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Current Natural Sciences & Engineering (CNS&E) International Journal publishes new, innovative and cutting-edge research in Natural sciences including physical, chemical, biological, agricultural and environmental sciences, metrology, and other related interdisciplinary fields. Scientific research results in the form of high-quality manuscripts, review articles, mini-reviews, reports, news and short communications are highly welcome.

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Preface



Prof. A C Pandey Director Inter University Accelerator Centre, New Delhi, India

Peer-reviewed publications are essential to effectively communicate research findings. However, the pressure to publish has led academics to submit their work to dubious journals that neglect editorial and peer-review processes, which sometimes compromises the quality of science. India's contribution to Open Access publications is lower than the world average, which is 4% compared to 25%. However, the annual growth rate of Open Access publications from India is 12.5%. India ranks fifth globally in terms of the total number of publications and sixth in terms of Open Access publications. I take pride in being associated with the CNSE International Journal, that is committed to publishing groundbreaking research papers through a rigorous peer-review process while upholding the highest ethical values for scientific communities across emerging disciplines. The journal covers the latest advancements in energy, materials science, environment, medical science, agriculture, and nuclear radiations for health & industrial technologies, including breakthroughs that deepen understanding of natural sciences. The CNSE journal's mission is to support scholars and faculty members who cannot afford exorbitant publishing charges in the name of open access to journals.



Prof. K K Pant Director, IIT Roorkee



Prof. Sanjay Behari Director Sree Chitra Tirunal Institute for Medical Sciences and Technology, Thiruvananthapuram, India.

I am happy to learn that first issue of Current Natural Sciences & Engineering (CNSE) International Journal is being published. This Journal is a peer reviewed comprehensive interdisciplinary journal in an open access mode and aims to publish new, innovative and cutting-edge research in the areas of Natural sciences including climate change, net zero carbon, Green Hydrogen, and sustainability. I am sure that the CNSE will be able to provide a unique platform to Scientists, Researchers & Engineers involved in the new science worldwide to publish their research findings for industries in the benefit of the society.

I am privileged to congratulate Prof Kotnala for envisaging the concept of CNSE, an International Journal that will serve as a platform to showcase scientific achievements in multi-disciplinary areas. I sincerely hope that publishing research papers through a rigorous peer reviewed process, maintaining high ethical values for scientific communities across emerging disciplines, will go a long way in fostering innovation. The journal covers current advancements in energy, materials science, environment, medical science, agriculture, as well as nuclear radiations for health & industrial initiatives. The CNSE journal's mission is to support all those scholars/faculty members who express the desire to have their research publications read and utilized by a diverse group of scientists in multiple fields. The journal, therefore, aptly addresses the multidisciplinary emphasis and the emergence from small silos in research, which is the need of the hour. The focus today should be on translating the end user experience into technological products and advances. I wish the journal my very best wishes.

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Prof. R K Sinha Vice Chancellor Gautam Buddha University, G Noida



Prof. Bhanooduth Lalljee President, Sustainable Agricultural Organisation, External Professor at MIE, Mauritius.



Dr. Indra Mani Vice-Chancellor, VNMKV, Maharashtra, India

I am privileged by my association with CNSE International Journal which has taken a big step to publish research papers through a rigorous peer reviewed process maintaining high ethical values for scientific communities across emerging disciplines. It majorly covers current advancements in energy, materials science, environment, medical science, agriculture, nuclear radiations for health & industrial technologies including breakthroughs to understand natural science more deeply. The CNSE journal's mission is to support all those scholars/faculties who cannot afford heavy publishing charges in the name of open access of the journals.

To the Scientific community, it gives me an immense pleasure and I am privileged as part of the editorial team and panel of reviewers to write a small note for this first issue of our journal, CNS and E, Current Natural Sciences and Engineering. Scientific research and publications are increasing exponentially with the IT age and Artificial Intelligence. However, many scientists, especially young scientists, are finding it difficult to publish in established high impact factor journals because of the very tough requirements of these journals and exorbitant publication fees. This new journal will give them a new opportunity and an avenue to make their scientific research findings and make them available to the general public. The Journal has a dedicated International team of reviewers and editors and papers submitted to the journal are processed quickly, effectively and efficiently without jeopardizing the rigorous scientific merit. I wish the journal plenty of success, wide readership and citations and long life.

