इतकी वाढ अपेक्षित आहे.त्यामध्ये शिवणकाम करणाऱ्या, विणणाऱ्या तसेच डिझाईन तयार करणाऱ्या लोकांची गरज आहे. [2]

वदलत्या फॅशननूसार रेडिमेड कपडे वापरण्याकडे जरी कल वाढत असला तरीही मापाने शिवलेले कपडे व्यक्तीमत्व खुलविण्यास जास्त मदत करतात. त्यामुळे या कलेचे महत्व वाढत आहे. तसेच रेडिमेड कपडे तयार करावयाच्या गारमेंट इंडस्ट्रीजमध्ये देखील हे कौशल्य प्रशिक्षण घेतलेल्या व्यक्तींचीच गरज असते. माहितीचे संकलन -

शिवणकला कौशल्य संपादनाने महिलांमध्ये होणाऱ्या वदलाचा अभ्यास करण्याकरीता शिवण कौशल्य आत्मसात केलेल्या १८ ते ४० वयोगटातील ५० महिलांना प्रत्यक्ष मेटून स्वत: तयार केलेल्या अनुसूचीद्वारे माहिती घेतली. [3], [4] ही माहिती घेताना त्यांची कौटुंबिक माहिती, शिक्षण यावरोवरच शिवण कौशल्य संपादनाने त्यांच्यामध्ये झालेले आर्थिक, सामाजिक बदल त्यांची निर्णयक्षमता, आत्मविश्वासात, राहणीमानात झालेल्या वदला संदर्भात माहिती संकलित केली.

माहितीचे विक्षेषण -

अनुसूचीद्वारे संकलित केलेल्या माहितीचे खालील उद्देशानुसार विभागणी करून त्याचे विश्लेपण करण्यात आले.

शिवण कौशल्य संपादनाने कुटुंवाच्या उत्पन्नात होणाऱ्या वदलाचा अभ्यास -

शिवण कौशल्य संपादन केलेल्या १००% महिलांच्या कौटुंबिक उत्पन्नामध्ये त्यांच्या कौशल्य प्रशिक्षणाने वाढ झालेली दिसून आली.



भागवण्यासाठी मिळकतीचा उपयोग

आकृती क्र. १ मध्ये दर्शविल्याप्रमाणे शिवण कौशल्य संपादन केलेल्या ३२% महिलांकडे स्वत:चे नाहन आहे आणि यामधील ९४% महिलांनी स्वत: मिळविण्यास सुरूवात केल्यानंतर वाहन पेतलेले दिसून आले. शिवण कौशल्य ^{संपा}दन केलेल्या महिलांमधील ७०% महिला या नोकरी करणाऱ्या असून त्यामधील ९१% महिला या नोकरीमध्ये ^{समा}धानी आहेत. आकृती क्र. २ मध्ये दर्शविल्याप्रमाणे कुटुंवाच्या गरजा भागविण्याकरीता आपल्या मिळकतीच्या ^{५०%} पेक्षा जास्त उपयोग करणाऱ्या महिला ४६% आहेत तर मिळकतीचा ५०% उपयोग करणाऱ्या १६% आहेत. 'Akshar Wangmay' UGC Care Listed, International Research Journal, ISSN: 2229-4929, July 2021, Special Issue, Volume-IV "Challenges of Higher Education in India to Compete with Global Level"

४०% उपयोग करणाऱ्या ८% आहेत. ३०% उपयोग करणाऱ्या महिला १२% आणि २०% उपयोग करणाऱ्या महिलांचे प्रमाण १८% आहे.

शिवण कौशल्य संपादनाने महिलांच्या निर्णय क्षमतेत तसेच आत्मविश्वासात झालेल्या वदलाचा अभ्यास



आकृती क्र. ३ - महिला म्हणून

घेतला जाणारा सल्ला

आकृती क्र. ४ - मतदानाला जाताना व्यक्तीगत निर्णय

शिवण कौशल्य संपादन केलेल्या १००% महिलांच्या आत्मविश्वासामध्ये वाढ झालेली दिसून आली. आकृती क्र. ३ मध्ये दर्शविल्याप्रमाणे घरामध्ये महिला म्हणून त्यांचे व्यक्तीगत निर्णय ६२% महिला स्वत: घेतात. ३०% पती, ४% आई, ४% सासू घेतात. तसेच ९२% महिलांना त्यांनी मिळविलेले पैसे त्यांच्या आवडी-निंवडी आणि इच्छेनुसार खर्च करण्याचे स्वातंत्र्य आहे. आकृती क्र. ४ नुसार ५६% महिला मतदानाला जाताना कोणाचाच सल्ला घेत नाहीत, ३६% महिला पतीचा सल्ला घेतात, ४% सासऱ्यांचा, २% भावाचा, २% मैत्रिर्णीच्या सल्ल्याने मतदान करतात. शिवण कौशल्य घेतलेल्या या महिलांमधील ८२% महिला वॅकेत वचत करतात. तसेच शिवण कौशल्य घेतलेल्या महिलांमधील ६६% महिलांना नवीन कौशल्य घेण्याची इच्छा आहे. आपल्या क्षेत्रातील अद्यावत माहिती घेण्याकरिता या महिलांमधील १४% महिला इंटरनेटचा वापर करतात, ४६% महिला यु ट्यूव द्वारे माहिती शिवण कौशल्याद्वारे महिलांना विकास प्रक्रियेत मुख्य प्रवाहात आणणे -

या उद्देशाने अभ्यास करता १००% महिलांमध्ये त्यांच्या कौशल्य संपादनाने समाजातील ओळखी वाढल्या आहेत. तसेच त्यांच्या मैत्रिणीमध्ये वाढ झालेली आहे. ६६% महिला वचतगटात आहेत, तर ९८% महिला वाष्ट्रवा जाएस माने आपल्या संबंधीत लोकांच्याकडे आनंदाचे कार्यक्रम असल्यास सहभागी होतात. संकलित माहितीमधील ७०% महिला थावण कौशल्याचा उपयोगाद्वारे नोकरी करीत आहेत. ३०% महिला शिवण कौशल्याद्वारे स्वयंरोजगार करीत आहेत. या महिलांमधील ९४% महिलांना घरातील कामाचा कधी-कधी ताण चेता. ६% महिलांना

कधीच येत नाही. १२% महिलांचे त्यांच्या कामामुळे मुलांच्या पालण-पोपणाकडे दुर्लक्ष होते. ४% महिला त्या करत

- १) १००% महिलांच्या कौटुंविक उत्पन्ना वाढ झाली.
- शिवण कौशल्य संपादनाने महिलांमधून होणारा वदल अभ्यासता खालील सकारात्मक वदल दिसून आले. २) १००% महिलांचा आत्मविश्वास वाढलेला दिसून आला. २) ९२% महिला आपल्या आवडी-निवडी व इच्छेनुसार पैसे खर्च करू शकतात.

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४) ६२% महिला आपले महिला म्हणून व्यक्तीगत निर्णय रचत: पेतात.

शिवण कौशल्य संपादनाने या महिलांनी स्वत:ची ओळख निर्माण केली आहे. अशा प्रकारची कौशल्य आत्मसात केल्यास महिलांचे सबलीकरण होऊन देशाच्या प्रगतीला हातभार लागेल. संदर्भ -

१) वैरागडे उज्वला, अग्रवाल अन्विता जून २००९ "वस्त्रशास्त्राची संकल्पना व फॅशन विद्यार्थनिंग" विद्या बुक्स औरंगाबाद

२) "Executive summary of Textiles and Clothing Sector-2012", https://nsdcindia.org/

- ३) घुरी नीलम जुलै २००८ "संशोधन पध्दती" फडके प्रकाशन कोल्हापूर
- ४) आढल्ये श्रीनिवास २०१५ "संशोधनशास्त्र परिचय" युनिव्हर्सल प्रकाशन पुणे

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"IMPLEMENTATION OF NEP-2020 GUIDELINES TO MAHARASHTRA "

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Abstract

NEP-2020 got importance from all strata of Indian society since this is the first Indian educational policy in the 21st century. The Indian education system is one of the largest and growing education systems in the world. With more than 1.5 lakh schools, more than 8.5 lakh teachers, more than 250 lakh students from 29 different states and 7 Union Territories coming from different social and economic conditions. As per the guidelines of NEP- 2020, MOE have designed application like UDISE + with the help of National Informatics Centre. Which provides accurate and timely data for policy making & decision making to MOE.

Further, NEP-2020 will create a strong, sustainable, reliable and objective assessment system for students from Primary to Higher Education. Which make efficient and skillfully employable students and helps to the increase in National Income.

After 35 years of National Policy on Education 1986, in which modifications undertaken in 1992 the present policy on education came which made tremendous changes in entire education system of India Changes suggested by NEP-2020 through the guidelines so far published shows its nature and importance.

NEP-2020 is aimed to create socio-economic and educational equality among the society (Education for all, Free Education). Further it aims to give world class facility & education to students from Nursery to Higher Education. To fulfil this, top 100/ renounced world's topmost Universities & Institutions permitted to open their campuses in Indian Subcontinent. To increase the literacy rate of all states and communities also the key objective of this policy. For accomplishment of this object Indian Government has adopted holistic approach towards, skill education, vocational education, professional education, health education, value education etc. from primary to higher education. Further this policy gave importance to Drop out students, teacher training, Academic Credit Banks and stress on Interdisciplinary / Multidisciplinary curricula. Though this policy helps to make India as a super power, its implementation has many Legal challenges. Through this research researcher will study the problems and also suggest some remedies to the challenges before implementing NEP- 2020.

Keywords: NEP, MOE, UDISE+, Drop outs, Holistic, Academic Credit Bank.

Introduction

Education is a concept created by human for the development of society. Human society is an element of the whole of nature. We see the change in natures in natural way, Evolution has proved this point. As human society is dynamic, the needs of this society change from time to time. To meet these changes, we have to inculcate the changes in socio, economic, religious, cultural and educational aspects of. Education is considered to be the most important and dynamic tool. Therefore, education has to take a step forward in these changes by thinking about the future of society.

Internet, Research in the Science & Technology, Communication & Computers has also brought many changes in the field of Education. If we see the educational system of developed countries, their nature of the examinations, and psychology of their students which looks very positive and helps to the growth of their country. By considering these educational tools and to bring aforesaid changes into Indian education system National Educational Policy-2020 have been introduced. This is the optimism, these changes in education will make our country advance.

Consistently made efforts and actions to sustain the educational thoughts flow accepted the deployment of educational streams is considered. The attitude of a person or group in the creation to deployment, to be ready to overcome the persistence of problems and if successful, could lead to the deployment of a stream in the educational thought becomes successful.

The aforesaid things will be possible, only when the participant among them will think they have all the information about streaming, they have Plan and will play a positive role in their hearts they thought about the usefulness of the stream. It is in this situation that the person acts according to the relevant thought flow. At the same time, the attitude and courage to accept outside thoughts are must among them. For the successful deployment, we need encouragement from others, Pre-Planning about action and flexibility for the improvement.

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According to H G Barnette, Innovation is any thought, behaviour or thing that is new and is qualitatively different from existing form.

For the applications of new educational trends Trainings, Orientation/Refresher courses, seminars, Conferences, workshops, such techniques can be used to utilize. Experts' guidance, use of social media and modern technology and literature will assist for the application.

In this way educational trends -streams origin, diffusion and applications enrich /grow thoughts, inculcate research culture, originate new ideas and increase in cooperation will develop.

Educational thought streams originate from activities. Their dissemination, acceptance and application give rise to new initiatives and from these new initiatives, new streams of thought are born.

Students up to class III of primary school needed basic / fundamental knowledge of script, language, mathematical arithmetic along with these they required to include environmental & health education in their curricula.

Process of implementation of NEP-2020

The new National Education Policy 2020 is inclusive and drives national development. In the last one-year U-Dias, the guidelines of Pragyaata, Nipun Bharat, Parakh, Sarthak have been disseminated by the Ministry of Education. These guidelines give an idea that how exactly the implementation of NEP-2020 took place. The new national education policy is conducive to the development of emerging India.

However, Maharashtra is one of the important states among six states selected for the effective implementation of the NEP-2020.

Difficulties in implementing NEP-2020 in Maharashtra

1. Teachers those working in rural and tribal areas and who do not Qualified the TET exam, but it is necessary to take important decisions about their salary.

As there is a vacancy of D. Ed / B. Ed teaching post Some teachers, are working since 7-8 years without pay or low pay so as to avoid the students educational loss. If the TET test has been mandated to aforesaid teachers then their service conditions become void. Researcher thinks It is also wrong to assume that only teachers who have passed the Teacher Eligibility Test can teach well. This should be considered in the new national education policy.

2. Every year's training of teacher's effects on their daily work, there is a possibility of adverse effect on health and family life of a teacher.

3. Indian constitution has given to every person the right to live and finances. Accordingly, private educational institutions have created many educational complexes in the course of time. For this, they have invested their own money, space, building and human resources. Although, some schools and colleges are not functioning properly and are not eligible to impart minimum standards of education though it becomes difficult for those private institutions to hand over and transfer their private property to the government.

4. To impart holistic education to all Social and economic equality needs to be established. While doing so, it is important to consider the human resource dependence on the relevant component. For example, the question of unemployment of private tutors will arise, so the central government needs to think about this.

5. NEP-2020 suggests & Plans examination reform system in 3rd, 5th,8th,12th standard Board examinations, but it is also necessary to know the difficulties to implement it.

6. It is necessary to give a definite outline of the dates and duration of the actual implementation of the new National Education Policy to the students, parents, teachers of the schools and colleges and the principals of the private institutions, otherwise a state of confusion and turmoil has arisen in their minds.

7. The terminology, abbreviations of guidelines created by NEP-2020 has made very complexity and difficulty to understand. Although Education Ministry should publish a dictionary of the abbreviations & terminology. So that the spread of information took place through teachers, students and parents which will be reduce difficulties in reading & understandings of NEP-2020 and which will save the time.

8. For the effective implementation of "Cluster School" scheme MOE has given excessive powers to DSE, SCERT like institutions as well as the DEO, BEO & BRC like officers. MOE must have to check, monitor & examine the transparency, efficiency and working conditions of the aforesaid institutions & officers. For the betterment of "Cluster School Scheme" aforesaid institutions & officers should undergo the online confidential feedback system and teachers, parents, industry, stakeholders, headmasters and administrators will be the respondents.

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9. Some government and private schools had built on the land donated by Philanthropes in the society for 99 years agreement. At present condition their contracts have expired, the question of space / land acquisition for those schools and colleges has arisen. The government also pay attention to this burning issue.

Although the researcher thinks that, these aforesaid issues and many other such things are the research-gap, the present research will throw lights on the above matters. There will also be some suggestions from researcher side.

Need of Feedback and Research for Policy Making

After the Independence of India, Central Government has established the Ministry of Education. UGC, NCERT, AICTE, NBA were established during the course of time for the development of higher education, technical education, school education. Further, NAAC like other autonomous bodies has maintained the quality of Higher Education. Every state has its own Primary & Secondary Education department which strives to develop the plans for respective department.

For the first time in India's history, a loan of Rs 4,000 crore has been taken from the World Bank as an investment option for the development of education.

NEP-2020 is India's first national education policy of the 21st century. This policy has been written by considering and studying all aspects of globalization in order to get the country ranked in the world educational rankings.

While the implementing of NEP-2020, The Ministry of Education have considered the opinions of organizations, Institutional leaders, teachers, students, parents, employers and other stakeholders. However, after taking feedbacks, opinions and considerations of above stakeholders in the education field is necessary to find errors or unintentionally made deficiency which will definitely enhance the efficiency of NEP-2020. Further if any ignored issues will be found in NEP which will be demolished by research and development cell of Central and State Governments. The interviews of Eminent educationalist and dignitaries in the field of education, institutional heads, teachers, parents and other stakeholders. Which will certainly help for policy making.

Social Relevance of NEP-2020

School is a replica of society. Good citizens are needed to build a better society, which accomplishes the school. That is why the future of the country is said to take place in school rooms. If we glance on socioeconomically developed countries, their education system is linked to the development of the country. Schools work to create a better generation. But the central & state government are responsible for providing the money, right kind of guidance and other resources to the schools. Education has the power to change and shape the future of the country.

Through NEP-2020, The Central Government has used the medium of Education as a weapon to eradicate social and economic inequality in the country. With the full development of the child, through NEP-2020 it is planned that students from rural and remote areas will get world class high quality free education.

NEP-2020 will not only be mandated by the Central Government to the states, but also it will require a referendum and public involvement for its effective implementation. For the successful implementation of NEP-2020 positive consciousness of society is also needed.

Concluding Remarks

NEP-2020 is a burning issue in contemporary India which constituents and has established ties with various stakeholders. Therefore, it is seen that there is excess of public interest in the present subject.

1. The National Education Policy-2020 is holistic, encompassing nation building and conducive to all. Which will lay the foundation for the building of modern India.

2. Under the "Cluster School Scheme" the process of merger of Kindergartens, Anganwadis/ Balvatikas, Nurseris, Government and Private Primary-Secondary Schools is very complex and intricate.

3. For effective implementation of NEP-2020, it is necessary to fill the entire vacancies of teachers and non-teaching staff.

4. The compulsion of TET as eligibility of teachers rendering services in tribal and remote area looks injustice, because they haven't paid salary since 8-10 years.

5. For the effective implementation of the NEP-2020, MOE will have to address the problems of the State Government and the private sector schools through circulars through face-to-face communication.

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6. To run "Academic Credit Bank" scheme for Higher Education will going to be complicated because the there are many differences in evaluations techniques and patterns of regional universities and local autonomous colleges. Also imposing charges for keeping virtual credits records of students from institutions burden.

7. NEP -2020 revises the school education structure as (5+3+3+4) and higher education strata 6 to 10. Due to which issue of increase in the additional Work Load to teacher founds. Already there are many vacant posts of teachers due to retirement and death due to covid-19. So, MOE has to take strict measures to fulfil the vacancies.

8. NEP-2020 will create livelihood problems for taking private tuition tutors. The government will have to try to accommodate them in the established education system and solve the problem of their livelihood.

9. In pursuing an interdisciplinary and multidisciplinary approach in higher education, while the merger of single faculty/weak colleges the Central Government will have to face judicial fight with them and also adopt a strict policy otherwise delay should take place.