I am delighted to know that the Current Natural Sciences & Engineering (CNSE) International Journal has published its first issue. I extend my warmest congratulations to everyone involved in this groundbreaking endeavor. This journal, a beacon of innovation and knowledge, is set to revolutionize the dissemination of scientific and engineering research. CNSE stands as a testament to the collective genius of scholars and engineers worldwide, offering a unique and expansive platform for sharing research that spans a diverse array of critical fields, from condensed matter and nanomaterials to digital agriculture and health science. The inclusion of key subjects underlines the journal's commitment to a broad spectrum of vital scientific areas, ensuring comprehensive coverage of the latest advancements. What makes CNSE particularly commendable is its approach to accessibility and global reach. By adopting an open access mode, free from heavy publishing charges, the journal not only fosters global visibility but also represents a significant step towards economical scientific publishing, particularly beneficial for Indian researchers.

Best wishes to the editorial board of the CNSE International Journal in their endeavor to enlighten minds and inspire a sustainable future through scientific excellence and innovation. May this journal soar to new heights, contributing significantly to the advancement of science and engineering for the betterment of society.

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Dr A K Srivastava Director, CSIR-AMPRI

I am pleased to announce the inaugural issue of the CNSE International Journal. The journal is committed to publish top-tier research in condensed matter and nanomaterials, engineering materials, sensors, green energy, environmental science, hydrogen energy, health science and technology, sustainable agriculture, and more. Our stringent editorial policy ensures only high-quality research makes it to publication, setting the journal on course to become a pioneer in the realm of science and engineering. Best wishes for the journal's success and influence in advancing scientific knowledge.



Dr. S.K. Jha, Outstanding Scientist & Head, Radiation Protection Section, BARC.

In the first issue of Current Natural Sciences & Engineering journal, we delve into cutting-edge and application-oriented research and innovative discoveries at the forefront of scientific inquiry in the fields of physical sciences, energy, metrology, nanoscience, chemical and environmental sciences. From advancements in energy technologies to breakthroughs in materials science, each contribution represents a significant step forward in our understanding of the natural world and its engineering applications. Application of nuclear technology is seen in almost all the aspects of life today; energy, water, health and food. As editor, I extend gratitude to our contributors for their passion and dedication. I welcome our readers to embark on a journey of discovery, curiosity, and collaboration, enriching our collective tapestry of knowledge and insight of the natural world.

Current Natural Sciences & Engineering 1 (1), 2024

Message from Chief Editor

Prof. (Dr.) R K Kotnala,

Former Chairman NABL, Raja Ramanna Fellow DAE & Chief Scientist, CSIR-National Physical Laboratory



Today, we all are witnessing severe adverse consequences of Global warming interlaced with abrupt Climate Change and ultimately it has resulted into a grave disastrous situation? It is due to the current levels of carbon dioxide (CO2) and other Green House gases (GHGs) beyond their limits in the atmosphere emitted mainly by industries, transportation, agricultural activities and energy production by fossil fuels, biomass. In 2023 earth atmosphere temperature rose to 1.5 degree Celsius and it triggered climate change conditions that resulted in melting 20% more ice from Greenland ice sheets. In the last two decades 5000 Giga tons of ice has been lost in Greenland alone, it is a very serious outcome of global warming! To circumvent the prevailing conditions of global warming, the United Nations, many countries & NGOs are working consistently to mitigate global warming.

Hence, Earth's Sustainability for we all, flora & fauna needs a sharp focus on the means of energy production by fossil fuels, biomass and other sources can be replaced immediately by renewable green & clean energy generated by Solar cells, Hydroelectric dams and other sources. Recently invented green & clean energy device Hydroelectric Cell is the biggest invention of 21st century in the green energy domain and it is an alternative to solar cell & fuel cell. A sustainable solution for ESG (Environmental, Social, and Governance) requires one of the strategic goals to reduce carbon (CO2) emissions. Green energy is the most sustainable solution to combat greenhouse gases emission.

Therefore, globally an immediate need is to adopt ESG, which can holistically support scholars & engineers' scientifically creative minds new ideas that can be scripted in the Current Natural Sciences & Engineering (CNSE) international journal. It is the most valuable journal on new science depository carved in the interest of the scientific fraternity, who are keen to disseminate science for the mother earth sustainability & mankind. It dwells mainly on the Green & Clean energy, Hydrogen energy, Environment, Net Zero Carbon, Health and Agricultural Science subjects to promote new, innovative and cutting-edge research in all areas of Natural Sciences.

The CNSE Journal is a unique platform to boost research impact globally and its editorial board comprises globally renowned S & T luminaries & advisory support from world top Institutes' leaders. Its main objective is to publish original scientific and technical papers, reviews, technical brief notes, research updates and news discussions on all aspects of natural sciences, engineering and interdisciplinary subjects. It is a comprehensive peer-reviewed interdisciplinary journal in an open access and it is free from heavy publishing charges with a global visibility. The CNSE journal is published by a nonprofit foundation VBF. The journal extends an opportunity for easy submission and quick publication of manuscripts.

I am sure Current Natural Sciences & Engineering international journal will serve society for their cause.

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Renewable Energy in India: Resource Availability, Waste Generation and Management

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Abstract: Energy security, environment and economy are the three major pillars of a country. These parameters not only secure a better quality of life for the citizens but also protect the country against an unwanted threat and economic crises. The energy need in India is primarily fulfilled by burning of the fossil fuels, but their reserves are limited and may deplete very soon. Also, they emit a large amount of CO_2 gas in the environment which is a key driver for the global warming. Therefore, to sustain the economy and protect the environment, India is focusing on the use of renewable energy; particularly solar and wind energy. In this article we have assessed the potential of these two energy sources in terms of material availability, waste generated and its disposal. At the end we have compared it with the well-established nuclear energy technology. Finding the future of a technology based on the raw material availability and its final treatment is necessary to make a self-reliant and sustainable technology, as India is progressing towards the same.

Keywords: Energy, Renewable, Global Warming, Material, Waste.

1. Introduction: Energy generation is one of the biggest challenges in today's world because its demand has increased remarkably in the past. To put forward the numbers: global energy consumption was about 146 EJ (1 $EJ=23.9\times10^6$ metric tonne oil equivalent) in year 1960 but has increased to 556.63 EJ in 2020 [1]. It has been predicted that the demand will further increase nearly by 50% in 2050. Total energy consumption of a country is driven by two factors (1) Population, (2) Energy spent per capita. Both these factors differ among countries depending upon their geographic location. technological advancement and, availability of resources. Henceforth: the need and the way to transform the energy industry also varies and a unique transformation path cannot be applied to all the countries together. Figure 1A shows a general trend of population growth and energy demand for different group of countries in near future. It can be seen from Figure 1A that in the Organisation for Economic Co-operation and Development (OECD) countries, Europe and Eurasia and America, the population is almost constant however in Africa. Middle East and Asia population growth is forecasted. In these group of countries the energy consumption is

also predicted to increase as compared to other countries and among them Asia will see the greatest expansion with ~40% of the world energy share by 2040 [2]. The majority of this share will be from China and India because of their, fast developing economies and high population. Figure 1B shows the energy consumption in the past and future for both these countries. Although from year 2000-2020 the energy demand in China has increased sharply but after that the growth projection is predicted to follow a linear increase however, in case of India it might increase exponentially. It is to be noted that by year 2025 the Indian population will surpass that of China to become the world's most populated country. The growing population and industrialization will result in more future energy demand for India. Presently, fossil fuel burning is the major sources of energy generation in India but their reserves are limited and it is estimated that with the current consumption rate the reserves will last only for 105 years in India [3]. Energy generation by fossil fuels is also one of the biggest contributors to CO₂ emissions and by an estimate account for around three-quarters of greenhouse gas emissions today and holds the

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key to averting the worst effects of climate change [4].



Figure 1A. Primary energy consumption and population growth in different group of countries in past and future years projected. 1B. Primary energy consumption in India and China in past and future projections.

It can be predicted with certainty that in future we will witness further increase if proper measures are not taken now. Various laws and climate policies are formed to regulate the emissions but the way these responsibilities are shared among different regions, countries and individuals is questionable. This is because the emissions differ for different countries and their per capita [4]. To compare, in 2020, China was one of the largest CO₂ emitters (Supporting Information (SI) Figure SF1A) but the per capita emissions are maximum for the Unites States (SI Figure SF1B). Although, India is much below the world average per capita CO_2 emissions but considering increasing population and industrialization, the emissions are predicted to increase creating an alarming situation for public health. The worse effects of climate change are even observed today.