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The following are some of the guidelines so far published be the MOE to implementation National Educational Policy-2020

i. (UDISE +) UNIFIED DISTRICT INFORMATION SYSTEM FOR EDUCATION PLUS

ii. NIPUN BHARAT - National Initiative for Proficiency in Reading with Understanding and Numeracy

iii. (Project Appraisal, Budgeting, Achievements and Data Handling System (PRABANDH))

iv. PRAGYATA guidelines

v. SARTHAQ

vi. PARAKH (Performance Assessment, Review, and Analysis of Knowledge for Holistic Development) vii. Academic Credit Bank for HEI

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डॉ॰ अनुभूति

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शुल्क

आजीवन (दस वर्ष): छह हजार रुपए वार्षिक शुल्क : एक हजार रुपए यह प्रति : चार सौ रुपए

प्रकाशित सामग्री से संपादकीय सहमति आवश्यक नहीं है। पत्रिका से संबंधित सभी विवाद केवल बिजनौर स्थित न्यायालय के अधीन होंगे। शुल्क की राशि 'शोध दिशा' बिजनौर के नाम भेजें। (सन् 1989 से प्रकाशन-क्षेत्र में सक्रिय)

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अनुक्रम

लोकवार्त्ता का स्वरूप⁄ डॉ॰ बाबूराम (डी॰लिट्॰) 11 मिथक की परिधि में उत्तरआधुनिकता-'अनंग'/ डॉ॰ निशा तिवारी 17 हिंदी गजल का आशावादी स्वर/ हरेराम समीप 24 मानवीय जीवन में भगवद्गीता के समत्त्व-योग की प्रासांगिकता/ डॉ॰ नरेन्द्रकुमार वेदालंकार 28 डाँ॰ कमलकिशोर गोयनका की अन्वेषी दृष्टि और प्रेमचंद/ अनिल कुमार पांडेय 34 मधु काँकरिया के उपन्यासों में नारीपात्र/ दीपा कमारी 39 कुँवरनारायण के काव्य में अभिव्यक्त मानवीय मूल्य/ दीपाली कुजूर 43 वैदिक वाङ्मय में राष्ट्रीय संवेदना और मूल्यबोध/ डॉ॰ ज्योति वर्मा 50 स्वयंप्रकाश की 'जो हो रहा है' कहानी में दलित-चेतना/ हरप्रीत कौर, डॉ॰ मुदुल जोशी 56 युवा-मनोविज्ञान और जैनेंद्रकुमार की कहानी/ जयश्री काकति 61 काला सच उपन्यास में नारी की दशा/ मंजु बाला 67 सर्वेश्वरदयाल सक्सेना के नाटकों में सामाजिक समस्या/ डॉ॰ नीरज शर्मा 70 मदनमोहन मालवीय के सामाजिक व शैक्षिक अवदान का अध्ययन 'कब आओगे महामना' उपन्यास के संदर्भ में/ प्रीति गुप्ता, डॉ॰ दीपिका विजयवर्गीय 75 इक्कोसवीं सदी की हिंदी कहानी : सहजीवनयापन समस्या (लिव-इन-रिलेशनशिप)/ डॉ॰ रमेश कुमार 81 हिंदी के आंचलिक उपन्यासों में जनजातीय समाज का धार्मिक एवं सांस्कृतिक स्वरूप/ सीमा रानी 89 होमवती देवी का हिंदी साहित्य में योगदान/ विक्रांत 94 हरियाणवी स्वॉॅंग की सैद्धांतिक परंपरा/ सुषमा रानी 99 रमणिका गुप्ता की आत्मकथा : 'आपहुदरी' शीर्षक की सार्थकता/ सुमित कुमार 105 जोखिम उठानेवाले औपन्यासिक नारीपात्र : एक पाठ/ डॉ॰ सिंधु एस॰ एल॰ 109 उषाकिरण खान की कहानियों में अभिव्यक्त लोकजीवन/ **अलका कुमा**री 114 उपन्यासकार प्रेमचंद का सामाजिक शिल्प-दर्शन/ रेनू 119 सुधा अरोड़ा के कथासाहित्य में चित्रित लोकविश्वास/ डॉ॰ सुनीता शर्मा, अरवीना शर्मा 124

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डाँ॰ अब्दुल कलाम के दुष्टिपथ में 'अग्नि की उड़ान' : साहित्य के विशेष संदर्भ में/ रुचि कुमारी शर्मा 130 डॉ॰ राजकुमार निजात के काव्य में सामाजिक यथार्थ/ गुरप्रीत कौर 136 'डरी हुई लड्की' उपन्यास में बदलते जीवनमूल्य/ डॉ॰ मंजु पुरी 142 योगरूब तथा यौगिकरूब पदों में भेद/ डॉ॰ मधुबाला सिंह 148 हिंदी के निर्मुण संतकवियों की जीवनदृष्टि के आधुनिक स्वर/ पिकी 152 रामचरितमानस के मार्मिक स्थल/ डॉ॰ महेश सिंह यादव 157 मुदुला सिन्हा और मैत्रेयी पुष्पा के नारी दृष्टिकोण का तुलनात्मक अध्ययन/ डॉ॰ अन्नाराम शर्मा, श्रीमती शकीला 163 उचल्या : भारतीय दलित साहित्य की प्रतिनिधि आत्मकथा/ डॉ॰ गोरख प्रभाकर काकडे 168 विभाजन की त्रासदी व कितने पाकिस्तान/ शिव कैलाश यादव 175 काव्यभाषा के बारे में तुलसीदास की मान्यताएँ/ डॉ॰ मुक्तिनाथ यादव 180 खयालनामा कहानी-संग्रह में सामाजिक स्थिति/ पुष्पा 184 मुस्लिम पारिवारिक जीवन के परिप्रेक्ष्य में शानी का साहित्य/ डॉ॰ आरिफ महात 188 ममता कालिया की कहानियों में नारी सशक्तिकरण/ रश्मि सिंह, डॉ॰ ललिता कुमारी 195 सूर्यकांत त्रिपाठी 'निराला' के काव्य में राम/ a डॉ॰ रश्मि कुमारी, राहुल कुमार यादव 201 अलका सरावगी के उपन्यास में नारी-अस्मिता/ डॉ॰ श्रद्धा हिरकने, डॉ॰ अनुसुइया अग्रवाल 207 संस्कृत मुक्तक परंपरा में 'आळ्वन्दारस्तोत्ररत्नम्' स्तुतिपरक मुक्तक का आलोचनात्मक अध्ययन/ **रमन शर्मा** 213 शरद जोशी के स्तंभ-लेखों में प्रशासनिक व्यवस्था पर व्यंग्य/ डॉ॰ राजकुमार 220 प्रवासी हिंदी कविता में भारत-बोध/ **रूपेश कुमार** 226 मध्यकाल में स्त्री-जीवन के विभिन्न पक्ष/ **डॉ॰ मीना** 230 भीष्म साहनी के उपन्यासों में नारी-चेतना/ संजय कुमार दुबे, डॉ॰ श्रद्धा हिरकने 234 प्रवासी जीवन-संघर्ष और साहित्य/ डॉ॰ मीना 239 आचार्य हजारीप्रसाद द्विवेदी का समसामयिक परंपरा विरोध/ डॉ॰ महेंद्रपाल सिंह 245 वृद्धजीवन की दर्दभरी दास्तान : रेहन पर रग्धू/ महेश बापुराव चव्हाण 248 ज्ञान चतुर्वेदी के व्यंग्य में सामाजिक व्यंग्य/ डॉ॰ गौकरण प्रसाद जायसवाल, दीपक कुमार 251

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मुस्लिम पारिवारिक जीवन के परिप्रेक्ष्य में शानी का स डॉ॰ आफि_।

हिंदी विभाग 🕅 विवेकानंद कॉलेज, कोल्हापुर (२)

हिंदी के महत्त्वपूर्ण कथाकार के रूप में शानी को नकारा नहीं जा सकती

हिंदी के महत्त्वपूर्ण कयाता. दुर्भाग्यवश यह कहना पड़ता है स्वतंत्रता के बाद की पीढ़ी के इस कथाकार के दुर्भाग्यवश यह कहना पड़ता है स्वतंत्रता के बाद की पीढ़ी के इस कथाकार के दुर्भाग्यवश यह कहना पड़ता हे पाया। शानी के साहित्य में स्वतंत्रता के काबिलियत के हिसाब से मूल्यांकन नहीं हो पाया। शानी के साहित्य में स्वतंत्रता के काबिलियत के हिसाब से मूल्यांकन नहीं हो पाया। शानी के साहित्य में स्वतंत्रता के काबिलियत के हिसाब से मूल्पाय किया गया है। स्वातंत्र्योत्तर हिंदी साहित्य में से मुस्लिम समाज-जीवन का बखूबी चित्रण किया गया है। स्वातंत्र्योत्तर हिंदी साहित्य में से मुस्लिम समाज-जीवन का बखूबी चित्रण किया गया है। स्वातंत्र्योत्तर हिंदी साहित्य में से मुस्लिम समाज-जीवन का बखूबी चित्रण किया गया है। स्वातंत्र्योत्तर हिंदी साहित्य में से मुस्लिम समाज-जीवन का बखूबी चित्रण किया गया है। स्वातंत्र्योत्तर हिंदी साहित्य में से मुस्लिम समाज-जीवन का बखूबी चित्रण किया गया है। स्वातंत्र्योत्तर हिंदी साहित्य में से मुस्लिम समाज-जीवन का बखूबी चित्रण किया गया है। स्वातंत्र्योत्तर हिंदी साहित्य में से मुस्लिम समाज-जीवन का बखूबी चित्रण किया गया है। स्वातंत्र्योत्तर हिंदी साहित्य में से मुस्लिम समाज-जीवन का बखूबी चित्रण करने वालों में शानी का स्थान महत्त्वपूर्ण है। से स मुस्लिम समाज-जीवन का अर्जुना से साहित्य-जगत को परिचित का स्थान महत्त्वपूर्ण है। उन्होंने से समाज-जीवन का यथार्थ चित्रण करनेवालों में शानी का स्थान महत्त्वपूर्ण है। उन्होंने से समाज-जीवन का यथार्थ चित्रण करनेवालों से साहित्य-जगत को परिचित का समाज-जीवन का यथाथ पित्र कि तास्तविकता से साहित्य-जगत को परिचित कराय के भारतीय मुस्लिम-समाज की वास्तविकता से साहित्य में देश के विभाजन की त्राप्र के भारतीय मुस्लिम-समाज का जारतीय साहित्य में देश के विभाजन की त्रासदी जिसके ब बुनियादी बातों को उछाला हो जाते. मुस्लिम समुदाय पर पड़ा प्रभाव एवं भारतीय मुस्लिम समुदाय के पारिवारिक, धार्मिक, से मे मु।स्लम सनुसान स्वार दिखने जीवन के संघर्ष की वास्तविक तस्वीर देखने मिलती है। आर्थिक एवं सामाजिक जीवन के संघर्ष की वास्तविक तस्वीर देखने मिलती है।

पूर्व सामाजिक जीवन-परिवार का इंसान के जीवन में बडा़ महत्त्व रहता है। पारिवारिक जीवन-परिवार का इंसान के जीवन पर ही जालवर कि भारवारिय आसी अच्छे-बुरे संस्कारों का आधार उसके पारिवारिक जीवन पर ही ज्यादातर निर्भर रहे। अच्छ-बुर संस्थार के से पहले वह अपने परिवार के संपर्क में आता है। अत: उसके के समाज का घटक बनने से पहले वह अपने परिवार के संपर्क में आता है। अत: उसके के समाज की पटक परिवार की अहम भूमिका रहती है। साथ ही परिवार के सदस्य के के बनन में उरायर गया के प्राप्त में चलते पारिवारिक जीवन का ढाँचा मजबूत बन्त ने अपने साहित्य में मुस्लिम समाज जीवन में व्याप्त पारिवारिक जीवन के विभिन का बखूबी चित्रित किया है। उनका साहित्य पारिवारिक जीवन का भरा-पूरा संसार प्रस्तु का यहाँ हम मुस्लिम पारिवारिक जीवन को विवाह, दापत्य जीवन एवं रिश्ते-नातों के फीट खोलने का प्रयास करते हैं।

विवाह-विवाह संस्कार एक ऐसी संस्था है जिसमें पारिवारिक जीवन को नींव खंड है। ये नींव जितनी स्वस्थ होगी, पारिवारिक जीवन की इमारत उतनी ही भव्य एवं कि हर समाज, धर्म में विवाह-संस्कार को पवित्र माना गया है। मुस्लिम समाज भी इससे आज है। शानी ने अपने साहित्य में मुस्लिम समाज में संपन्न होते विवाह का चित्रण किया के जल' उपन्यास में फूफी के शादी के प्रसंग में मुस्लिम समुदाय व्याप्त रस्म-रिवाज का चित्रण देखने मिलता है। दुल्हन दूल्हे के घर आते ही संदल की रस्म अब बा दूल्हे-दुल्हन हथेलियों में जरा-जरा संदल लगाया जाता गया और रोशन फूफा ने छोटे कां संदल वाला हाथ उठाकर, चौखट के ऊपर वाली दीवार पर ऐसे धर दिया कि कौतिय जाए।" रस्म पूरी होने के बाद मुहल्ले-पड़ोस की औरतें नेग के लिए रज्जू मियाँ का सके देती है। रज्जू मियाँ की बहाने-बाजी पर एक पडोसन कहती, 'अरे, जब बेटे की सार्क

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ही और घर में बहू आ रही है तो उतना बड़ा कलेजा रखो। जैसे-तैसे रज्जू मियाँ के हाथ ही और इसे ब्योध और हैंसी के बाद वह एक रूपया हुआ और अंत में पडोधी कि हाथ बहर मने हुई, जो गह छोड़कर हटने लगे तो उनकी नामकली ने हो और घर म नए सियों के बाद वह एक रूपया हुआ और अंत में पड़ोसी बिना उसे हो और है बोच और हैंसी के बाद वह एक रूपया हुआ और अंत में पड़ोसी बिना उसे मान हो ही राह छोड़कर हटने लगे तो उनकी नाराजगी के भय से, शरमाणपत्ने ने कि बह शादी प्रबलित हास-परिहास का जिन्म ते हैं, ब्यान को इकर हटने लगे तो उनकी नाराजगी के भय से, शरमाशरमी वी रुपए अने कुए वूँ ही राह छोड़कर हटने लगे तो उनकी नाराजगी के भय से, शरमाशरमी वो रुपए अने कुए वूँ ही राह शादी प्रचलित हास-परिहास का चित्रण जीवंतता के साथ ज्याने के साथ भाष होता है। आ होता है।

ा _{होता} है। ह^{त होता} प्र^{भाज} में संपन्न होते विवाह में व्याप्त प्रधाओं को शानी ने साहित्य में चित्रित किया मुहितम समाज एवं परिवार पर पड्ते प्रधावों का वास्तविक विवास क्रिक्टिल होता है। हित्य समाज हुस्तिम समाज है कि कारण समाज एवं परिवार पर पड्ते प्रभावों का वास्तविक चित्रण उनके साहित्य में र^{ह द्वार्थी} के कारण समाज में शरीअत के नाम पर 'बहुविवाह' की प्रथा प्रवर्धित के ह^{वाओं के कारण} समाज में शरीअत के नाम पर 'बहुविवाह' की प्रथा प्रचलित हो चुकी है। ह^{वि} है। मुस्लिम समाज में शरीअत के नाम पर 'बहुविवाह' की प्रथा प्रचलित हो चुकी है। है सिली अपने स्वार्थ के लिए अक्सर शरीअत का हवाला देते नजर आले के है। मुल्ला है। मुल्ला के लिए अक्सर शरीअत का हवाला देते नजर आते हैं। इस्लाम में के लोग अपने स्वार्थ के लिए अक्सर शरीअत का हवाला देते नजर आते हैं। इस्लाम में के लोग अपने स्वार्थ को चार विवाह करने की अनुमति है लेकिन इसके आपने नजर के स्वार्थ के अनुसार पुरुष को चार विवाह करने की अनुमति है लेकिन इसके आपने नजर के स्वार्थ के स्वार हैं लेग अपन स्तान विवाह करने की अनुमति है लेकिन इसके अपने कानूनी नियम हैं, के अनुमार पुरुष को चार विवाह करने की अनुमति है लेकिन इसके अपने कानूनी नियम हैं, के अनुमार एक का कत्तेव्य है। इस्लाम में बहुविवाह की मान्यता के पीछे प्रेरिजनी के अनुसार उत्त कर्त्तन्य है। इस्लाम में बहुविवाह की मान्यता के पीछे ऐतिहासिक पार्श्वभूमि बहुविवाह हा एक का कर्त्तन्य से पूर्व अरब में स्त्रियों की स्थिति बडी दयनीय की जार्श्वभूमि हर एक को उदय से पूर्व अरब में स्त्रियों की स्थिति बड़ी दयनीय थी। उसे समाज में की स्थति बड़ी दयनीय थी। उसे समाज में हित हरे. हो था। उनका क्रय-विक्रय भेड़-बकरियों की तरह किया जाता था। एक पुरुष बिना हो था। उनका क्रय-विक्रय भेड़-बकरियों की तरह किया जाता था। हो के एक साथ अपने हरम में अनेक स्त्रियाँ रखता था। त्र उत्पारण को तरह वि के एक साथ अपने हरम में अनेक स्त्रियाँ रखता था। के उदय से पूर्व पुरुष को चाहे किन्ने की

हर^{क के} प्^क से पूर्व पुरुष को चाहे जितने भी विवाह करने का अधिकार प्राप्त था, हर्सनम में अंकुश लगाया गया। इस्लाम के उदय के बाद पहले की स्थितियों में सुधार हर्सनम में अंकुश लगाया गया। इस्लाम के उदय के बाद पहले की स्थितियों में सुधार क जोधत (कानून) के अनुसार एक पुरुष को विशेष परिष्धित्रणों से जाना के हर्स्याम पहल को स्थितियों में सुधार के अनुसार एक पुरुष को विशेष परिस्थितियों में चार विवाह करने के ही गई। लेकिन इस पर तंबीह के तौर पर करआन में उपाय हराजा में चार विवाह करने हे दी गई। लेकिन इस पर तंबीह के तौर पर कुरआन में स्पष्ट कहा गया है कि 'अगर करके तम इसाफ न कर परनेने के कै हर हो कि यतीम लड़कियों से शादी करके तुम इंसाफ न कर सकोगे तो और औरतों में जो हर हा कि नगर सकाग ता और औरतों में जो बन्दी लगे तुम उनसे शादी कर लो, दो-दो, तीन-तीन, चार-चार, लेकिन अदल न रखने का का ला अ कि एक ही काफी है।'' इससे स्पष्ट होता है कि एक ही औरत से शादी करने में भलाई है, कि नाम औरतों से शादी करने पर सभी के साथ जंगान न हो है व एक से ज्यादा औरतों से शादी करने पर सभी के साथ इंसाफ करना मुश्किल होगा। दिली के तहत किसी एक की ओर झुकाव ज्यादा होने से अपने बीवियों में इंसाफ करने से चूक का परणामस्वरूप अल्लाह के यहाँ गुनहगार होगा। कुरआन में स्पष्टता से कहा गया है कि हा भारत से कहा गया है कि ह बीवियों में इंसाफ न कर सकोगे, अत: एक ही पर बस करो। फिर भी इस्लाम में बहु-विवाह ह इ.सन्यता संबंधी तरह-तरह की अटकले लगाई जाती हैं।