Energy is also closely related to the economy as it ultimately enables investments and technologies that create jobs and drive growth among countries. Gross domestic product (GDP) of a country is a measure of economic growth. Many studies have been carried out in the past to understand the relationship between energy consumption and GDP [5-7]. It was observed that India is an energy dependent economy and portrays a bidirectional causal relationship between energy consumption and GDP [8]. It is postulated that the Indian economy will grow at the rate of 5% per year in comparison to world average of 3% and to achieve this growth, India needs massive amount of energy [8].

2. Solar and Wind energy contribution in India: Considering the stated facts together, it is certain that India needs large amount of energy to cater to its needs and in order to maintain the health of the environment a shift from fossil fuels to other low carbon or CO₂ neutral energy sources is absolute necessary. The primary condition is that the sources should be deployed economically and generates energy in a sustainable manner. For energy sources such as this, solarphotovoltaics, concentrated solar power, wind, geothermal, hydroelectric, wave, tidal. nuclear, corn-ethanol, cellulosic-E85 and coal with carbon capture and storage technology have been explored in India and their potential is evaluated in terms of various parameters such as abundance, scalability, greenhouse gas emissions, land use and, technological advancement [9]. Based on these parameters, it was found that the solar and wind energy has the largest potential for India because of their ultimate renewability and large scalability [9-11]. Considering this, Indian government is promoting these technologies and many solar and wind energy plants have come up in recent years. Researchers have also evaluated the potential of these two energy sources for India using different approaches. Lu et. al. [11] have used the cost optimization model to evaluate the best possible energy mix for India, taking cost, storage, power demand, inter-regional grid connectivity and capacity factor into account and suggested that 80% of the India's energy demand in 2040 can be met by renewable; in particular solar and wind energy. In their prediction they have assumed that the combined energy output of these two sources will be 3800 TWh assuming a growth rate of 6.5% per annum. We did a calculation wherein the actual energy generated from these two sources in 2021 and 2022 was taken [12] and the same growth rate factor was applied (Supplementary Sheet 1, SI). From the calculation it was found that the combined energy potential of these sources in 2040 will be 484.15 TWh; almost 8 times less the value taken by Lu et. al. for designing energy distribution in India. To look into it further, we checked the growth of solar and wind energy

in last 10 years in India and their contribution in the installed capacity for electricity generation and in total energy consumption per year in electricity sector (Supplementary Sheet 2, SI). The results are plotted in Figure 2. It is evident that the wind energy is almost at its saturation and its growth and use in electricity sector is almost constant. In fact its contribution in the overall electricity generation has decreased in past two years (Figure 2C) which suggest that this sector is not growing as per the rate at which electricity demand is growing. Looking at the solar energy, it is seen that this sector has seen a remarkable growth in last 5 years and the growth rate of as high as 80% has been achieved. Thanks to the geographical location of India because of which solar energy is available in surplus amount. Figure 2B shows that the contribution of solar energy in total installed power (GW) is >14% however, the overall energy generated per year is much less $\sim 4\%$ in 2021. This is because of the interim nature of this energy source and the energy is not available all the time to extract.

A detailed analysis on the growth trajectory of solar and wind energy sources in different countries has been carried out by Cherp et. al. [13]. They have shown that it follows S-shaped curve where initially the growth will be slow; then it accelerates followed by saturation. The same type of growth pattern has also been observed as shown in Figure 2C. From the results it is seen that the wind energy has attained a stable growth while solar is in its growing phase. Cherp et. al. [13]. have also shown that the maximum growth rate that wind and solar energy can attain in a large country like India is $\sim 1\%$ and 1.1%, respectively of the total electricity output. Considering this fact and the contribution of solar and wind energy in the total electricity generated (GWh/y); ~4% in 2021, it is envisioned that these two sources in total will contribute maximum 50% to the total electricity output by 2040 as against the ambitious estimation of 80% suggested by Lu et. al. [11]. This suggests that a technological innovation and better planning is needed to achieve the much higher growth rates. Jacobson et.al. [10] have mentioned that 100%

energy demand by 2035 can be met by renewable particularly wind, water and solar energy. For the study they have considered electrification of most of the processes including heating and cooling and transport as as collaboration among different well countries. For example India is grouped with Bangladesh, Sri Lanka, and Nepal but considering today's geopolitics nothing can be assured. Also, looking at the current energy distribution in India, this seems to be a highly ambitious estimation. Tiewsoh et. al. [8] have used the long-range energy alternative planning (LEAP) model for predicting the contribution of various energy sources in electricity generation for India in 2030 and commented that solar and wind energy are the major renewables for India but the contribution from nuclear energy cannot be ignored because of its continuous supply and ~9-15% contribution in the overall electricity generation which will come from this sector. Here we would like to emphasise that in 2021 the power sector represents only 18.2% of the overall energy consumption [14,15] in India. As India along with the world is trying to move more towards the processes driven by the electricity, in future the electricity demand will increase further that in turn will require more energy from renewable and low carbon energy sources. Therefore, it is important to understand the advantage and limitations of these energy sources to reach to a better planning.

The merits and demerits of an energy source are decided by many factors as described in Figure 3. Many of these parameters such as availability and scalability, greenhouse gas emissions, water use, effect of climate, public acceptability and job creation for different energy sources has been discussed earlier by many researchers [1,8,9,11,13,16,17] and in detail by Jacobson et. Al [9]. Herein, we will forecast the future of solar and wind energy sources for India by evaluating their performance in terms of various parameters connects the GDP, energy that and environment together. Our major focus will be on material availability, and waste generated as these parameters are of equal importance to



Figure 2A. % growth of solar and wind energy. 2B and 2C. % Contribution of solar and wind energy in installed power (GW) and total energy (GWh/y) used in electricity sector respectively.

preserve the biodiversity and sustain the economy in a densely populated country like India. We will be very brief with other parameters and only mention wherever required.

2.1. Solar energy: First, we will discuss the solar energy. Solar energy is the conversion of sunlight into electricity using photovoltaics (PV), or concentrated solar power (CSP). This idea was led by the discovery of photovoltaic effect in 1839 [18] and the first solar cell based on silicon was reported in 1954 with an efficiency of $\sim 6 \%$ [19]. Since then the solar cells have shown а commendable improvement and now contribute $\sim 3.4\%$ of the world electricity share which was $\sim 0.01\%$ in 1990 [16,19,20]; and anticipated to reach 25% by 2050 [1,16,19,21]. The potential of solar energy can be understood by the fact that an one hour equivalent of this energy was more than the energy used by the world in one year [21] and because of this it is sought as one of the important contributors in energy mix, particularly in India because of high intensity reaching the surface. However this energy source is not available all the times and the fluctuation pose a major limitation in using solar energy to meet the continuous demand. Capacity factor is an important term that basically measures how often a plant is running at maximum power compared to its nameplate potential. It is a measure of reliability of a plant. A plant with capacity factor of 100% means it is producing maximum power all the time.

Capacity Factor = Actual unit electricity output/Maximum possible output.

Capacity factor for solar energy is calculated for last 8 years in India (Supplementary Sheet 3, SI) and it was observed that the value ranges between 11-18% which means that the maximum energy that can be drawn from solar is much less as compared to their nameplate potential. Moreover, this energy is not in continuous supply that poses a major limitation on grid stability and powerful storage batteries are needed to store solar energy. Numerous research is also going on to develop techniques



Figure 3. Various parameters to evaluate the performance of an energy source.

that can convert solar energy into hydrogen via water splitting in electrolyzers and use directly hydrogen as a fuel [22]. But it has not come in the public domain yet.

Let us talk about the materials needed for solar energy harvesting. First of all, a suitable material that absorbs the solar energy and converts it into useful power with high efficiency is needed. Of all the materials discovered [16,22,23], silicon is the most used material and silicon-based solar cells (mono and poly-crystalline silicon) cover over 80% of the world's installed capacity today [16]. CdTe, CuInSe and CuInS are also prominent materials for solar energy harvesting because of their low cost and better mechanical properties, but have low efficiency. Several advanced technologies such as dye sensitized solar cells, quantum dot solar cell, perovskite based solar cells, organic solar cells etc. [22] have been developed for solar energy harvesting. They have been tested on laboratory scale and are yet to emerge at the plant scale. Today, Si, Cd, Te, In, and Cu are the main components of a solar cell absorbing material. Ag is used in solar cell solution as electrolyte. So for solar cell technology to grow and reach at its maximum potential these elements should be available. If we look at the reserves for these elements; as of 2021 Ag reserves in total is 5,30 billion tons out of which 4,74 billion ton is mainly concentrated in Peru, Australia, Russia, China, Poland, Unites States, Mexico, Chile and Bolivia [24]. In India, there are no native silver deposits except the small and unique Bharak deposit in Rajasthan with an estimation of ~29000 tons. Also it is estimated that the Ag deposit will be completely washed off in next 200 years and the world will reach at the same scenario as that of fossil fuel for now [25].