शानी ने अपने साहित्य द्वारा बहुविवाह के कारण पारिवारिक जीवन में होते बदलाव एवं बल को सजीव रूप में अंकित किया है। 'काला जल' उपन्यास में बी-दारोगिन अपने पति मिर्जा की बातिर दूसरी शादी बिलासपुर वाली से करवाती है। लेकिन जिस गर्मजोशी बह बिलासपुर वाली को ब्याह लाती है, उसके घर आते ही उसके साथ सौतेला व्यवहार करने न्तते है। उसे मिर्जा के पास ज्यादा फटकने नहीं देती। मिर्जा के साथ उसे अकेला देखती तो क्सी-न-किसी बहाने से उसे मिर्जा से अलग करवाती है। वह हर वक्त काम में मश्गूल रहे म्नीलर घर के सारे काम उससे करवा लेती है। फिर भी भुले बिसरे वह कभी मिर्जा के साथ क्रेली पाई जाती तो बी-आपा उसे ताने देती रहती, 'फुर्सत मिल गई, महारानी जी? इतनी जल्दी च्चॅ निकल आईं? थोड़ी देर और लाड़-चोंचले कर लेतीं।'⁴ इतने पर न रुक आगे कहती, 'और ये की किसे दिखाती है? छिनाल, हरामजादी, कामचोर निवाला हाजिर'' इस तरह घर का माहौल ह दिन किसी-न-किसी कारण तंग रहता, जिसे देख मिर्जा उकता जाते। एक दिन बी- दोरागिन

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को चिल्लाते देख मिर्जा गुस्साते हैं, 'अरे चोप्प... हर बात की हद होती है। जब देखता है पीछे लगी है। उसका रहना मुश्किल कर दिया है। जलन से ऐसी ही मरी बा रही थे के शादी क्यों करवाई? मैं भी कमबख्त इसके चक्कर में आकर एक अच्छी काभी थे ते जिंदगी से खेल बैठा।" इस प्रसंग से स्पष्ट हो जाता है कि बहुविवाह वाले घर ये पुर्व के तरह चला जाता है। परिवार बिखरता है। बहुविवाह करनेवाला व्यक्ति किसी-न कियी के से खेल जाता है जिसका एहसास उसे वक्त के गुजरने के बाद होता है। शानी ने कियी के से खेल जाता है जिसका एहसास उसे वक्त के गुजरने के बाद होता है। शानी ने कियी के बी-दारोगिन और बिलासपुर वाली के प्रसंग को बड़ी जीवंतता के साथ चिक्रि किये स्थिति में दूसरी बीवी की होनेवाली मानसिक कचोट को शानी ने बिलासपुर वाली क्रा के दिखाने का प्रयास किया है।

दिखाने का प्रयास किया है। बहुविवाह के कारण दूसरी पत्नी और बच्चे की होती दुर्गति का चित्रण 'रहीम के कहानी में देखने मिलता है। रहीम के पिता की किराने की दुकान थी। दुकान से पुनाफा होते का और वे अमीर हो गए। अमीर होते ही पहली पत्नी और बच्चों के होते हुए उन्होंने रहीम के शादी कर ली। जब तक ये जिंदा थे रहीम और उसकी माँ की जिंदगी मजे से के मुश्किल से दस के रहे होंगे कि उनके पिता उनकी माँ, सौतेली माँ और सौतेले बहने। 'रही छोड़कर चल बसे। उनके चालीसवें के बाद रहीम के सौतेले बड़े भाई ने सारी जायतार, कि की माँ ने बहुत हाथ-पाँव मारे, पर कुछ हुआ नहीं।'' अत: जिंदगीभर रहीम और उसकी माँ को अलग कर दिया रह में जिंदगी गुजारते रहे। घर, जायदाद सब से बेदखल होकर लाचार जिंदगी गुजारने के लिए मज्यू के गए। इस तरह कह सकते हैं कि शरीअत के अनुसार भले ही पुरुष एकाधिक विवाह कर सकते पर वास्तव में वह सबके साथ न्याय नहीं कर पाता और अंत में परिवार बँट जाता है।

पर पासाय न पुरु पुरुष से साम समुदाय में प्रचलित विवाह की दुर्गति को भी चित्रित किया है 'छल' कहानी में राशिद भाई चालीस पार होने के बाद शादी करते हैं। गरीबी, असमर्थत कि उनके स्वभाव के चलते उनका ब्याह फलता नहीं। ब्याह के पाँच वर्ष बाद तक दो बच्चों के का बने राशिद भाई वक्त से पहले ही बुढ़ापे को पा जाते हैं। घर में अकसर बीवी के साथ झाहे से राशिद भाई वक्त से पहले ही बुढ़ापे को पा जाते हैं। घर में अकसर बीवी के साथ झाहे से राशिद भाई को इंसान से जानवर बनते देर नहीं लगती। रोज घर-मुहल्ले में तमाशा चलता रहत है दोनों एक-दूसरे के खानदान की बखिया उधेड़ देते हैं। मार-पीट छीना-झपटी करते हैं। एक-दूस को फूहड़ गालियाँ बकते हैं और अपने जीवन को जहन्नुम बना लेते हैं। अनमेल विवाह के चले ही 'गुलमोहर का पेड़' कहानी में साहिरा के जीवन की त्रासदी देखने मिलती है। अठारह कस की कुँआरी साहिरा चालीस पार इसरार भाई की दूसरी पत्नी बन जाती है। साहिरा के जीवन का चित्रण कहानी में लेखक इस प्रकार करते हैं–'सचमुच, साहिरा की जिंदगी में सिर्फ ढेर सारे की और सफेद पन्ने रह गए हैं, जिन्हें एक बार उलट देना भर काफी है। जैसे कोई नया-नया खूल में दाखिल होकर नई काफी खरीदे और एक-दो सफे लिखे कि स्कूल ही छूट जाए।⁸ इस कथन से स्पष्ट होता है कि अनमेल विवाह के कारण स्त्री-जीवन के दु:ख की कोई सीमा नहीं रहती कहना गलत न होगा कि शानी ने मुस्लिम समुदाय में प्रचलित विवाह संस्कार का यथार्थ किय किया है।

दांपत्य जीवन-पारिवारिक जीवन में दांपत्य संबंध को महत्त्वपूर्ण स्थान प्राप्त है। असल में सभी संबंधों का निर्माण इसी संबंध के माध्यम से होता है। मुस्लिम समाज में दांपत्य संबंध को

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बड़ी गरिमा प्रदान की गई है। पति-पत्नी को एक-दूसरे का आधार माना गया है। कुरआन में एक बड़ी ^{गरिमा} प्रदान की स्वह (अल्लाह) ऐसा है कि जिसने तुम्हें सिर्फ एक जान से पैदा किया और ब^{ड़ी} फरमाया है कि 'वह (अल्लाह) ऐसा है कि जिसने तुम्हें सिर्फ एक जान से पैदा किया और ^{जगह} करमाया जोड़ा बनाया, ताकि वह अपने जोड़े से सुकन हासिल को 19 जोन्हें ^{अन्य} फरमाया है। ज^{गह} फरमाया है। ^{अन्य} फरमाया है। ^{अन्त} फरमाया है। ^{अन्त} फरमाया है। ^{अन्त} कोड़ा बनाया, ताकि वह अपने जोड़े से सुकून हासिल करे।" और फिर एक और _{उसी से} उसका जोड़ा के रिश्ते को अलग ढंग से समझाया है–' वह तम्हाम जिल्लान के क _{अभि से} उसका जाएं। _{3सी से} उसका जाएं। _{3सी से} उसका के रिश्ते को अलग ढंग से समझाया है–'वह तुम्हारा लिबास है और तुम उनके _{जगह नहो।} ¹⁰ इससे स्पष्ट होता है कि इस्लाम में दांपत्य रिश्ते का बहा महन्द्र के जात ्रा_{ह पति}-पत्म स्पष्ट होता है कि इस्लाम में दांपत्य रिश्ते का बड़ा महत्त्व है और तुम उनके _{जगह हो।} ™इससे स्पष्ट होता है कि इस्लाम में दांपत्य रिश्ते का बड़ा महत्त्व है क्योंकि यही वह ^{तिबास} हो। [™]इससे इंसान सुकून (आनंद) प्राप्त कर सकता है। जिम तान किस्तान _{तिबीस हो।} रहे _{तिबीस हो।} रहे _{तिबीस हो।} निससे इंसान सुकून (आनंद) प्राप्त कर सकता है। जिस तरह लिबास इंसानी जिस्म की _{रि^{र्गी} ज माहौल और असर से सुरक्षा करता है उसी तरह हा जरी जीता है} रिश्^{ती हैं जिसस} रे. और असर से सुरक्षा करता है उसी तरह हर बुरी चीजों से पति-पत्नी भी हर खराब माहौल और असर हो।

हर एक- इसरे के लिए सुरक्षा कवच हैं। सर के 1919 के मुस्लिम जीवन की बारीकियों को बखूबी चित्रित किया है, जिसमें शानी ने साहित्य भें मुस्लिम जीवन की बारीकियों को बखूबी चित्रित किया है, जिसमें शाना ने अखूबा चित्रित किया है, जिसमें _{प्रमुख रूप} से दांपत्य जीवन भी आता है। उनके साहित्य में दांपत्य जीवन में पनपते प्यार, र्_{प्रमु}ख रूप र जावन म पनपते प्यार, र्_{मु}ख रूप र जावन म पनपते प्यार, अ^{पनापन, झगड़ा, तकरार, अजनबीपन आदि अनेक रूप देखने मिलते हैं। 'काला जल' उपन्यास} अ^{पनापन, रागपुग} अ^{पनापन, रागपुग} हो को बी-दारोगिन के दांपत्य जीवन के मधुर पलों को मार्मिकता से चित्रित में लेखक ने मिर्जा जैसे ही मिर्जा की बिलासपर वाली से टागरे जाती के क में लेख^क ने को से ही मिर्जा की बिलासपुर वाली से दूसरी शादी हो जाती है तब इन दोनों के किं^{बी} है, लेकिन जैसे ही मिर्जा की बिलासपुर वाली से दूसरी शादी हो जाती है तब इन दोनों के किया ^{ह, राज्य} छ जाता है। पति-पत्नी के रिश्ते में किसी तीसरे के आ जाने से इनके बीच _{रिश्तों} में खटास आ जाता है। पति-पत्नी के रिश्ते में किसी तीसरे के आ जाने से इनके बीच रि^{रती म} अप्र पर आ जान स इनक बीच ब^{द्रती त्यवहार} में आनेवाले बदलाव को शानी ने 'काला जल' में बबन के अम्मी-अब्बा के ब^{द्रती} अर्जन्त किया है। जो पत्नी अपने पति की लंगी राजने के भ बर्दलत व्ययस्य न अभग क अम्मा-अब्बा क बर्दलत व्ययस्य ने चित्रित किया है। जो पत्नी अपने पति की लंबी उमर के लिए दुआ माँगते नहीं थकती, मध्यम से चित्रित किया है। जो पत्नी अपने पति की लंबी उमर के लिए दुआ माँगते नहीं थकती, माध्यम स्वाप्ताप्त करतूतों पर बहुआ देने से भी नहीं कतराती। बबन के अब्बा दूसरी औरत के बही उसकी गलत करतूतों पर बहुआ देने से भी नहीं कतराती। बबन के अब्बा दूसरी औरत के वही उसमा बही उसमा वक्कर में फँसकर अपने घर को बरबाद करने पर तुल जाते हैं। अम्मी के समझाने पर भी नहीं बक्कर में फँसकर जपने जोगी गुनाना घर से जिल्लाने के वक्कर मा गरा का जान्या पर भा नहा बक्कर मा राज्या का समझान पर भा नहा मानते बल्कि उसे ही खरी-खोटी सुनाकर घर से निकालते हैं। तब उसके मन से बहुआ निकलती मानत बारप्त राज राज राज सत्यानाश हो जाएगा। खुदा कभी भला नहीं करेगा। देखना, यही उलट जवानी है, अर, ७ है, अर, ७ है, अर, ७ कोई सुम्हें कोई कोई कुत्ता भी नहीं पूछेगा।''' इस कथन से स्पष्ट होता है कि

काढ़ राग राज्य स स्पष्ट होता दांपत्य जीवन में पनपती मधुरता विपरीत परिस्थितियों में जहर बनने से भी नहीं कतराती। 'बीच के लोग' कहानी में शानी ने पति-पत्नी में उत्पन्न हमेशा झगड़ों से उनके रिश्ते को जोड़नेवाले नाजुक धागे में बनती ढेर-सी गठानों को दर्शाया है। इस गठानों को पाटते-पाटते शम्मी आश्राणार के सहब के रिश्ते की मिठास खत्म हो जाती है। वकील साहब पाकिस्तान चले जाते आपा वकील साहब के रिश्ते की मिठास खत्म हो जाती है। वकील साहब पाकिस्तान चले जाते आण न्या के तहत शम्मी आपा हिंदुस्थान में रह सुहागन बेवा का जीवन ढोने के लिए ह जार के जाती है। पति-पत्नी के रिश्ते में पनपते कड़वाहट का जीवंत चित्रण 'रहीम चाचा' मण दे कहानी में देखने मिलता है। रहीम चाचा और सकीना के बीच हरदम झगड़ा होता रहता है। घर का _{माहौल हमेशा} तंग रहता है जो रिश्ता सुकून को पाने का आधार होता है वही रहीम चाचा के जीवन से सुकून को दूर करने का कारण बन जाता है।

पति-पत्नी एक-दूसरे का सबसे बडा़ आधार होते हैं। इसका चित्रण 'नंगे' कहानी में हुआ है। कठिन हालात में रूबीना अपने पति का हरदम साथ और प्यार देते नजर आती है, जिसके कारण घोर आर्थिक कठिनाइयों में भी इनके रिश्ते की मिठास बरकरार रहती है। रूबीना के माध्यम से लेखक ने समर्पिता पत्नी का आदर्श रूप प्रस्तुत किया है, जो हर हालत में अपने पति, बच्चे, परिवार और सगे-संबंधियों को एक सूत्र में बाँधे रखने में सफल होती है, जो किसी भी रिश्ते को बिखरने नहीं देती।

शानी ने अपने साहित्य में मुस्लिम जीवन को प्रस्तुत किया है। आर्थिक अभाव में जी रहे

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रायलब कोवव का झजीव विद्रण इनके झाहित्य में देखने पिलता है। आर्थिक मध्यव के का लंत-राल्वे को होनेकाली सार्वाधक कजोट अनेक कहानियों में देखने पिलती है, किसे के बाबा'. 'को', 'एक धकाव का घर', 'आईता', 'जली हुई रस्त्री' आरि प्रमुख है। 'कसे राखा'. 'को', 'एक धकाव के काएण वाहित भीर सफिया के रिहते में पनगती कप्रयापति है राहती' में आर्थिक अधाव के काएण वाहित भीर सफिया के रिहते में पनगती कप्रयापति है राहती' में आर्थिक अधाव के काएण वाहित भीर सफिया के रिहते में पनगती कप्रयापति है करने हो भी संकोच करते हैं। पति पत्नी अपनी छोटी छोटी जरूततों को एक न्राने के प्रतान है, 'पनि क्रांग के पर देखने फिलती है। पति पत्नी अपनी छोटी छोटी जरूततों को एक न्राने के प्रतान के करने हो भी संकोच करते हैं। सफिया एक दिन झिड़ाकते हुए वाहित से कहती है, 'पनि का आपसे?' जनाब देने से पहले ही वाहित हर जाता है कि पता नहीं क्रम कोनमी बात करेगा के पर सफिया कहती है, 'पाविडेंट फंड के पैसे पिलोंगे, तो भी ला तोगे? बहुत रितों से का पर सफिया कहती है, 'पाविडेंट फंड के पैसे पिलोंगे, तो भी ला तोगे? बहुत रितों से का प्रताह संचत कर पहले वह भीरे से मुस्कृराया, फिर जरा जोर से बनाई हुई हैमी हैमता हुआ के तत्वाव को बख्बूबी उड़ेल दिया है। निष्कर्भताः कह सकते हैं कि शानो ने अपने महिला के संबंधों के विविध पहलुओं को वास्तविकता के साध चित्रित किया है, जिसमें कहीं भी _{तार्थी} नहीं है।

नहीं है। रिश्ते-नाते-मानव जीवन में रिश्तों का अपना एक अलग स्थान एवं पहल्ब है। अपनों के इंसान एकांगी है और वह रह भी नहीं पाता। इंसान के अपने, उसके रिश्ते जितिब में पाए जाते हैं। शानी के साहित्य संसार में भी रिश्तों के विविध रूप दिखाई देते हैं, जिन्न आत्मीयता और प्यार है; तो कहीं टकराव, दरार और अजनबीपन है। इन सबका शानी ने कार्य चित्रण किया है।

चित्रण किया है। 'काला जल' उपन्यास में रिश्तों की जमघट-सी नजर आती है, जिसमें लेखक ने का और फूफी के परिवार के माध्यम से मानवीय रिश्तों की शृंखला प्रस्तुत की है। इसमें लेखक ने का रिश्ते की वास्तविकता को बखूबी चित्रित किया है। फिर चाहे वो रज्जू मियाँ और फूफी क सास-ससुर का रिश्ता हो, बी-दारोगिन और बिलासपुर वाली का सौतन का रिश्ता हो, बजन के मोहसिन का भाई का रिश्ता हो, त्रिवेदी काका और बब्बन के पिता का दोस्ती का रिश्ता हो, बजन के फिर बब्बन और सल्लो आपा का मधुरता से युक्त भावपूर्ण रिश्ता हो, सभी रिश्तों के पहला हो का शानी ने सच्चाई एवं ईमानदारी के साथ मार्मिक रूप में प्रस्तुत किया है, जो कहीं भी कृत्रि के गढा हुआ महसूस नहीं होता।

भेदा हुआ महसूस पुरा हाआग ऐतबार और अपनेपन में रिश्ता मजबूत बनता है। जब रिश्तों में खटास आ जाती है तक रिश्ता बोझ बन जाता है। रिश्ते की इस कशमकश को शानी ने अपनी कहानी 'डाली नहीं फूल में बड़े ही मार्मिकता से व्यक्त किया है। सबीहा के पिता के मरने के बाद वह अपनी बड़ी क बाजी और युनूस भाईजान के पास रहने आती है। एक दिन बाजी युनूस को सबीहा के का दिल्लगी करते हुए देखती है। उस दिन से वह सबीहा से खफा रहने लगती है। उससे ज्यात क नहीं करती। हर बात में उसकी कमियाँ निकालने लगती है। लोगों के सामने उसे दुल्हात हा उसके बदबख्ती का बयान करने लगती है। यह सब देख सबीहा भी अंदर-ही-अंत बैक उठती है। बाजी और सबीहा के रिश्ते में पड़े इस दरार को लेखक ने बड़े ही संजीरनी के का प्रस्तुत करते हुए कहा है, 'शायद सबीहा और बाजी को बाँधनेवाली डोर कमल के नल बैसे क जो टूटने के बावजूद भी अपने सिरों से निकले चंद बारीक और नाजुक रेशों से जुड़ी हुं ही

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्यहाँ लेखक ने उनके रिश्तों के बीच मिटती मिठास को व्यक्त करते हुए यह भी दिखाने क है। किया है कि भले इनके रिश्तों में कड़वाहट पनप रही है, फिर भी वे एक-हम्मे के जि