Silicon is abundantly available in nature but mostly found in SiO₂ form. Solar cell needs silicon in highly purified form. Silicon purification is an extremely difficult and energy intensive process. The market is majorly dominated by China and in 2019 it produced ~4.5 million tons of pure silicon that accounted for ~64% of global production. Though India is among the top 15 producers, its production was 60,000 tons which is <1%of global production (7 million tons) in 2019 [24]. India has imported most of its solar cell material from China in the past few years. Although the government is putting a lot of efforts for the local self-reliant technology still the correlation between the technological development, its implementation and demand looks far from the meeting point.

For thin film solar cell, Cd, Cu, In, Se and S are needed. Cadmium is generally recovered from zinc ores and sphalerite is the most economically significant zinc ore mineral for Cd recovery. The world production of cadmium was estimated at 25,600 tonnes in 2018. Most of the world's primary cadmium is produced mainly in China, Republic of Korea, Japan, Canada, Kazakhstan, Mexico, Russia and Peru. India has imported ~6,904 tonnes of Cd in 2018-19 from China, Japan, Republic of Korea, Mexico and Peru [24]. Indium is also majorly produced in China followed by South Korea and Canada. Cu is produced majorly in Chile, United States, Indonesia and Peru. In Se production also United States, China. Germany, Japan, Belgium, Russia are the leaders. This suggests that most of the materials used for solar cell fabrication are either not present or not manufactured in India and for solar cell technology, India is heavily dependent on the imports from other countries. Figure 4 shows on maps the important materials for solar energy along with their reserve sites.

2.2 Wind Energy: Let's move to the other renewable energy source that is wind energy. Wind is considered to contribute significantly in fulfilling the future energy demand. Even today, it is one of the major contributors of renewable energy share in the total energy portfolio. Wind farms consist of both onshore and offshore wind farms. Onshore wind power generates electricity using wind farms constructed on land which require a large amount of land and high wind speed. In most of the cases these wind farms are constructed in rural areas that can lead to habitat loss and compete with other usages of the land.



Figure 4. Countries with the reserves of raw materials for solar cell fabrication.

Offshore wind power generates electricity using wind farms constructed in water body usually sea. These wind farms do not require a large land but their construction and maintenance cost are significantly higher as compared to the onshore farm. In wind farms, mechanical energy of wind is converted to the electrical power using wind turbines and electric generators [24]. Wind energy has tremendous potential and according to an estimate the total amount of economically extractable power from the wind is more than what the world uses from all sources. Various models support this claim via top-down and bottom-up approaches. Using top-down" calculation, Kleidon [25,26] has shown that 18-68 TW power could be extracted from wind energy. Archer and Jacobson [27] did calculation using "bottom-up" approach and estimated that 72-170 TW power could be extracted practically. However, a recent study by Miller [28] does not support this claim and says that the estimates are too high by a factor of about 4. Wind energy has evolved a lot since its inception in 1982 and the kind of growth and potential it has shown is exceptional [29]. In 2019, wind contributed $\sim 2\%$ of the global energy demand [30].