है।²³ इहाँ लेखक ग जनन गरावे के सिंहतों में कड़वाहट पनप रही है, फिर भी वे एक-दूसरे के साथ है।²³ किया है कि भले इनके रिश्तों में कड़वाहट पनप रही है, फिर भी वे एक-दूसरे के साथ प्र^{दास} और एक-दूसरे को सहने के लिए मजबूर हैं। हैर एक-दूसर का पर 'नंगे' कहानी में शानी ने 'दूल्हे भाई' जैसे रिश्तेदार को प्रस्तुत किया है जिसे घर में कोई ---- फिर भी रख लेता है। जैसे-जैसे वक्त गुजरता है वह घर का जिसे घर में कोई

रह⁴ (नमें) कछाम से रख लेता है। जैसे-जैसे वक्त मुजरता है वह घर का हिस्सा बन जाता है। त्र^{द्वना} नहीं चाहता फिर भी रख लेता है। जैसे-जैसे वक्त मुजरता है वह घर का हिस्सा बन जाता है। र^{द्वना} का वाचक कहता है, 'यह दूल्हे भाई अब हमारे कोई नहीं फिर भी वैसे क्ले जाता है। रख^{ना न}हीं चहिता गगर ... रख^{ना न}हीं चहिता गगर ... इह^{ानी} का वाचक कहता है, 'यह दूल्हे भाई अब हमारे कोई नहीं फिर भी कैसे इतने जाता है। कहानी की उन्हें हटाकर कुछ सोचा ही नहीं जा सकता। कई बरस हए भेरी प्रक्र आपने-से रहाती का वाचक पाला के कुछ सोचा ही नहीं जा सकता। कई बरस हुए मेरी एक बदनसीब इहींनी के उन्हें हटाकर कुछ सोचा ही नहीं जा सकता। कई बरस हुए मेरी एक बदनसीब इन गए हैं कि उन्हें हटाकर रिश्तेदार बने थे, पर बीच में ही आपा शय से उन जो क कि अप हैं कि अप स्थान रिश्तेदार बने थे, पर बीच में ही आपा कई बरस हुए मेरी एक बदनसीब ब^{न गए} हैं कि अप स्थान रिश्तेदार बने थे, पर बीच में ही आपा क्षय से उठ गई। एक बदनसीब आ^{दा के} पल्लू से बँधकर रिश्तेदार बने थे, पर बीच में ही आपा क्षय से उठ गई। रिश्ता ब्रुटा। बो के पत्लू से दुआ लेकिन बीमारी और अभाग्य से उनकी नौकरी भी जाती रही और दूसरी आ^{दा} के बच्चे को लेकर पिछले दो बरस से मायके जा बैठी है। इधर तभी रही और दूसरी आग दूसरा ब्याल छन्म उनकी दूसरा बच्चे को लेकर पिछले दो बरस से मायके जा बैठी है। इधर तभी से दूल्हे और दूसरी _{बीवी अ}पने बच्चे को नया कर लिया है; हालाँकि अम्मी को उनका रहना कभी प्रमंह उन्हें भाई ने _{बीवी} अपने बण्प नाम कर लिया है; हालाँकि अम्मी को उनका रहना कभी पसंद नहीं आया। जब पुरा^{ने} रिश्ते को नया कर लिया है; हालाँकि अम्मी को उनका रहना कभी पसंद नहीं आई ने पुराने रही तो दामाद से क्या रिश्ता?'' इस प्रकार शानी की कहानियों में जिन्हों आया। जब पुराने रिश्ते का परप पुराने रिश्ते का परप ब्रेटी ही नहीं रही तो दामाद से क्या रिश्ता?'' इस प्रकार शानी की कहानियों में रिश्तों की अजीब ब्रेटी टी नहीं रहीने मिलती हैं।

बाँ देखन गराण के कहानी में भाभी और देवर के रिश्ते की मिठास देखने मिलती है। 'जनाने का फूल' कहानी में भाभी और देवर के रिश्ते की मिठास देखने मिलती है। 'जनान पर के जसलम रिश्ते में आयशा का देवर लगता है लेकिन उनका रिश्ता कुछ-कुछ दोस्ती जैसा बन जाता असलम असलम को अपने गुजरे कल की बातें बताती है। शानी ने हम फिरोजन असलम रिश्त न आ आ जाने गुजरे कल की बातें बताती है। शानी ने इस रिश्ते का अंकन बखूबी है। आयशा असलम और अपनेपन के साथ तकरार और रूठना मनजा की जाता है। आयशा असरा में सिठास और अपनेपन के साथ तकरार और रूठना मनाना भी नजर आता है। किया जिसमें मिठास और इसीन का दोस्ताना नजर आता है जिपमें का जिस आता है। किया जिसने स्वित्त भी नजर आता है। 'दोजखी' कहानी में वाचक और हसीन का दोस्ताना नजर आता है जिसमें अपनापन एवं प्यार तो

त ज्यापार के शानी ने अपने साहित्य में रिश्तों के विविध पहलुओं को बखूबी चित्रित किया है। राणा तर्रते-नातों की हर कोने से चिकित्सा की है। उनमें पनपते प्यार, अपनापन, तकरार, नोक-झोंक न्तर्गत चित्रण किया है। इसके उपरांत ऐसा महसमा रोज के फिर्मा के स्वित किया है। रिश्ते-नोता प्राप्त, अपनापन, तकरार, नोक-झोंक आदि का मार्मिक चित्रण किया है। इसके उपरांत ऐसा महसूस होता है कि 'रिश्तों' में अलगाव आदि को पांच हो। इसी कारण तो वह अपने साहित्य में रिश्तों में पनपती खटास, उसमें पड़ी शानी को तो बेबाकी से चित्रित करते हैं लेकिन उन्हें टूटते हुए नहीं दिखा पाते। आखिर में उलझे दारों को तो बेबाकी से चित्रित करते हैं लेकिन उन्हें टूटते हुए नहीं दिखा पाते। आखिर में उलझे दरारा को भा हुए रिश्तों में कोई-न-कोई ऐसी सिरों को जरूर दिखाते हैं जो उसे जोड़े रखती है। पूरी तरह से हुए परणा नहीं होने देती बिल्कुल कमल की नाल की तरह जिसके टूटने के बाद भी उसके कई अलग पुरुष पूर्ण पर बाद भा उसक कई सिरे एक-दूसरे से जुड़े रहते हैं। अत: कह सकते हैं कि शानी के साहित्य में पारिवारिक जीवन का यथार्थ चित्रण मिलता है।

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देवेश ठाकुर

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• वर्ष-15 ● अंक 31 ● अप्रैल - जून 2022● पूर्णांक 69 मूल्य 100 रुपए • प्रधान संपादक - देवेश ठाकुर • संपादक - डॉ. सतीश पांडेय



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प्रबंध संपादिका : परीक्षक विद्रत मंडल : (Peer Review Team) प्रोफेसर ताकेशी फुजिई डॉ. रोहिणी शिवबालन अध्यक्ष, हिंदी विभाग प्रधान संपादक-प्रकाशक ः टोक्यो युनिवर्सिटी फॉर फॉरेन स्टडीज, टोक्यो 2) प्रो. (डॉ.) देवेन्द्र चौबे डॉ. देवेश ठाकुर जवाहरलाल नेहरू विश्वविद्यालय, नई दिल्ली संपादक : 3) प्रो. (डॉ.) वशिष्ठ अनुप डॉ. सतीश पांडेय हिन्दी विभाग, काशी हिंदू विश्वविद्यालय, संयुक्त संपादक ः वाराणसी (उ. प्र.) 4) डॉ. नरेन्द्र मिश्र डॉ. प्रवीण चंद्र बिष्ट प्रो. हिंदी, मानविकी विद्यापीठ, इंग्नु मैदानगढी, डिजिटल संपादक : दिल्ली110068 डॉ. मनीष कमार मिश्रा 5) प्रो. (डॉ.) करुणाशंकर उपाध्याय प्रोफेसर, हिन्दी विभाग, संपादकीय-संपर्कः मुंबई विश्वविद्यालय, मुंबई बी-23, हिमालय सोसाइटी, 6) डॉ. अनिल सिंह असल्फा. अध्यक्ष, हिन्दी अध्ययन मंडल, मुंबई घाटकोपर (प.), मुंबई-400 084. विश्वविद्यालय, मुंबई टेलिफोन : 25161446 7) प्रो. (डॉ.) सदानंद भोसले Email: sameecheen@gmail.com प्रोफेसर, हिन्दी विभाग, website-www.http//: सवित्रीबाई फुले पुणे विद्यापीठ, पुणे sameecheen.com 8) प्रो. (डॉ.) शरेशचंद्र चुलकीमठ विशेष : पूर्व अध्यक्ष, हिन्दी विभाग, 'समीचीन' में प्रकाशित रचनाओं में व्यक्त कर्नाटक विश्वविद्यालय, धारवाड विचार संबद्ध रचनाकारों के हैं। संपादक- डॉ. अरुणा दबलिश प्रकाशक की उनसे सहमति आवश्यक नहीं है। सभी विवादों का न्याय-क्षेत्र मात्र मुंबई पूर्व प्राचार्य, कनोहरलाल महिला स्नातकोत्तर महाविद्यालय, मेरठ (उ. प्र.) होगा। सभी पदाधिकारी पूर्णरूप से अवैतनिक।

स्वामी, मुद्रक, प्रकाशक : देवेश ठाकुर ने प्रिंटोग्राफी सिस्टम (इंडिया) प्रा. लि., 13/डी, कुलां इंडस्ट्रियल एस्टेट, नारी सेवा सदन रोड, नारायण नगर, घाटकोपर (प.) मुंबई-400 086 में छपवाकर बी-23, हिमालय सोसाइटी, असल्फा, घाटकोपर (प.), मुंबई-400084 से प्रकाशित किया।

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आदिवासी अस्मिता का पक्षधर कवि-अनुज लुगुन

डॉ. आरिफ शौकत महात

वैश्वीकरण ने समूचे विश्व को बदल दिया है। दुनिया ने विश्वग्राम की जो संकल्पना देखी वह साकार हो गई। भूमंडलीकरण के चलते बदलाव की धारा पूरे विश्व भर में प्रवाहित हुई, जिसने विकास के नाम पर विश्वभर में पैर फैलाए। सन् 1991 के बाद विकास की यह धारा भारत तक पहुँची। विकास के नाम पर उदारीकरण एवं मुक्त व्यापार की चपेट में भारत के मूल निवासी या कहें आदिवासी आ गए। आदिवासियों ने आदिम काल से जंगल को अपना घर समझ उसे सहेज कर रखा था। औद्योगिक विकास के नाम पर अहिस्ता-अहिस्ता आदिवासियों के दोहन की कहानी शुरू हो गई। औद्योगिक विकास से संबंधित सारे संसाधन इन्हीं आदिवासियों के जल, जमीन, जंगल में मौजूद थे जिसके चलते आदिवासियों की जमीन को अधिग्रहित कर उन्हें हासिल करने का सिलसिला शुरू हो गया। आदिवासियों की जल, जमीन, जंगल को अधिग्रहित करना वास्तव में उनके मूल अधिकारों के हनन तक पहुँचा जिसके चलते संघर्ष की चिंगारी ने जन्म लिया। अपनी ही मस्ती में जीने वाले इन आदिम जनजातियों के जीवन में नवीन समस्याओं ने दस्तक दी। इस संघर्ष ने ही उनकी अस्मिता को चकनाचूर करने के साथ उनकी आदिवासियत को खतरे में डाला।

'आदिवासियों की अस्मिता का प्रश्न जहाँ उनके नाम की परिभाषा से गहरा संबंध रखता है, वहीं वह उनकी सामाजिक संरचना और जीवन यापन के साधन जल, जंगल, जमीन से जुड़ा है। उसका उद्गम उसकी पहचान को पुष्ट करता है, तो उसकी विरासत भाषा, शिक्षा, संस्कृति और जीवनशैली पहचान को जिंदा रखती है। इनकी रक्षा किए बिना उसकी अस्मिता की रक्षा नहीं हो सकती है।' वास्तव में देखा जाए तो आदिवासियों की अस्मिता उनके जल, जंगल, जमीन से जुड़ी हुई है। उनके उन अधिकारों से जुड़ी हुई है जो प्राकृतिक संसाधनों पर आधारित हैं। विकास के नाम पर सबसे ज्यादा हल्ला उनकी इसी अस्मिता पर हुआ है। विकास के नाम पर सरकारों द्वारा उनके जमीनों का अधिग्रहण शुरू हुआ। फिर उस जंगल की चीजों पर कानूनी रोक लगा दी गई, जिससे वह अपनी जीविका चलाते थे। जिस जल, जंगल और जमीन को वह अपना सब कुछ मानते थे, जिससे उनकी परंपरागत अस्मिता जुड़ी हुई है, जिससे उनकी भाषा, संस्कृति, परंपरा, रीति-रिवाज जुड़े हुए हैं उन्हीं से उन्हें वॉचित करने की कोशिश निरंतर जारी रही। इसी के चलते आदिवासी अस्मिता के नए प्रश्न उभरकर सामने आए जिसे हम अनुज लुगुन की कविता में देख सकते हैं।

अनुज लुगुन मुण्डारी भाषा के चर्चित युवा आदिवासी कवि हैं। उनकी कविताओं में आदिवासी जन समुदाय की पीड़ा दृष्टिगोचर होती है। आपका जन्म 10 जनवरी, 1986

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को झारखण्ड के सिमडेगा जलडेगा पहान टोली में एक मुंडा परिवार हुआ। आपने अपना शोध कार्य 'मुंडारी आदिवासी गीतों में आदिम आकांक्षाएँ और जीवन-राग' बनारस हिंदू विश्वविद्यालय से पूरा किया है। आपके बारे में रमणिका गुप्ता लिखती हैं- 'उनकी कविताओं में केवल झारखंड ही नहीं, पूरे देश का आदिवासी इतिहास झाँकता है- शौर्य बोलता है- और संग-संग चलता है चिंतन... दर्शन। अनुज लुगुन, इतिहास, संस्कृति, उत्साह, उम्मीद, संकल्प, हक और हौसले के कवि हैं। खूबसूरती की उनकी अपनी ही परिभाषा है, व्याख्या है, जो प्रचलित व पारम्परिक व्याख्या से भिन्न है- खतरनाक होने की हद तक सत्य और तथ्य के नजदीक है।'² अतः कह सकते हैं अनुज लुगुन वर्तमान दौर के आदिवासी अस्मिता एवं संघर्ष की बात बेबाकी से रखने वाले एक संवेदनशील एवं सशक्त कवि हैं।

90 के दशक से भारत में विकास के नाम पर और आदिवासियों को मुख्यधारा में सम्मिलित करने के इरादे से जो विकास की भूमिका तैयार की गई वह आदिवासियों को उनके जल, जंगल, जमीन से दूर ले जाने वाली साबित हुई। विकास का यह अनचाहा प्रवाह आदिवासियों के जीवन को विस्थापन, पलायन, भुखमरी, बेरोजगारी आदि नई समस्याओं से भर दिया। इन्हीं समस्याओं से दो-दो हाथ करना आदिवासियों को संघर्ष के रास्ते पर ले आया। नई पीढ़ी के आदिवासियों ने शिक्षा ग्रहण कर अपनी जनजातियों की समस्याओं की तरफ सारी दुनिया का ध्यान खींचा। अपने समाज के सामाजिक एवं परंपरागत सांस्कृतिक हितों की रक्षा के लिए आवाज उठाना शुरू किया जिसके लिए उन्होंने अपने संगठन भी बनाए। उनका यह प्रयास राजनीतिक, साहित्यिक मंच से होते हुए अग्रेषित हुआ। आदिवासियों ने अपने इतिहास की जड़ों को नए सिरे से खोजने का प्रयास किया और अपनी समस्याओं का, अपने होने के भाव का, अपनी अस्मिता को बचाए रखने की जद्दोजहद का आगाज साहित्य के माध्यम से शुरू किया।

आदिवासी अस्मिता पर निरंतर चोट करती इस व्यवस्था के खिलाफ अनुज लुगुन अपना आक्रोश व्यक्त करते हैं। उनका मानना है कि इस व्यवस्था के चलते विकास के नाम पर चल रही अंधी दौड़ में सरकार हमारे ही जल, जंगल, जमीन से हमें बेदखल कर रही है। वह हमसे यहाँ के निवासी होने का सबूत माँगते हैं। अपनी 'ससान दिरी' कविता में कवि इसका जवाब देते हुए कहते हैं-

'इन मृत पत्थरों पर जीवित है / हमारी सैकड़ों पुश्तों की विरासत /

लेकिन सरकारी पट्टों पर / इनका कुछ पता नहीं है /

ये हमारे घर हैं और इस तरह / हम बेघर हैं सरकारी पट्टों पर'3

आदिवासियों का यह संघर्ष सिर्फ उनकी अस्मिता एवं अस्तित्व टिकाए रखने के लिए नहीं है बल्कि इसके साथ पर्यावरण (जल-जंगल-जमीन) को बनाए रखने की उनकी जद्दो-जहद भी है। अपने संघर्ष की बात करते हुए कवि इस बात की ओर भी इशारा करते हैं-

समीचीन

अप्रैल-जून 2022

'हम तैयार होते गए / नए मोर्चों पर लड़ाई के लिए / सरकारी चेहरे की तरह पत्थर नहीं है / इनमें जंगल के लिए लड़ते हुए / एक पेड़ की कहानी है / जो धराशायी हो गया / नफरत की कुल्हाड़ी से / एक डाल की कहानी है / जो पंछियों को पनाह देते-देते टूट गई / एक फूल की कहानी है / जो बसन्त के आने से पहले झुलस गया'⁴

इस संघर्ष की बात करते हुए कवि कहते हैं कि यही ससान दिरी के सैकड़ों पत्थर (जो इनकी सांस्कृतिक विरासत वाले पत्थर हैं। जो इन्होंने उनके पुरखों की कब्र पर गाड़े हैं) इन्हें न्यायपूर्ण हस्तक्षेप करने के लिए हमेशा अमादा करते हैं। इनका यह न्यायपूर्ण हस्तक्षेप धरती को बचाने की प्रामाणिक लड़ाई है। यहाँ न्यायपूर्ण हस्तक्षेप बड़ा मायने रखता है।

आदिवासी अस्मिता असल में नक्सली विद्रोह एवं प्रशासकीय अत्याचार के बीच की धारा है। वास्तविक रूप में आदिवासी न तो लाचार बनकर जीना चाहते हैं और ना ही विरोध को हिंसा तक ले जाकर नक्सली। इन दोनों से परे जो आदिवासियों की मूल प्रवृत्ति है उसे वह बचाना चाहते हैं। अपने जल, जंगल, जमीन एवं जीवन पर अपना अधिकार एवं उसकी रक्षा के लिए प्रतिबद्धता यही आदिवासी अस्मिता का मूल स्वर है।

'मैं गीत गाना चाहता हूँ' कविता में कवि इसी की ओर इशारा करते हैं। उनका विद्रोह एवं संघर्ष उनके अस्तित्व को टिकाए रखने का माध्यम भर है। जिस बंजर जमीन को अपने खून से सींचा, उस फसल पर जब कोई और अपना अधिकार जताने आ जाता है तो उसे समझाते हैं। आदिवासियों के समझाने के तरीके को भी कवि यहाँ पर व्यक्त करते हैं-

'हमें गुरिल्ले और छापामार तरीके खूब आते हैं / लेकिन हमने पहले गीत गाए / माँदर और नगाड़े बजाते हुए उन्हें बताया कि देखो /

फसल की जड़ें हमारी रगों को पहचानती हैं / फिर हमने सिंगबोंगा से कहा कि / वह उनकी मति शुद्ध कर दे / उन्हें बताए कि फसलें खून से सिंचित हैं''

इनका संघर्ष सीधे हथियार नहीं उठाता बल्कि इनका संघर्ष अपने अस्तित्व को टिकाए रखने का न्यायपूर्ण हस्तक्षेप करता है। अपने अधिकार के लिए आदिवासी सभी न्यायोचित रास्तों से होकर गुजरते हैं। सबसे बड़ी अदालत पहुँचने से पहले इनकी फसलें एवं इनके अधिकार रौंदे जाते हैं। अब यह घायल आदिवासी या कवि की भाषा में कहें तो शिकारी चट्टान के टीले पर बैठकर रौंदी जा चुकी फसलों को देख रहा है। शहीद हुए साथियों को, भूखे बच्चे और औरतों को देख रहा है। इसे अफसोस नहीं है बल्कि उसकी चाहत यही है कि वह अपनी फसल का सम्मान लौटाना चाहता है। अपनी आदिवासी अस्मिता बनाए रखना चाहता है। अपने अस्तित्व के लिए संघर्षरत रहना चाहता है। इसलिए वह कहता है-

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'मैं एक बूढ़ा शिकारी / घायल और आहत /

लेकिन हौसला मेरी मुट्टियों में है और / उम्मीद हर हमले में /

मैं एक आखिरी गीत अपनी धरती के लिए गाना चाहता हूँ !'°

इनका यह आक्रोश इस व्यवस्था को लेकर है जो हिमायती होने का दावा तो करता है लेकिन कार्यवाही कुछ नहीं करता-

'हम दुखी हैं कि हमारी पत्नी और बच्चे फर्जी मुठभेड़ में मारे गए हैं'

मारे जाने का दुःख तो है ही लेकिन दुःख इस बात का भी है कि इस खबर को पड़ोस वाला भी नहीं जानता। उनकी इस खबर को उसकी वास्तविकता के साथ पहुँचने ही नहीं दिया जा रहा। संविधान के तहत न्याय के रास्ते पर ये चल तो रहे हैं लेकिन यह रास्ता है कि कभी खत्म होने का नाम ही नहीं लेता। इसे स्पष्ट करते हुए कवि कहता है-

'न्यायाधीशों के रास्ते थकाऊ, घुमावदार और अंतहीन-

कई पीढ़ियों से जारी है उनके यहाँ चक्कर काटने का हमारा सिलसिला'7

कवि यहाँ आदिवासियों की समस्या के प्रति उदासीन प्रशासकीय व्यवस्था, मीडिया एवं न्याय व्यवस्था पर भी करारा प्रहार करता है। विकास की अंधी दौड़ ने दुनिया को क्या दिया पता नहीं लेकिन प्रकृति से बहुत कुछ लिया। यह प्रकृति से लेना या इसका होता दोहन इतना विनाशकारी एवं बर्बर है जिसकी आँच में सबसे पहले मूलनिवासी, जंगल निवासी आदिवासी झूलसे और देर सबेर सारी दुनिया झूलसेगी।

विकास के नाम पर प्रकृति एवं आदिवासियों का होता शोषण आदिवासी कविताओं में प्रमुख रूप में देखने को मिलता है। जो आदिवासी जल, जंगल, जमीन को अपना सब कुछ मानते थे उन्हें वहाँ से बेदखल कर दिया गया। सरकारी कागज में उनका कहीं नाम दर्ज नहीं। जिस जंगल से वे अपनी जीविका चलाते उसकी हर चीज पर पाबंदी लगाई गई। परिणाम स्वरूप कुछ संघर्षरत बन बागी कहलाए गए कुछ विस्थापित हो गए। विस्थापन की समस्या को लेकर रमणिका गुप्ता लिखती हैं 'सरकार ने विकास के नाम पर बड़े-बड़े बाँध बनाए जिससे लाखों लोग विस्थापित हुए। हमारे देश की विकास नीति का लक्ष्य होना चाहिए था विकास में सबको समान अधिकार की प्राप्ति। लेकिन ऐसा नहीं हुआ। विकास तो हुआ, पर कुछ चुनिंदा लोगों का असंख्य लोगों की कीमत पर, खासकर आदिवासियों की कीमत पर। राष्ट्रहित के नाम पर आदिवासी लोगों की जमीन अधिगृहित कर उन्हें विस्थापित ही नहीं किया गया, बल्कि उनके संदर्भ में सॅविधान में प्राप्त मूल अधिकारों का भी उल्लंघन किया गया। इन विकास परियोजनाओं से इन आदिवासी प्रदेशों अथवा क्षेत्रों का आर्थिक संतुलन भी बिगड़ गया।'⁸ आदिवासियों के विस्थापन की समस्या रोज-ब-रोज गहराती जा रही है। इसी संदर्भ में अनुज लुगुन अपनी कविता 'शहर के दोस्त के नाम पत्र' में अपनी इस पीडा को दर्शाते हुए कहते हैं कि

'यहाँ से सबका रुख शहर की ओर कर दिया गया है /

कल एक पहाड़ को ट्रक पर जाते हुए देखा / उससे पहले नदी गयी /

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अब खबर फैल रही है कि / मेरा गाँव भी यहाँ से जाने वाला है'?

आदिवासियों का विस्थापन हो रहा है लेकिन जंगल में लोहे के फूल खिल रहे हैं। विकास की आड़ में बाजार सजे हैं लेकिन सवाल यह है कि यह बाजार किसके हैं और खुले किसके लिए हैं। इस ओर इशारा करते हुए रमणिका गुप्ता कहती हैं- 'पूँजीपतियों के विकास व वन दमन के लिए आदिवासियों के विशाल जनसमूह को निस्सहाय बना दिया। उन्हें इस हालत में रखने की साजिश रची गई ताकि वे पूँजीपतियों के लिए सस्ते मजदूर बनकर उनके हित-साधन की दमनकारी मशीन का एक पूर्जा बन जाएँ।'¹⁰

कवि का दुःख अपनों के प्रति है जो विस्थापित हो रहे हैं। प्रकृति की गोद से निकलकर कंक्रीट के जंगलों में भटकने के लिए जहाँ पर उनका कोई नहीं। और यह वह बखूबी जानता है कि यह कंक्रीट के जंगल उनकी सहजता एवं सरलता के साथ उन्हें जीने नहीं देंगे जैसा कि प्राकृतिक जंगल देते हैं। कंक्रीट के जंगल उनकी आदिवासियत को, मासूमियत को बड़ी ही शान से कुचलेंगें। औद्योगीकरण के चलते रेलवे, स्लीपर, कागज लोहा और अन्य तरह के उद्योगों के लिए कच्चे माल एवं खनिज संपदा के लिए आज जंगलों और पहाड़ों को देखा जाने लगा है। जिसके चलते विकास का नया खेल शुरू होता है। जिसमें शुरुआती मुद्दों में आदिवासियों को मुख्यधारा में लाया जाना प्रमुख रहता है। फिर आदिवासी एवं उनकी आदिवासियत को बनाए रखने एवं बचाए रखने का खेल उन्हीं के जमीन से बेदखल कर उन्हें विस्थापित होने के लिए मजबूर करने की हद तक बढ़ जाता है। इसी समस्या की ओर इशारा करते हुए कवि अपनी कविता अघोषित उलगुलान में आदिवासियों के आक्रोश, संघर्ष एवं पीड़ा को वाणी देते हैं। इस तरह अपने ही जंगल में शिकार करने वाले खुद शिकारी बनते जा रहे हैं, इसका मार्मिक चित्रण प्रस्तुत कविता में देखने मिलता है। आदिवासियों के संघर्ष एवं विस्थापन की दशा को व्यक्त करते हुए कवि कहता है-

'लड़ रहे हैं' आदिवासी / अघोषित उलगुलान में /

कट रहे हैं वृक्ष / माफिया की कुल्हाड़ी से /

और बढ़ रहे हैं कंक्रीट के जंगल / दान्डू जाये, तो कहाँ जाये? /

कटते जंगल में / या- / बढ़ते जंगल में ... ?'''

व्यवस्था के विरुद्ध विद्रोह का स्वर कवि ने आदिवासी औरतों के द्वारा भी उद्घाटित किया है। अपनी 'उलगुलान की औरतें' कविता में कवि आदिवासी औरतों के इसी बदलते स्वरूप को चित्रित करते हैं। अब आदिवासी औरतें बालों में श्रृंगार का फूल खोंसने के बजाय साहस का फूल खोंसती है। कवि कहते हैं-

'पगडंडियों से गलियों से बाहर / आँगन में गोबर पाथती माँ /

सदियों बाद स्कूल की चौखट पर पहुँची बहन / लोकल ट्रेन से कूदती हुई /

दफ्तर पहुँची पत्नी और भोर अँधेरे / दौड़-दौड़ कर खेतों की ओर /

चौराहे की ओर आवाज उठाती / सैकड़ों अपरिभाषित रिश्तों वाली औरतें /

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खतरनाक साबित हो रही हैं' 12

आदिवासी औरतों का यह बदलता रूप चिंता का विषय है। वह खतरनाक हो रही है धरती के दुश्मनों के लिए लेकिन धरती से प्रेम करने वालों के लिए वो उतनी ही खूबसूरत है, ऐसा कहने से भी कवि नहीं चूकते।

निष्कर्षतः हम कह सकते हैं कि अनुज लुगुन वर्तमान दौर के आदिवासी समुदाय की वास्तविक तस्वीर प्रस्तुत करने वाले सशक्त कवि है। इनकी कविताओं में आदिवासियों का इतिहास, संस्कृति, उत्साह, उम्मीद सब कुछ छलकता है। साथ ही विकास के नाम पर बदलते आदिवासी समुदाय के परिवेश को एवं उनकी पीड़ा को यथार्थ रूप में दर्शाने का काम वह बखूबी करते हैं। उनकी कविता संघर्ष का रास्ता अख़्तियार करती है लेकिन उनका यह संघर्ष विनाश के लिए नहीं बल्कि आदिवासियों की अस्मिता एवं अस्तित्व बनाए रखने का न्यायोचित हस्तक्षेप भर है। संदर्भ :

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 पु. 66
- 12. वही, पृ. 56

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प्रस्तावनाः

प्राचीन भारतीय संस्कृतीमध्ये स्त्रियांना आदराचे स्थान दिलेले आहे. प्राचीन भारतीय ग्रंथ व लेखकांमध्ये स्त्रियांसंबंधी परस्परविरोधी विचार पहावयास मिळतात. जरी काही ग्रंथांमधून त्यांच्या चरित्राबद्दल कटू आलोचना केली असली तरी शास्त्र व महाकाव्यामध्ये स्त्रीला महत्त्वपूर्ण आदर्शची प्रतिष्ठा मिळाली आहे. शतपथ ब्राह्मणांमध्ये स्त्रीला पुरुषाची अर्धांगिनी समजले आहे. (अर्धो हवा एष आत्मनो) महाभारतामध्ये गृहिणी हीच गृह आहे असे म्हटले आहे. स्मृतीग्रंथामध्ये सुद्धा स्त्रियां प्रती प्रशंसामुक्त विचार व्यक्त केलेले आहेत.

यत्र नार्यास्तू पूज्यन्ते रमन्ते तत्र देवता।

यत्रैतास्तू न पूजन्ते सर्वास्तत्राफलाः क्रिया।।

- मनु ३.५६

मनुस्मृतीमध्ये स्पष्टपणे म्हटले आहे की, जेथे स्त्रियांचा आदर केला जाते तेथे देवतांचा वास असतो. जेथे त्यांचा सन्मान होत नाही तेथे सारी कामे निष्फळ ठरतात. कोणत्याही त्रिकालदर्शी महर्षि असो अथवा महापुरुष त्यांचा जन्म मातेच्या गर्भातूनच होत असतो. परंतु स्त्रीजातीबद्दल त्यांचा फतवा आहे. 'न स्त्री स्वातंत्र्यामर्हति' अनादी काळापासूनच वेद आदी शास्त्रानुसार स्त्रिया पारतंत्र्यात राहतात व पतिव्रत पालन करतात.

गुप्तकालीन साहित्य आणि कलेमध्ये स्त्रियांचे आदर्श रूप वर्णन केलेले आहे. परंतु व्यावहारिक दृष्टीने समाजामध्ये स्त्रियांचे स्थान खालावलेले होते. स्त्रियांसंदर्भात त्या काळामध्ये काही गोष्टी विकसित झाल्या. त्यांचे शिक्षणाचे अधिकार, धार्मिक बाबी, प्रथा-परंपरा, सतीप्रथा, पडदापद्धत इ. गोष्टीच्या रुपात पहावयास मिळते. उद्देश :

गुप्तकाळामध्ये स्त्रियांच्या शिक्षणाचे आपल्याला साहित्यिक प्रमाण पहावयास मिळते. स्त्रियांना पत्नी, माता, कन्या म्हणून त्यांना आदराचे स्थान होते. तरीसुद्धा जून २०२२ इतिहासाचार्य वि.का.राजवाडे संशोधन मंडळ,धुळे.

संशोधक

आपल्याला पहावयास मिळते की, स्त्रियांची स्थिती गुप्तकाळामध्ये खालावलेली होती. त्या काळातील काही सुशिक्षित महिलांचा उल्लेख जरी सकारात्मक बाब असली तरी शूद्र जातीच्या स्त्रियांना तो अधिकार नव्हता. गुप्तकालीन स्त्रियांच्या जीवनातील शैक्षणिक, वैवाहिक, आर्थिक, राजकीय, सामाजिक असे विविध पैलू स्पष्ट करणे व त्यांच्या वर्तमान स्थितीच्या प्रासंगितकेची चर्चा करणे हा या शोधनिबंधाचा मुख्य उद्देश आहे.

स्त्रीशिक्षण :

गुप्तकाळातील उच्चवर्गीय स्त्रियांना शिक्षणाचा मर्यादित अधिकार होता. परंतु शूद्र स्त्रिया मात्र शिक्षणापासून वंचित होत्या. कालिदासाने 'अभिज्ञानशाकुंतलम्' मध्ये 'अनुसूया' हिला इतिहासाचे ज्ञान असल्याचे म्हटले आहे. 'अमरकोश'मध्ये शिक्षिकांसाठी उपाध्याया व आचार्या या शब्दांचा उल्लेख केला गेला आहे. उच्चवर्णीय समृद्ध कुटुंबातील मुलींना साहित्य व संस्कृतीचे शिक्षण दिले जाई. गुप्तकाळात 'भट्टारिका' ही विदूषी होऊन गेली. दक्षिणेत स्त्रिया संगीत, नृत्य या कलांचे जाहीर प्रदर्शन करीत. गुप्तकाळात शूद्रांप्रमाणे स्त्रियांनाही रामायण, महाभारत, पुराणे यांचे श्रवण करण्याची अनुमती दिली गेली होती. सनति, शतक्ष्पा आध्यात्मिक ज्ञानामध्ये निपुण होत्या. राजशेखरच्या 'काव्यमीमांसा' वरून समजते की, स्त्रियासुद्धा कवयित्री होत्या. विविध कलांमध्ये पारंगत असलेल्या स्त्रियांचा उल्लेख ही पहावयास मिळतो. जशी मालती, माधवची 'मालती' चित्रकलेमध्ये निपुण होती. परंतु 'याज्ञवल्क्य स्मृती'मध्ये कन्येचा उपनयन व वेदाध्ययनासाठी निषेध दर्शविला आहे. तसेच या काळातील स्त्रियांचा उपनयन संस्कार बंद झाल्याने विवाह हाच त्यांच्यासाठी उपनयन समजला जावू लागला व त्यामुळे लहान वयात लग्न होत असल्याने शिक्षण घेण्यात अडचणी निर्माण झाल्या. त्यामुळे या काळातील स्त्रियांचा सामाजिक दर्जा खालावल्याचे पहावयास मिळते. राजकीय कार्य :

सातवाहनांच्या विरुद्ध गुप्तांच्या राज्यामध्ये राजकीय उत्तराधिकारी विशुद्ध रुपाने गुप्तकाळामध्ये पितृसत्ताक पद्धत होती. गुप्त काळातील सम्राटांनी आपल्या मातेच्या नावाचा उल्लेख केलेला आहे. गुप्तकालीन अभिलेखांची ही विशेषता पहावयास मिळते की, यावर राण्यांचे नाव अंकित करण्यात येऊ लागले. सगळ्यात

😧 इतिहासाचार्य वि.का. राजवाडे संशोधन मंडळ, धुळे. संशोधक प्रथम चंद्रगुप्त प्रथम याने लिच्छवी राजा वृषदेव तेरावा याची कन्या कुमारदेवीशी प्रथम पश्राण होता व 'प्रयागप्रशस्ति'मध्ये राणी कुमारदेवीचा उल्लेख केला विवाह केला होता व 'प्रयागप्रशस्ति'मध्ये राणी कुमारदेवीचा उल्लेख केला गेलेला आहे. गुप्तकालीन शिक्क्यांची नाविन्यता पहावयास मिळते की, आता शिक्क्यांवर राजासोबत त्याच्या पत्नीची आकृती अंकित करण्यात आली. याचे पहिले साक्ष गुप्तांचे प्राचीनतम स्वर्णशिक्के चंद्रगुप्त कुमारदेवी प्रकाराने मिळायला सुरुवात होते. याचबरोबर त्याचे राज्यदंपती व विवाहप्रकार पहावयास मिळतात. समुद्रगुप्त कुमारदेवीचा पुत्र असल्याने त्यांना 'प्रयागप्रशस्ती'मध्ये 'लिच्छविदौहित्र' म्हटले गेले आहे. समुद्रगुप्ताची पत्नी दत्तदेवीने अश्वमेघ यज्ञामध्ये भाग घेतला होता. कुमारदेवी व प्रभावतीगुप्ताचा अपवाद सोडल्यास कोणतीही गुप्तकालीन महिला प्रशासनाशी संबंधीत नव्हती. कुमारदेवीने आपला पती चंद्रगुप्त प्रथम सोबत शासन केले आहे. द्वितीय चंद्रगुप्ताची मुलगी प्रभावतीगुप्ताने वाकाटक राज्याची संरक्षिका म्हणून कार्यभार सांभाळला होता. प्रभावती गुप्ताच्या वेळी वाकाटकांवर चंद्रगुप्त द्वितीयचा प्रभाव अत्यधिक होता. हेच कारण आहे की, तिने आपल्या पुना ताम्रपत्रामध्ये आपल्या पतीच्या गोत्राचा उल्लेख न करता आपल्या पित्याच्या गोत्राचा (धारण गोत्र) उल्लेख केला आहे. यावरून समजते की गुप्तकाळातील स्त्रियांचा राजकारणातील सहभाग अगदी नगण्य स्वरूपात होता.

स्त्रियांचे धनसंबंधी अधिकार :

प्राचीन भारतीय सभ्यतेमध्ये वैदिक काळापासूनच पती-पत्नी दोघांनाही पारिवारीक संपत्तीचे संयुक्त अधिकारी मान्य केलेले आहे. विवाहाच्या वेळी पती ही प्रतिज्ञा करतो की, तो आर्थिक बाबींमध्ये आपल्या पत्नीच्या अधिकाराची व हिताची उपेक्षा करणार नाही. मनुस्मृतीमध्ये म्हंटले आहे की, आपल्या पत्नीची योग्य निर्वाह व्यवस्था केल्याशिवाय पती परदेशगमन करू शकत नाही. गुप्तकालीन स्मृतीमध्ये स्त्रियांच्या संपत्तीसंबंधी अधिकारांना मान्यता देण्यात आली. तसेच हे अधिकार अधिक विस्तारलेले दिसून येत आहेत. तसेच पुरुषांच्या स्थायी मालमतेवर स्त्रियांचा अधिचय कार्यों प्रतीय काहेत. तसेच पुरुषांच्या स्थायी मालमतेवर स्त्रियांचा अधिकार असतो आणि स्त्री धनासोबत ती ही मालमत्ता विकू शकते अथवा गडाण के जन्मी अथवा गहाण ठेवू शकते. याज्ञवल्क्य हा पहिला स्मृतीकार आहे, ज्याने पतीच्या पत्रविरहीत निधनानंत जिल्ला के पतिला स्मृतीकार आहे, ज्याने पतीच्या पुत्रविरहीत निधनानंतर स्त्रिला पतीच्या संपत्तीचे अधिकारी मानले आहे. विधवांच्या जन २०२२ (20)

इतिहासाचार्य वि.का.राजवाडे संशोधन मंडळ,धुळे.

संशोधक

संपत्तीसंबंधीच्या अधिकाराची त्यांनी उदारपणे व्याख्या केलेली आहे. त्यांनी उत्तराधिकारी म्हणून पुत्रानंतर त्या स्त्रीस अधिकार दिलेले आहेत. याज्ञवल्क्य व बृहस्पती यांनी स्त्रीला पतीच्या संपत्तीची उत्तराधिकारी मानली आहे आणि तिच्यानंतर कन्येला. बृहस्पती आणि नारदांनी म्हटले आहे की, कन्यासुद्धा पुत्रासमान संतती आहे. म्हणून जर पुत्र नसेल तर कन्येचा पित्याच्या संपत्तीवर अधिकार असेल. कात्यायनाने पत्नीला 'धनहरि' (संपत्ती प्राप्त करणारी) म्हटले आहे आणि ती जीवंत नसल्यास कन्येला. परंतु नारदासारख्या शास्त्रकारानुसार ज्या व्यक्तिस मूलबाळ नसेल त्याची संपत्ती राज्याने अधिग्रहीत केली पाहिजे आणि राजाचे हे कर्तव्य आहे की, त्याने विधवांचे पालनपोषण करावे. या काळात विधवांचे जीवन खडतर होते म्हणून काही विचारवंतांनी तिच्या संपत्तीविषयीचे अधिकार स्वीकारले आहेत.

स्त्रीधन:

हिंदू व्यवस्थाकाराने स्त्रियांना चलसंपत्तीमध्ये पूर्ण अधिकार प्रदान केलेला आहे. स्त्रिला विवाहाच्या वेळी भेट म्हणून मिळालेली रत्नभूषणे, अलंकार, बहुमूल्य वस्त्रे यांसारख्या वस्तूंवर तिची मालकी असल्याचे सर्वच प्राचीन स्मृतीग्रंथांत म्हटले आहे. त्यांच्यानुसार विवाहाच्या वेळेस वधूचे मातापित्याकडून ते सासू-सासरे यांनी ज्या भेटवस्तू दिलेल्या असतात त्यास 'स्त्रीधन' असे म्हटले जाते. स्मृतीग्रंथांच्या अध्ययनातून आपणास स्त्रीधनाविषयी विस्तृत माहिती मिळते. मनुने स्त्रीधनाचे सहा प्रकार सांगितले आहेत.

१) पित्याद्वारे कोणत्याही वेळी मिळालेला उपहार.

२) मातेद्वारे दिलेला उपहार.

- ३) भावाद्वारे दिलेला उपहार.
- ४) पतीद्वारे विवाहानंतर दिलेला उपहार.
- ५) विवाहाच्या वेळी इतरांकडून मिळालेले उपहार.
- ६) विवाहानंतर कोणाकडूनही मिळालेले उपहार.

स्त्रीधनाची दोन भागामध्ये विभागणी केलेली आहे.

- १) सौदाकीय;
- २) असौदाकीय

इतिहासाचार्य वि. का. राजवाडे संशोधन मंडळ, धुळे. संशोधक) इतहाला भाषा होतहाला भाषा भाषा, पिता किंवा पतीकडून प्राप्त धन स्वतः जवल सौदाकीयानुसार कन्या माता, पिता किंवा पतीकडून प्राप्त धन स्वतः जवल सादाकायानुराग् न हेवू शकते व त्याच्यावर तिचा पूर्ण अधिकार असेल. तसेच दुसऱ्या नातेवाईकांकडून ठेवू शकत व त्या ज्यायर स्व किंवा साधनाकडून प्राप्त झालेले स्त्रीधन असौदाकिय समजले जाते. सौदाकीय किंवा साधनाकडून प्राप्त झालेले व्यक्ति क्या क्या कार्या के क्या किवा सायगापद्धा तरा तरी ती असौदाकीय धन उपयोगात आणू शकते, धनावर तिचा अधिकार असला तरी ती असौदाकीय धन उपयोगात आणू शकते, धनावर गापा आन्य गाही. कात्यायनानुसार स्त्री आपली संपत्ती (स्त्रीधन) विकृ भए जिस समाण ठेवू शकते. परंतु नारदाच्या म्हणण्यानुसार स्त्रीचा स्त्रीधनामधील केवळ चलसंपत्तीच विकता येईल. ज्या स्त्रिया व्यभिचारी, अपवित्र, चांगले आचरण असणाऱ्या नव्हत्या त्यांना स्त्रीधनापासून वंचित करण्याचे विधान शास्त्रकाराने केलेले आहे.

'अप्रजस्त्रीधन भर्तृब्राहादिष् चतुर्ष्वपि।

दृहितृणा प्रसुता चेच्छेषेशु पितृणामि तत।।'

- याज्ञवल्क्य २, १४५

प्रारंभी स्त्रीधनाचे क्षेत्र संकुचित होते. त्यामध्ये वस्त्रे, आभुषणे येत. नंतरच्या काळात ते व्यापक बनले. शेवटी स्त्रीधन हे उत्तराधिकारामध्ये कन्येला देण्याबद्दल कोणीही विरोध केला नाही.

विवाह:

प्राचीन हिंदू समाजाचा सर्वाधिक महत्त्वपूर्ण संस्कार म्हणजे 'विवाह' होय. ज्याचे महत्त्व आजही विद्यमान आहे. गृहस्थाश्रमाचा प्रारंभ याच संस्काराने सुरु होतो. याचा शाब्दिक अर्थ आहे वधूला वराच्या घरी घेऊन जाणे अथवा पोहोचवणे. प्राचीन भारतीय समाजामध्ये यास पवित्र धार्मिक संस्था म्हणून मान्यता मिळाली. ज्याचा उद्देश पती व पत्नीच्या सहयोगाने विभिन्न पुरुषार्थ पूर्ण करणे आहे. याचा आदर्श फक्त यौनसुख प्राप्त करणे नसून संतती उत्पत्तीला धर्मगत आधार बनला.

'अपत्नीको नरो भुप कर्मयोग्यो न जायते।

ब्राह्मणः क्षत्रियो वापि वैश्यः शूद्रोऽपि वा नृपः।।

- याज्ञवल्क्य १.५१

याज्ञवल्क्याने स्पष्ट लिहिले आहे की ब्राह्मण, क्षत्रिय, वैश्य, शूद्र कोणीही असो; जर तो विवाहीत नसेल तर तो कर्म करण्यायोग्य नाही. शक्यतो सजातीय विवाह होत होते. कधी-कधी खालच्या वर्णातील स्त्रियांचे उच्चवर्णामध्ये विवाह

(22)



😭 इतिहासाचार्य वि.का.राजवाडे संशोधन मंडळ,धुळे.

स्राधक

होत होते. अशा विवाहांना 'अनुलोम' विवाह म्हटले जात होते. स्मृतीग्रंथ यांना मान्यता देतात. गुप्तकाळामध्ये मुलींचा विवाह सामान्यत: १२-१३ वर्षाची असताना होत असत. 'याज्ञवल्क्य' नुसार स्त्रियांचा विवाह हाच त्यांचा उपनयन संस्कार आहे. ऋतुप्राप्ती पूर्वीच कन्येचा विवाह करावा असा आदेश स्मृतीतून देणेत आला आहे. पुराणामधूनही स्त्रीच्या विवाहाची वयोमर्यादा कमी करण्याचीच प्रवृत्ती आढळून येते. या काळात स्त्रियांच्या स्थितीमध्ये निरंतर ऱ्हास होताना पहावयास मिळतो. स्त्रियांच्या अज्ञानामुळे स्मृतीकारांनी हा सिद्धांत मांडला की पती हा पत्नीचा देव आहे आणि तिचा धर्म आहे त्याची आज्ञा पाळणे व पूजा करणे. उपनयन समाप्ती व बालविवाहाच्या प्रचलनामुळे तिला समाजामध्ये अत्यंत खालच्या स्थितीमध्ये आणून ठेवले.

बहपत्नीत्व :

गुप्तकाळामध्ये बहुपत्नीत्वाची प्रथा राजघराणे, सरदार व श्रीमंत लोकांपुरतीच मर्यादित असावी. या काळात ही प्रथा पहावयास मिळते. गुप्तकाळातील उच्चवर्णीय लोक जास्तीतजास्त जमीन अर्जित करीत असत. ज्यामुळे त्यांच्यात एकापेक्षा जास्त पत्नी असल्याची उदाहरणे पहावयास मिळतात. पत्नीला खाजगी संपत्ती मानले जावू लागले. बहुपतीत्वाची प्रथा फार थोड्या प्रमाणात पहावयास मिळते. प्राचीन भारतीय संस्कृतीमध्ये एक विवाह आदर्श समजला जातो. हिंदू शास्त्रकार काही विशिष्ट परिस्थितीमध्येच पुरुषांना दुसरी पत्नी असण्यासाठी अनुमती देतात. वात्स्यायन, नारद, मनु यांच्या विवरणावरून लक्षात येते की, बहुपत्नीत्वाच्या पाठीमागे पुत्रप्राप्ती हा उद्देश असावा.

विधवाविवाह:

स्त्रिला समाजात जे काही मानाचे स्थान व सामाजिक दर्जा प्राप्त होत असे तो केवळ एखाद्याची पत्नी म्हणूनच मिळत असे. स्त्रीच्या वैवाहिक जीवनाचा आधार फक्त तिचा पती असे. गुप्तकालीन कालखंडामध्ये आपल्याला स्त्रीच्या पुनर्विवाहाबद्दल दोन मते पहावयास मिळतात. बृहस्पतीनुसार विधवांनी आजन्म ब्रह्मचर्याचे पालन करावे. व्रत, उपवास, तप, दान करावे किंवा सती जावे, परंतु पुनर्विवाह करू नये. परंतु नारद व पाराशर यांनी विधवा विवाहास अनुमती दिलेली आहे. 'अमरकोश'मध्ये विधवा पुनर्विवाहासाठी 'पुनर्भू' शब्दाचा वापर

इतिहासाचार्य वि. का. राजवाडे संशोधन मंडळ, धुळे. संशोधक केला गेला आहे. या काळामध्ये विधवांची स्थिती चांगली नव्हती. एकदा का केला गेला आह. या पाळा केला गेला आह. या पाळा आपला पती गमावला की स्त्रीचा सामाजिक दर्जा संपूर्णपणे नष्ट होत असे. विधवा आपला पता गमापुरा। या राग प्रधानां का मां होऊन तिचे जिणे कंटाळवाणे. स्त्रीचे सर्व सुख, सन्मान, आशाआकांक्षा नष्ट होऊन तिचे जिणे कंटाळवाणे. असहाय्य, अर्धमृत आणि अपमानास्पद होत असे.

नियोग प्रथा :

ग प्रथाः प्राचीन समाजामध्ये नियोग प्रथा ही प्रचलित होती. ज्या अतर्गत पतीविरहीत स्त्रिया पुत्रप्राप्तीसाठी दिरासोबत अथवा स्वतःच्या गोत्रातील व्यक्तिसोबत संबंध ठेवू शकते. पती रूग्ण असेल, नपुंसक असेल अशा परिस्थितीमध्ये सुद्धा अशा प्रकारचा संबंध स्थापित केला जात होता. अशा संबंधातून जन्माला येणाऱ्या पुत्राला क्षेत्रज पुत्र म्हणजे जात होते व तो आपल्या मृतपित्याच्या संपत्तीचा उत्तराधिकारी होता. स्मृतीग्रंथांनी नियोग प्रथेला अत्यंत कठोर प्रतिबंधांतर्गत मान्यता दिलेली आहे. मनू, याज्ञवल्क्य व नारद यांच्यानुसार नियोगीला विधवेसोबत एक पुत्र जन्माचाच अधिकार आहे. कालांतराने या प्रथेची अत्यंत निंदा करण्यात आली. मनूने त्यास पशुधर्माची संज्ञा दिली आहे. बृहस्पतीने ह्या प्रथेस निषिद्ध मानले आहे. अन्य शास्त्रकारसुद्धा ह्या प्रथेची निंदा करतात. सतीप्रथा:

सती जाण्याची अमानुष चाल ही भारतीय समाजाला लागलेले गालबोट व लांछनास्पद गोष्ट होती. मृत पुरुषाच्या विधवा पत्नीने भारतीय स्त्रीवादाचा आदर्श या नात्याने मृत पतीच्या चितेवर स्वतःला जाळून घेऊन सहगमन करावयाचे असे. पतीच्या निधनानंतर त्याच्या पत्नीला सती जाण्यासाठी प्रेरित केले जाई. गुप्तकाळातील साहित्य 'मृच्छकटिक' मध्ये चारुदत्ताची पत्नी सती गेल्याचे उदाहरण पहावयास मिळते. पहिले ऐतिहासिक सती गेल्याचे प्रमाण ५१० ई. मधील भानुगुप्ताच्या ऐरण अभिलेखामध्ये मिळते ज्यात गोपराज (सेनापती) च्या मृत्युनंतर त्याची पत्नी सती गेल्याचे पहावयास मिळते. गुप्तकाळामध्ये ह्या प्रथेला लोकप्रियता मिळाली नाही आणि त्याला कोणतीही शास्त्रीय मान्यता ही मिळू शकली नाही. पडदापद्धत :

पडदापद्धतीचा प्राचीनतम उल्लेख महाकाव्याच्या वर्तमान संस्करणामध्ये जून २०२२



🙀 इतिहासाचार्य वि.का. राजवाडे संशोधन मंडळ, धुळे.

(१०० ई.पू.) मध्ये प्राप्त झालेला आहे. पडदा पद्धत उत्तर भारतात प्रचलित होती. साहित्यामध्ये याचा उल्लेख केला गेला आहे. परंतु दक्षिण भारतामध्ये पडदापद्धत अस्तित्वात नव्हती, कारण अजिंठा, एलोरा, सांची व भरहत येथील चित्र, नाटक, मुद्रांवर ज्या राण्यांचे चित्र आहे त्यात त्यांनी कोठेही पडदा घेतलेला दिसून येत नाही, यावरून पडदापद्धत दिसून येत नाही. स्त्रिया स्वतंत्रपणे वावरत होत्या. परंतु कुलीन वर्गातील स्त्रियांमध्ये पडदा पद्धत दिसून येते. गुप्तकाळात पडदापद्धत जास्त विकसीत नव्हती. फहियान, ह्युएनत्संग व इत्सिंग यांनी या प्रथेचा उल्लेख केलेला नाही. 'मृच्छकटिक'मध्ये वसंतसेनेला पडदा धारण करण्यासाठी विरोध करताना पहावयास मिळते. माघच्या व भवभूतीच्या रचनांमध्ये पडदापद्धत प्रचलित असल्याची माहिती मिळते. स्त्रिया बंधनात जरी असल्या तरी त्यांना स्वतंत्रपणे वावरण्याची मुभा होती. त्यांना अनोळखी लोकांशी बोलण्याची परवानगी नव्हती. गुप्तकाळामध्ये पडदापद्धत पूर्णपणे नाही परंतु सामान्य पद्धतीने उच्चकुलीन वर्गातील स्त्रियांसाठी पहावयास मिळते, सामान्य स्त्रियांसाठी नाही. स्त्रीव्यवसाय:

गुप्तकाळात उच्चवर्णीय स्त्रियांना उदरनिर्वाहाचे साधन नव्हते. कनिष्ट दोन वर्गांतील स्त्रियांना त्यांच्या उदरनिर्वाहासाठी अर्थार्जन करण्याची मोकळीक होती. त्यामुळे त्यांना थोडेफार स्वातंत्र्य मिळाले. मात्र तशाप्रकारे स्वातंत्र्य उच्चवर्णीय स्त्रियांना नाकारण्यात आले होते. वैश्य आणि शूद्र स्त्रिया शेतीची विविध कामे आणि घरगुती कामे करीत असल्यामुळे त्यांच्या पतीचे त्यांच्यावर अधिपत्य नसे. दक्षिण भारतात स्त्रियांकडे प्रशासनातील महत्त्वपूर्ण पदे असत. स्त्रिया, कलाकार, कवयित्री, गुप्तचर, शिक्षिका म्हणून कार्य करीत होत्या. परंतु गुप्तकाळात बालविवाह होत असल्याने स्त्रियांना शिक्षण घेता येत नसे. तरी उच्चवर्णीय स्त्रियांनी शिक्षण घेतले तरी त्या उदरनिर्वाहासाठी सर्वस्वी पतीवर अवलंबून होत्या, हे त्यांना समाजामध्ये दुय्यम स्थान मिळण्यामागचे प्रमुख कारण आहे. गणिका :

गणिका समाज जीवनातील एक सामान्य अंग होत्या. गणिकांकडे पाहण्याचा समाजाचा दृष्टीकोन भावूकही नव्हता आणि उपेक्षितही नव्हता. समाजाच्या दृष्टीने गणिका समाजाचे अत्यावश्यक अंग होत्या. गणिकांना दिल्या जाणाऱ्या प्रशिक्षणाचे

संशोधक

😧 इतिहासाचार्य वि. का. राजवाडे संशोधन मंडळ, धुळे. कर्णन 'कामसुत्रात' येते. त्या काळात गणिकांचा व्यवसाय तेजीत होता व उच्च वर्णन 'कामसुत्रात' येते. त्या काळात गणिकांचा व्यवसाय तेजीत होता व उच्च वर्णन 'कामसुत्रात थत. (पा प्राप्त प्रतिष्ठा होती. 'विदिशा'तील साहसी दर्जाच्या गणिकांना समाजात काही प्रमाणात प्रतिष्ठा होती. 'विदिशा'तील साहसी दजोच्या गाणकाना समाजात. नवयुवकांनी गणिकांबरोबर केलेल्या क्रीडांचे वर्णन कालिदासाने केलेले आहे. नवयुवकाना गाणपगणपान्त्र अत्सवाच्या वेळी उत्सवात सहभागी होण्यासाठी मोठचा संख्येने गणिका/वेश्या उत्सवाच्या प्रधा अस्ति विशाखादत्तच्या 'मुद्राराक्षस'मध्ये आहे. वृद्ध वेश्यांना रस्त्यावर आल्याचा उल्लेख विशाखादत्तच्या 'मुद्राराक्षस'मध्ये आहे. वृद्ध वेश्यांना रस्त्यावर आएपापा उत्तराज्य 'कुट्टनी' म्हटले जात होते; ज्या नवीन वेश्यांना मार्गदर्शकाचे काम करीत होत्या अणि यासाठी त्या त्यांच्या कमाईतील एक हिस्सा घेत. दयनीय परिस्थितीत जगर गराज असलेल्या कुमारिकांना वेश्याव्यवसायामध्ये आणले जात होते. 'कुट्टनीमतम'चे रचनाकार दामोदरगुप्त यांनी म्हटले आहे, 'जो वेश्यांच्या जाळ्यात अडकणार नाही तो जीवनात सुखी राहील.'

मूल्यमापन:

प्राचीन भारतीय ग्रंथांमध्ये व लेखकांमध्ये स्त्रियांसंबंधी परस्परविरोधी विचार मांडलेले आहेत. काही ग्रंथांमध्ये त्यांच्या चरित्राबद्दल दोष दाखवून त्यांची कट्र आलोचना केली गेली आहे तर शास्त्रामध्ये व महाकाव्यामध्ये महत्त्वपूर्ण आदर्शाची प्रतिष्ठा स्त्रिला मिळाली आहे. शतपथ ब्राह्मणांमध्ये स्त्रीला पुरुषाची अर्धांगिनी म्हटले आहे, (अर्धो हवा एष आत्मनो). मनूने स्पष्ट लिहिले आहे की, मातेचे स्थान हे पित्यापेक्षाही श्रेष्ठ असते. गुप्तकाळातील समाजामध्ये स्त्रियांप्रती सामान्यपणे उदार व आदरपूर्वक विचार मांडण्यात आले आहेत. पत्नी, माता, कन्या म्हणून तिचा सन्मान करण्यात आला आहे. गुप्तकाळातील शिक्क्यांवर कुमारदेवी व लक्ष्मीचे चित्र उच्चवर्गातील स्त्रियांच्या सन्मानाचे प्रतीक होते. गणिकांना समाजामध्ये महत्त्वाचे स्थान होते तरी सुद्धा आपल्याला पहावयास मिळते की, धर्माचा आधार घेऊन त्यांच्यावर सामाजिक बंधने लादली गेली. संदर्भ :

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्रियः, यथ साधना गर्ना नद्यता, हा तार्क्षभा छोड ५८ दे से भाग हे है.

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EMERGING TRENDS IN ONLINE SHOPPING BEHAVIOR OF E-SHOPPERS IN SANGLI DISTRICT

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Abstract:

Online shopping is most emerging area of shopping today. About 40% of Indian population engaged in online shopping at the end of May 2020. Online shopping means selling of the goods directly to the consumer by using electronic media. Consumer gets his product by visiting different websites which are available for online shopping. Different types of e-retailers as well as e-wholesalers are available and consumer can shop online by using mobile, computers, laptops etc. As the days changes buying behavior of online shoppers is also going to change. Wide range of factors are affected on e-shoppers behavior like price, manufacturer/ producer, discount availability, price, shopping mood, availability of money, desire of goods etc. The present research paper attempts to study e-shopping buying behavior of customers, factors affecting purchase decisions, satisfaction level of customers along with some concluding remarks.

Keywords: e-shopping, electronic media, customers, behavior

Introduction:

E Commerce is an electronic commerce which includes trading of goods and services through electronics media. E -shopping is the act of purchasing products or services over the internet. Over the years such online shopping is getting more and more popularity because people find it is convenient and easy to shop whenever needs at per his own choice as per his own place. The important benefit that Eshopping has instead of traditional shopping one can no need to wait for a long time to search the product from store to store.

Objectives of the Study:

- To studye-shoppingbuyingbehavior of customers.
- 2. To find out factors influencing purchase decision regarding e-shopping.
- To know the satisfaction level of customers regarding e-shopping.

ResearchMethodology:

- 1. Research Design :Researcher used diagnostic research design for the present research.
- 2. Data Required: Present study requires demographic details of individuals like age, marital status, occupation, family income, place of internet access, use of internet, different products and services shopped online, factors that influenced purchasing decisions, factors or elements that affects buying decisions, etc. are required to know

நவீனத் தமிழாய்வு (பன்னாட்டுப் பன்முகத் தமிழ் காலாண்டு ஆய்விதழ்) 23-24 டிசம்பர் 2021 – சிறப்பிதழ் (ISSN: 2321-984X) Modem Thamizh Research (A Quarterly International Multilateral Thamizh Journal) 23-24 December, 2021 - Special Issue (ISSN: 2321-984X) Third International Multi-Disciplinary Conference On "Emerging Trends in Humanities, Commerce, Management, Science and Technology 2021. (IMCET – 2021)" Organized by: Rayat Shiksan Sanstha's Balwant College, Vita, Maharashtra.

International Journal of Mechanical Engineering

Detection of Leaf Disease using Residual Neural Network

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Abstract - The Deep residual learning framework has achieved great success in image classification. This paper represents the training of a screened leaf image data set to recognize a particular feature of leaf disease symptoms using convolutional neural networks. The new way of methodology and training used to facilitate the easy and rapid implementation of the system in practice. "The trained model" is able to identify two types of mango "leaf diseases", "healthy leaves" and allowing plant leaves to be distinguished from their surroundings. This paper describes all the steps from capturing the images, assessed by agricultural experts to form a dataset, and train a dataset using different neural architecture. A deep Residual framework ResNET used to perform deep CNN training. The ResNETs are easy to optimize and can easily gain better accuracy. The experimental results obtained from different neural ResNET architectures such as ResNet18, ResNet34, ResNet50, ResNet101 achieved accuracy from 94% to 98%. From the trained model accuracy, the ResNET with 18 layers model with 98% accuracy is selected for deployment. The application will help farmers to identify and facilitate the decision making, quick and efficient leaf disease. *Index Terms* - CNN, Deep Learning, Mango Disease, Neural Network

INTRODUCTION

India is one of the largest producers of "mango crop" worldwide. Many people in India region are farmer's dependent fruit production. However, the country is not so developed in this present time behind the international market for exporting due to quite "less yield" and quality enhancing of different fruit due to "bacterial growth" in crop. The development of bacteria in plants presents in specific parts of different plant and leaves which are major factors for continuous decrease of "nurturing growth" in the coming years for the agriculture. There are various diseases which affect the crops greatly. The specific diseases impacts and that results in the "irregular shaped" "black patches" which can be seen distributed over the "leaf surface". Along with that, the "fungus" can present at "damp situations" in the "patches". Thereafter, these "patches" begin in some small shapes but also they occupy the whole area of that leaf as well as fruit and then it result in "rotten fruit" or "rotten leaves". It is important to identify and control these types of different diseases in their initial state. Therefore, it is important to prevent "the diseases" in the early stage of affecting "the basic operation" of the plant body such as "transpiration", "Photosynthesis", "pollination", "germination", "fertilization" etc. Thereafter, these types of diseases are occurred because of the "pathogens" such as "fungi", "bacteria" and "viruses". It requires monitoring continuously of the body of the plant which is a "time consuming process". This is also required to find out some specific methods to identify the diseases on those plants at early stages of the process (Ramcharan Amanda, Peter, Babuali, James, & P., 2017). So the latest method researcher is going to develop for detecting plant leaf disease which will be more accurate and less time consuming.

DISEASES

Disease categories: There are two common diseases in mango plant leaves as shown in Figure 1. Each of the leaf diseases has unique symptoms and unique features, these features can help to categorize and differentiate infected plants by deep learning algorithms. Deep neural networks led to a number of progresses in the classification of images.

Anthracnose: The specific disease can cause the decrement to young fruits and flowers. It affects fruits during the storage .It produces "blossom blight", "leaf spot", "twig blight", "wither tip", and "fruit rot" symptoms. "Foliage" and "Tender shoots" are impacted which can cause dieback of the branches in earlier stages. Different types of infection destroy the whole "inflorescence" that results in "no setting of fruits". Furthermore, young fruits that are infected can have "shrivel", "black spot" and "drop off". Therefore, fruits are infected at "mature stage" continue the "fungus" and that can cause serious loss at the time of "storage", "transit" and "marketing" (Ullagaddi & Raju, 2014).

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Disease Symptoms

Red rust: It is due to an "alga", which is identified in the "growing areas" of leaf. Due to the "algal attack" the deduction in "photosynthetic activity" as well as "defoliation" of leaves occurred and "lowering vitality" of the "host plant". Furthermore, the specific disease can be identified by recognizing the "rusty red spots" on the "leaves and petioles" as well as "bark of young twigs" and is "epiphytic" in nature. Initially the spots are present in "greenish grey" color and "velvety in texture". After that, they turn "reddish brown". The "slightly elevated" spots on the leaves sometimes "coalesce" and then form into "larger" and "irregular spots". The disease occurs commonly in "closely planted orchards".

DATESET

To resolve the "presence and incidence" of leaf disease, nearly "3319 samples" from about "20 fields" were collected systematically from the production areas across Konkan

("3,319 samples"; "20 fields"). After using expert diagnostics, it is identified that "infected plants" represents nearly 3% of the entire number of fields that are sampled. Thereafter, the "infected fields" were searched geographically in two provinces of Konkan area i.e. Ratnagiri, Sindhudurg in West Maharashtra.

Field	Localization(city)	Number of plants
Field1	Regional Fruit Research	400
	Station Vengurle, Dist.	
	Sindhudurg	
Field2	Mango Research Sub Centre	885
	Rameshwar (Girye), Tal.	
	Devgad, Dist. Sindhudurg	
Field 3 to	Mango Orchids in	460
Field 20	Sindhudurg, Ratnagiri	
	Table 1	

Samples collected from various fields

When we use "deep neural networks", it requires three different dataset for developing a specific model (Y A Nanehkaran, Chen, & Tian, 2020). The "training set" is the first set of the network and the set is a gathering of different images that are used by the specific network which helps the network to learn the parameters automatically that are hidden like "weights" and "biases". The validation set, the second set is used to adjust the "hyper parameters" manually, these are the "essential settings" which is unable to be learned in the time of the training (Ramcharan Amanda, Peter, Babuali, James, & P., 2017). The photos collected by camera of both healthy and unhealthy leaves were splatted into 3 categories Healthy, Anthracnose and Red rust under the supervision of experts from agriculture representing each class rather than splitting it into binary.

Class	Number of Original Images	Training (70%)	Testing (15%)	Validation (15%)
Healthy Images	566	396	85	85
Anthracn ose	702	492	105	105
Red Rust	608	426	91	91

Table2

Images for each category of leaves captured by camera

"Data Augmentation": "Data augmentation" is an effective strategy that makes the practitioners capable of significantly increasing the "diversity of data available" for "the training models", without gathering any new information. "Data augmentation techniques" such as "cropping", "padding", and "horizontal flipping" are generally used to train the "large neural networks" (Bharath, 2020). "The Augmentation factors" used for data augmentation are

Augmentation Factor
Rotation Range = 60
Width_shift_range = 0.2,
Height_shift_range = 0.2
Shear_range = 0.2
$Zoom_range = 0.2$
Brightness_range = [0.5, 1.0]
Figure 2

Augmentation factor used to increase dataset

To create effective and efficient "Deep Learning models", the "validation error" decrease along with the "training errors". "Data Augmentation" is a effective technique for using to achieve this. "The augmented data" represents an important as well as comprehensive set of all "possible data points", and it reduces the gap between the "training set" and "validation set", along with that any sets for future testing. After "Augmentation" the images in the "training data", "Validation data" and "Testing data" are shown as below:

Class	Number	Training	Testing	Validation
	of Original			
	+Aug.			
	Images			
Healthy	1939	1769	85	85
Images				
Anthracnose	2423	2213	105	105
Red Rust	2390	2208	91	91

Table 3

Datasets after Data Augmentation

TRANSFER LEARNING

"Transfer learning" supports the usage of CNNs when the amount of training data is small, in the context of "crop diseases identification" (Nag & Sangskriti, 2020). These methods help to get higher "generalizability" because the network had gained knowledge before to hand out with a high number of different examples. There are a total of two different ways to carry out "transfer learns" such as "fine-tuning" and "feature extraction". In the feature extraction, the "weights of pre-trained model" keep intact and use embedding and made to train the "new classifier" on the specific data. "Fine-tuning" uses the heaviness of the "pre-trained model" to evaluate the training and the model parts. A training strategy is selected depending on technical and thematic consideration such as number of "images", "computing capacity", "availability of architecture" and "pre-trained weights" in comparison with the specific data that are used. We used transfer learning to improve generalizability and computation time. After fixing all of the hyper parameters, the model is retrained by integrating the specific images used during validation and training into a global training set. In this research we used 4 different CNN architectures (ResNet18, ResNet34, ResNet50, and ResNet101).We used the augmented dataset with a background class.



Figure 3 Residual Learning Blocks

The ResNet 18 and ResNet34 are 2 layers deep while ResNet50 and ResNet101 are 3 layer deep .The "18 layer network" is the subspace of the "34 layer network" but still it performs effectively. If the network is deeper, ResNet performs by a significant margin



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TRAINING AND EVALUATION PHASES

In this paper we present a simpler and more flexible architecture that uses ResNets' learning, utilizing the split-transform-merge approach for layers. The important challenge is to get a model which is trained and is capable of describing unseen and new in machine learning. Over-fitting happens when the input sample number becomes small in comparison with the learning capability of the specific network. Furthermore, over-fitting does not support learning about the "general characteristics" and instead it identifies the "noise of the training set". When we try to run the model on this input data, accuracy looks great. Thereafter, "deep learning of neural networks" is trained using the "stochastic gradient" that descent "optimization algorithm". The rate of learning is a "hyper parameter" that controls the changes in the model in order to respond to the "estimated error" every time that the model "weights are updated". The learning rate for all four architectures ResNet18, ResNet34, ResNet50, and ResNet101 is discussed here.

The learning rate of models



Learning Rate for ResNet18, ResNet34, ResNet50, ResNet101 architectures

The best values of the hyper parameter were found through "tuning techniques" to improve the model. This tuning was performed using the Learning Rate Finder (LRF), which compared these settings with one another until it found the optimal learning rate for the model which is shown in Figure 5.

In Figure 5, The Train loss, Error Rate and Accuracy of the Model are given for validation dataset given by all four CNN architectures ResNet18, ResNet34, ResNet50, ResNet101.



Figure 6 Validation Loss, Error Rate, Accuracy for each CNN architecture

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The confusion matrix for all 4 networks is given below.



Confusion Matrix for four CNN Architectures for validation dataset

RESULTS AND DISCUSSIONS

Learning Rate Finder: Observing Figure 5, it can be identified that the specific network model was capable to start "model learning" rate from "1e-6" to "1e-1". Initially the oercentage of learning was very less and the network became powerless to gain knowledge. The minimum loss was observed at "1e-1" and then a loss up to 1e⁻⁰ was faced then decreased. The CNN Model accuracy for validation set is given below at the optimized learning rate is 98% for ResNet18, 96% for ResNet34, 98% for ResNet50 & 96% for ResNet101.

Architecture	Resnet 18	Resnet 34	Resnet 50	Resenet
				101
Accuracy	0.987261	0.961783	0.98082	0.968153
		Figure 8		
	Accura	cy for validati	ion set	

"Precision", "Recall", "F1-Measure" as well as these are described in "Eqs". (1)–(4). "Precision" is the process to predicted measure "true positive values" appropriately to the entire count of "positive predicted observations". "Recall" is the process to measure the count of "positive class predictions" created with different "positive predictions". "F-Measure" is the process to measure that maintains balance between "the precision" and "recall" (Eq. (3)) (Sambasivam & DuncanOpiyo, 2020).

	True positive	
Precision = True pos	itive + False positive	(1)
True	positive	(2)
T rue posit	tive + <u>False</u> negative	
F = Measure = 2 * =	Precision *Recall	(3)
I = Measure	Precision + Recall	
Accuracy =	True Positive + True Negativ	e
Theedrace,		

True Positive+True Negative+False Positve+False Negative

"Performance Evaluation": In "Data Science", evaluation of a "model performance" is very essential and the most used "performance metrics" in classification are, "confusion matrix" ["normalized", "non-normalized", "accuracy", "precision sensitivity"].

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Classes	Precision	Recall	"F1 Score"
Healthy	0.96	0.95	0.95
Anthracnose	0.9519	0.9428	0.9473
Redrust	0.9750	0.9652	0.9700

CONCLUSIONS

The performance of our model indicates effective results for classification of diseases like anthracnose and red rust .It shows the result by training CNNs using an "imbalanced data". Different techniques and methods are used to create a remarkable study. The ResNet18 model in Figure 8 had shown the best accuracy for the validation set. Therefore, while integrating this model into a mobile application we considered both the result for validation set as well as the precision, recall and F1 score rate. This mobile application will be useful for farmers or agricultural extension workers. The farmers can use the smart phones for "real-time monitoring" and the lession of "mango infections" for ensuring that "necessary prevention methods" can be used.

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TOTAL STEREOSPECIFIC SYNTHESIS OF (3*E*,7*Z*)-TETRADECADIENYL ACETATE, THE MAJOR SEX PHEROMONE COMPONENT OF THE POTATO PEST Symmetrischema tangolias

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(3E,7Z)-Tetradecadienyl acetate, the major sex pheromone component of the potato pest *Symmetrischema tangolias* (Gyen), was stereoselectively synthesized from the commercially available 3-bromo-1-propanol via the stereospecific reduction of alkyne with lithium aluminum hydride (LAH) and the Wittig reaction.

Keywords: (3*E*,7*Z*)-tetradecadienyl acetate, pheromones, *Symmetrischema tangolias*, reduction, W ittig reaction, green metrics calculation.

Solanum tuberosum L. (potato) is cultivated all around the world because of its significance in human consumption and one of the cheapest staple food materials and richest sourcea of starch, dietary fibers, vitamins, and minerals. Thus, such a noteworthy crop is produced predominantly throughout the world, but this crop is severely damaged by various pests. To overcome such problems, researcher are making efforts towards controlling such pests by various measures such as use of chemical pesticides, biopesticides, and pheromones [1].

For environment friendly agriculture, two best practices are accessible, such as integrated crop management (ICM) and integrated iest management (IPM) [2]. Among them, in the ICM system the pheromones are the most frequently used and the most rapid technique for mating disruption, controlling pest, and mass trapping [3].

A literature review reveals that significant effort has been focused on the eco-friendly synthesis of sex pheromones by multistep reaction pathways, among which are protection [4], alkylation [5], reduction [6], acetylation [7], oxidation [8], and the Wittig reaction [9]; these are most widely used reactions towards the synthesis of various sex pheromones of the female moth.

The potato tuber moth *Symmetrischema tangolias* (Gyen) is recognized as a severe pest on potatoes in the field as well as in storehouses [10].

The use of insect pheromones by mass trapping and mating disruption techniques has shown promising results in controlling distressing insect pests [11].

There are very few reports on identification and synthesis of sex pheromone. In 1995 the Griepink et al. [10] isolated and identified the sex pheromone components from the female moth's gland. The main chemical components of the sex pheromones of *Symmetrischema tangolias* are (3*E*,7*Z*)-tetradecadienyl acetate and *E*-3-tetradecenyl acetate, which

were identified in the pheromone in the ratio 2:1, while Ragoussis et al., effectively investigated the synthesis of (3E,7Z)-tetradecadienyl acetate with the help of the Wittig and Knoevenagel reactions [13].

It is a very challenging task to synthesize sex pheromones stereoselectively and stereospecifically with a high overall yield and enhanced isomeric purity using a simple method. To enhance the isomeric purity and overall yield, our research group tried to address the economical, highly efficient stereoselective synthesis of (3E,7Z)-tetradecadienyl acetate. This is achieved by using stereospecific reduction and the Wittig reaction at key stages with a simple base to get stereospecific (E,Z) isomeric purity of the pheromone (1) in 99% yield by GC.

(3E,7Z)-Tetradecadienyl acetate (1), the core constituent of the pheromone of *Symmetrischema tangolias*, was synthesized by a stereoselective and stereospecific method, as mentioned. This method consists of six experimental steps (Scheme 1).

At the initial stage, to eliminate the terminal alcoholic group on both sides, a well-established protection reaction of 3-bromo-1-propanol was carried out by the reported method, which gives 2-(3-bromopropoxy)-tetrahydro-2Hpyran (2). It was employed as a starting material. Further, an alkylation is carried out with 3-butynol using LiNH₂ in liquid NH₃ to afford 7-(tetrahydro-2*H*-pyran-2-yloxy)hept-3-yn-1-ol (3) with 85% yield. An (E)-allylic bond exists in the targeted molecule; hence, to access this (E)-allylic bond, we further carried out a stereospecific and stereoselective reduction of the alcohol to the corresponding 7-(tetrahydro-2H-pyran-2-yloxy)hept-3-en-1-ol (4) in the presence of LiAlH₄ in diglyme, obtaining a good yield (84%) under heating conditions. The (E)-allylic bond in compound 4 was confirmed by gas chromatography (GC), indicating that it was predominant at retention time 8.511 with 98% purity.

Particulars	MI	%RME	%CE	%AE	Yield, %
Step I	8.76	11.4	79.65	72.40	62
Step II	6.59	15.17	83.85	85.64	84
Step III	4.80	20.82	93.24	87.54	80
Step IV	3.2	31.21	59.8	67.18	86
Step V	29.52	3.38	60.7	98.82	60
Step VI	34.08	2.93	15.24	41.26	35
	\sim			10	
$a \xrightarrow{1}{3} Br = a$	$\rightarrow 12 \begin{bmatrix} 3\\ 3\\ 0 \end{bmatrix} = 12 \begin{bmatrix} 3\\ 3\\ 0 \end{bmatrix}$			$0^{\frac{1}{8}}$	
$0^{\frac{1}{3}}Br$	$\rightarrow 12 \left(\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$			$0^{\frac{7}{8}}$	

TABLE 1. Green Metrics Calculations

a. 3-Butynol, LiNH₂, liq. NH₃, -78°C; *b.* LAH, diglyme, 140°C; *c.* CH₃COCl, pyridine, 0°C, DCM; *d. p*-TSA, r.t., DCM; *e.* PCC, 0°C, DCM; *f.* PTB, Wittig salt, -78°C, THF

HO

Scheme 1.

The resulting alcohol 4 was then acylated by using acetyl chloride and pyridine in dichloromethane to give the 7-(tetrahydro-2*H*-pyran-2-yloxy)hept-3-en-1-yl acetate (5). It was purified by column chromatography using hexane-ethyl acetate in 9:1 ratio to give an 80% yield. Then the tetrahydropyranyl group was deprotected by using *p*-toluenesulfonic acid in methanol to give 7-hydroxyhept-3en-1-yl acetate (6) in 78% yield. Compound 6 was oxidized subsequently in the presence of pyridinium chlorochromate (PCC) and sodium acetate in dichloromethane to give (3E)-7-oxohept-3-en-1-yl acetate (7) in 60% yield. Wittig olefination of (3E)-7-oxohept-3-en-1-yl acetate (7) was carried out with *n*-heptyltriphenylphosphonium bromide in the presence of potassium tertiary butoxide in THF at -78°C to produce the (Z)-stereoselectivity with 99% isomeric purity of the targeted molecule (3E,7Z)-tetradecadienyl acetate (1) in 35% yield. The stereochemical properties obtained by the Wittig reaction due to saturated aliphatic nonstabilized triphenylphosphonium ylides when reacted with primary aliphatic aldehydes in nonpolar solvents (such as THF) at -78° C in the absence of free salt led to primarily (Z)-olefins.

The target molecule was confirmed on the basis of spectroscopic data. All the spectral data, IR, ¹H NMR, ¹³C NMR, and DEPT, showed good agreement with the corresponding pheromone structure (3E,7Z)-tetradecadienyl acetate (1), while the GC report shows 99% (E,Z) isomeric purity. Finally, all the products of each step were confirmed by mass spectrometry.

Synthesis of sex pheromones is a multistep process, and it is a challenging task to follow green chemistry principles. The green metrics have been considered as an evaluator of environmental sustainability in diminishing the amount of theoretical waste. The green metrics consist of parameters like mass intensity (MI), reaction mass efficiency (RME), carbon efficiency (CE), and atom economy (AE). The MI stands for yield stoichiometry, and the RME stands for yield and excess catalytic amount of reactant excluding solvent. The CE shows the gain or loss of carbon atoms in the conversion of reactant to product, and finally AE gives provides a theoretical calculation of the process and environmental efficiency. The standard values of green metrics under ideal conditions are MI \approx 1%, RME \approx 100%, %CE \approx 100, and %AE \approx 100. To explain the greenness of the present synthesis, we have studied green metrics calculations [14].

The greater yields of the product indicate that significant RME values and moderate yield generate moderate RME values. Furthermore, the percent CE of step 1 is 79.65%, while at step 6 the percent CE is 15.24%, demonstrating a remarkable conversion. Finally, the percent atom economy of step 1 is 72.40%, and that at step 6 is 41.26%, indicating maximum conversion of starting materials into product and minimum waste.

EXPERIMENTAL

General. All chemicals used were purchased from Sigma-Aldrich and used as such. The ¹H and ¹³C NMR spectra were recorded in DMSO-d₆ (δ 2.5) on a Bruker instrument (300 MHz, 400 MHz for ¹H NMR, 75 MHz for ¹³C NMR) using TMS as an internal standard. IR spectra (KBr) were recorded on a Bruker FT-IR spectrometer, in cm⁻¹.

Gas chromatography-mass spectrometric (GC-MS) analyses were carried out on a Hewlett-Packard 5890-5970 system, equipped with a SPB-1 capillary column (20 m \times 0.25 mm, 0.33 µm film thickness, Supelco, Sigma-Aldrich Ltd., Greece): carrier gas, helium, 1 mL/min; injector temperature, 230°C;

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oven temperature, 50°C for 5 min isothermal and then raised to 250°C at a rate of 4°C/min and then held for 10 min; ion source temperature, 220°C; interface temperature, 250°C; mass range, 40–500 amu; EI, 70 eV. GC analyses were carried out on an Agilent 6890 N chromatograph either in a polar capillary column CP-Wax 52 CB (30 m×0.32 mm, 0.25 µm film thickness, Varian Inc., CA) or in a nonpolar capillary column SPB1 (20 m × 0.32 mm, 1.0 µm film thickness, Supelco, Sigma-Aldrich Ltd.): carrier gas, helium, 1 mL/min; injector temperature, 200°C; oven temperature, 60°C for 5 min isothermal and then raised to 250°C at a rate of 4°C/min and then held for 15 min.

Thin-layer chromatography (TLC) was performed on 0.25 mm precoated silica gel 60 F 254 glass plates, and column chromatography on silica gel, 60–120 mesh size (Merck & Co., Darmstadt, Germany). All commercial reagents and solvents were used as supplied. All reactions of air- and water-sensitive materials were run in oven-dried glassware under nitrogen. Air-sensitive solutions or liquids were transferred with glass syringes. Wittig salt *n*-heptyltriphenylphosphonium bromide was prepared by treatment of 1-bromoheptane with triphenyl phosphine in acetonitrile. Tetrahydrofuran was distilled from sodium benzophenone ketyl.

7-(2-Tetrahydropyranyloxy)-hept-3-yn-1-ol (3). About 500 mL ammonia was collected in a 2 L three-neck reaction flask attached to an ammonia condenser; to that, 1 g ferric nitrate and Li metal (8 g, 1121 mmol) were added portionwise. After 45 min, 3-butyn-1-ol (41 mL, 538 mmol) was added dropwise. Half an hour later, 3-bromopropanol - OTHP 2 (100 g, 448 mmol), HMPA (20 mL), and THF (200 mL) were added in 1 h. Then the reaction was maintained for 2 h, and the ammonia was allowed to evaporate. The reaction mixture was quenched with solid ammonium chloride (50 g) and saturated ammonium chloride solution (100 mL). The reaction mixture was extracted with diethyl ether (1 L) and washed with water $(3 \times 100 \text{ mL})$, followed by saturated sodium chloride solution (50 mL). Then sodium sulfate (50 g) was added, and the crude product was concentrated and then purified by column chromatography to give alkylated product 3 as a colorless oil, 81 g (85%). IR (KBr, v_{max}, cm⁻¹): 2938.9 (CH), 3438 (OH). ¹H NMR (300 MHz, CDCl₃, δ, ppm): 1.64–1.43 (4H, m, 2CH₂), 1.73–1.64 (4H, m, 2CH₂), 2.20–2.15 (2H, m, CH₂), 2.32–2.27 (2H, m, CH₂), 3.0 (1H, br.s, OH), 3.42–3.35 (2H, m, CH₂), 3.57-3.52 (2H, s, CH₂), 3.79-3.67 (2H, m, CH₂), 4.95 (1H, s, CH). GC-MS (Purity) = 99.04%. Observed GC-MS *m/z* 211.1 $[M-1]^{-}$ (calcd for C₁₂H₂₀O₃, 212.28).

7-(2-Tetrahydropyranyloxy)-hept-3(*E*)-en-1-ol (4). Enynol **3** (100 g, 471 mmol) was added slowly with stirring to an ice-cold solution of lithium aluminum hydride (35.79 g, 943 mmol) in diglyme (450 mL). After heating for 1 h at 140°C, the mixture was decomposed by careful dropwise addition of cold water (2 mL) and 6 M sodium hydroxide (25 mL). The solution was then filtered, and the solid was washed with diethyl ether (5 × 100 mL). Then the combined filtrate was washed with brine (50 mL) and dried with sodium sulfate (20 g). The reaction mixture was concentrated, and the residual oil was purified by column chromatography to give the product as a colorless liquid 4 (85 g, 84%). IR (KBr, v_{max} , cm⁻¹): 2937 (CH), 1642 (C=C). ¹H NMR (300 MHz, CDCl₃, δ , ppm): 5.51–5.31 (2H, m, 2CH), 4.5 (1H, br.s, OH), 3.83–3.64 (2H, m, CH₂), 3.56–3.52 (2H, m, CH₂), 3.46–3.32 (2H, m, CH₂), 2.59 (2H, s, CH₂), 2.22–2.16 (3H, m, CH₂), 2.09–2.02 (2H, m, CH₂), 1.78–1.54 (6H, m, 3CH₂). GC (Purity)=98.05%. Observed GC-MS *m/z* 214.2 [M]⁺ (calcd for C₁₂H₂₂O₃, 214.30).

7-(2-Tetrahydropyranyloxy)-hept-3(E)-enl Acetate (5). To a solution of alcohol 4 (50 g, 23 mmol), dichloromethane (100 mL) and pyridine (24.5 mL, 303 mmol) were added in one portion. and the mixture was cooled to 0°C. Then acetyl chloride (20 mL, 280 mmol) was added slowly along with dichloromethane (20 mL). The reaction mixture was poured onto ice, and the layers were separated. The aqueous layer was extracted with dichloromethane $(3 \times 100 \text{ mL})$. The combined organic layers were washed with water $(3 \times 100 \text{ mL})$ and brine (10 mL) and then dried with sodium sulfate (20 g). Removal of the solvent and purification of the residue by column chromatography yielded acetate 5 as a colorless oil (48 g, 80%). IR (KBr, v_{max}, cm⁻¹): 1738 (C=O), 2939 (CH). ¹H NMR (300 MHz, CDCl₃, δ, ppm): 1.50–1.97 (5H, m, CH₂, CH₃), 1.98–2.02 (8H, m, 4CH₂), 2.17–2.26 (2H, q, CH₂), 3.25-3.43 (2H, m, CH₂), 3.61-3.77 (2H, m, CH₂), 3.92-4.00 (2H, m, CH₂), 4.47-4.50 (1H, m, CH), 5.27-5.48 (2H, m, 2CH), GC (Purity) = 92.84%. Observed GC-MS m/z 256.2 [M]⁺ (calcd for C₁₄H₂₄O₄, 256.33).

7-Hydroxyhepta-3(E)-enyl Acetate (6). A solution of protected acetate 5 (40 g), 4-toluene-sulfonic acid (0.5 g), and methanol (50 mL) was stirred for half an hour at room temperature. A solution of 5% sodium bicarbonate (5 mL) was added to the reaction mixture, and the solvent was removed. The residue was extracted with diethyl ether $(3 \times 100 \text{ mL})$, and the combined ether extracts were washed with brine (20 mL) and dried with sodium sulfate (20 g). The solution was evaporated in vacuo, and the residue was subjected to column chromatography to give hydroxy acetate 6 as a colorless oil (25 g, 78%). IR (KBr, v_{max}, cm⁻¹): 1642 (C=C), 1737 (C=O), 2936 (CH), 3626 (OH). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 1.56–1.69 (2H, m, H-6), 2.01–2.15 (5H, m, CH₃) 2H-5), 2.25–2.40 (3H, m, HO 2H-2), 3.62 (2H, t, H-7), 4.07 (2H, t, H-1), 5.35–5.61 (2H, m,H-3, 4). GC (Purity) = 96.08%. Observed GC-MS m/z 112 [M-60]⁺ (calcd for C₉H₁₆O₃, 172.22).

7-(Acetoxy)hepta-3(E)-enal (7). Pyridinium chlorochromate (37 g, 174 mmol) and sodium acetate (4.7 g, 58 mmol) were suspended in anhydrous dichloromethane (200 mL) and cooled to 0°C. Then the alcohol 6 (20 g, 116 mmol) in dichloromethane (20 mL) was added in one portion to the mechanically stirred solution. After 15 min the cooling bath was removed and the resultant mixture stirred for 2 h at room temperature. It was diluted with dry diethyl ether (50 mL) and filtered through a pad of Celite. The filtrate was concentrated in vacuum to give the corresponding crude aldehyde, which was subjected to column chromatography to give aldehyde 7 as a colorless liquid (12 g, 60 %). IR (KBr, v_{max}, cm⁻¹): 1642 (C=C), 1727 (C=O), 2951 (CH). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 2.04 (3H, s, <u>CH₃</u>), 2.31– 2.36 (4H, m, 2H-5, 2H-2), 2.36-2.52, (2H, t, 2H-6), 4.05-4.08 (2H, t, H-2), 5.47–5.51 (2H, m, H-3, 4), 9.76 (1H, t, CHO).

GC (Purity) = 94.88%. Observed GC-MS m/z 142 [M – 28]⁺ (calcd for C₉H₁₄O₃, 170.20).

(3E,7Z)-3,7-Tetradecadienyl Acetate (1). The aldehyde 7 (8.67 g, 504 mmol) was dissolved in THF (20 mL) and slowly added to a stirred and cooled (-78°C) freshly prepared solution of the *n*-heptylidenetriphenylphosphorane [prepared by addition of a solution of potassium tertiary butoxide (12.69 g, 113 mmol) to a suspension of *n*-heptyltriphenylphosphonium bromide (25 g, 566 mmol) in THF (100 mL)]. After the addition, the reaction mixture was stirred for 1 h at the same temperature and then brought to room temperature while stirring. The reaction mixture was quenched with saturated ammonium chloride solution (50 mL) and diluted with diethyl ether (100 mL). Then it was washed with water $(3 \times 50 \text{ mL})$ and brine (20 mL) and dried over sodium sulfate (20 g). Subsequent evaporation of the solvent under vacuum and column chromatography afforded the pure pheromone acetate 1 as a colorless oil 4.5 g (35%). IR (KBr, v_{max}, cm⁻¹): 1658 (C=C), 1741 (C=O), 2923 (CH). ¹H NMR (400 MHz, CDCl₃, δ, ppm, J/Hz): 0.87–0.90 (3H, t, J=6.9, H-14), 1.27–1.30 (8H, m, 4×CH₂), 2.02–2.08 (9H, m, CH₃-COand $4 \times CH_2$, 2.31–2.32 (2H, q, H-2), 4.05–4.08 (2H, t, J=6.9, H-1), 5.35–5.36 (4H, m, H-3, 4, 7, 8). ¹³C NMR (300 MHz, CDCl₃, δ, ppm): 13.94, 20.65, 22.56, 27.01, 28.89, 27.16, 29.58, 31.70, 31.88, 32.62, 63.86, 125.36, 128.67, 130.20, 132.71, 170.56. ¹³C NMR (300 MHz, CDCl₃, δ ppm): 20.64, 22.55, 126.66, 127.48, 128.85, 129.24, 130.74. GC (Purity) = 95.56%. Observed GC-MS m/z 252.2 [M]⁺ (calcd 252.39).

In summary, cheap and commercially available 3-bromo-1-propanol is a very useful reagent for the preparation of pheromone (3E,7Z)-tetradecadienyl acetate (1), the main pheromone component of the potato tuber moth *S. tangolias* (Gyen). It was synthesized in six steps, and the products can be easily purified by column chromatography. The steps involved are simple, highly stereoselective, and cost effective, and the procedures easily scalable, which makes this method useful in producing the pheromone for the control of the serious insect pest *Symmetrischema tangolias*.

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