India ranks fourth among world in terms of wind energy installations with an installed capacity of ~42 GW [12]. The Government is

promoting wind power projects through private sector investment by providing various fiscal and financial incentives. Like solar energy, wind power also has certain drawback that needs to be overcome to utilize its power fully. Wind power is not a steady power source and varies greatly with geography and time. Therefore, it cannot meet the demand at all times and must be used with other power sources to ensure a reliable supply [31]. Capacity factor for wind energy is calculated (Supplementary Sheet 3, SI) for last 7 years in India and the value range between 12-20% which suggests that like solar energy wind is also an intermittent energy source that needs to be stored. In India wind has attain a steady growth as already shown in Figure 2. The development of wind power in India began in the 1990s, and has significantly increased in the last few years. By current estimation [12] the overall potential for wind power in India is 302 GW at 100 m height and 2% land availability out of which 42 GW is already installed in 2022 that measures $\sim 10\%$ of the total electricity generated in India. Although the estimates for wind potential have increased a lot in past several years because of exploration of new sites; for prediction let us take the current estimates and look at the energy requirement in India and numbers suggested by other researchers. Consumption of overall energy in India's electricity sector was ~18.2% in 2021. This suggests that apart from the electricity sector a large amount of energy is consumed in India. Considering the maximum potential of wind energy, it can contribute ~ 75% at max in the overall installed power at 2021 level which means that the wind energy potential in India's energy demand is limited. Veers et. al. [32] have already mentioned that to extract reasonable amount of energy from wind, a large gap still exist that has to be complemented by aggressive research and policy decisions. Now let us look at the materials needed to convert wind energy into electricity.

Primary raw material in a wind turbine is steel (60% to 71%), cast iron (12% to 16%), fiber glass, and epoxy (11%) and glass/ceramic (6%), tool steel (6%), stainless steel (3%), aluminum (1% to 4%), and copper (0.7% to 2%). India has reserves for these elements. Rare earths elements neodymium, praseodymium, dysprosium and terbium are used to manufacture neodymium-iron-boron (NdFeB) permanent magnets. These magnets are used as components in generators for wind turbines. These elements are mostly concentrated in China [33]. In 2019, 67% of these oxides are produced in China while only 1% is produced in India. Interestingly China is also the biggest consumer of rare earth oxides with \sim 70-75% consumption. The importance of these elements can be seen by a whopping 243% and 103% increase in the price of neodymium and dysprosium respectively from 2020 to 2022. A detailed analysis of mineral availability for wind energy in India has been given by Verma et. al. [34] The reserve of rare earth elements in different part of the world is depicted in Figure 5.

Next we move on to the batteries. As mentioned that because of the intermittent nature of solar and wind energy strong batteries are needed to store them. In this context energy density of a battery is an important parameter that states the amount of energy stored within a given volume or weight. Most of the storage batteries use Li ion and for the best Li ion batteries the energy density is in the range of 150-300 Wh/Kg [35,36]. Considering India's overall energy requirement, the amount of Li needed only to store the solar and wind energy will be $\sim 10^{12}$ considering 100% storage kg [37] (Supplementary Sheet 4, SI) and the business as usual scenario. Energy efficiency of various processes increases upon electrification and Jacobson et. al. [10] have shown that the energy requirement of India can be decreased by 50% if all the processes are electrified by 2050. Considering this scenario and only storage the Li requirement will be $\sim 10^{11}$ kg. The total Li reserves in world are estimated to be $\sim 21 \text{ X } 10^9 \text{ kg in } 2020 \text{ [38]}$. Although new reserves are being explored continuously to meet the global Li demand and $\sim 80 \text{ X } 10^9 \text{ kg}$ of potential resources are identified in 2020



Figure 5. Countries with reserves of rare earth elements for wind energy harvesting.

[38]. This suggests that the total Li requirement to meet the solar and wind energy storage requirement is close to total terrestrial Li reserves. Because of high demand of Li, its prices have been increased 3.5 times in last 5 years [39]. India has very less reserve of Li; ~1600 tons which was discovered last year only in Mandya, Karnataka. A huge deposit of ~5.9 million tons of Li has also been found very recently in Jammu and Kashmir.

3. Sustainable waste management plan: After the implementation of any technology it is essential to assess the waste generated out of it and opt for the necessary measures to protect the environment. Since solar cell uses enormous amount of material, it implies that a huge amount of waste may be generated. The efficiency of a solar module deteriorates with time because of induced heat and humidity. These processes generate defects in the ultimately material that decrease the performance of the solar module and therefore needs to be replaced. In general, the lifetime of a solar module is expected to be \sim 25-40 years before the nominal efficiency drops by 20% [40,41]. IRENA has carried out a study to estimate the waste generated for different countries from the solar panel. For India they have estimated that it will generate ~600 GW from solar from which ~4.5 million tons of waste will be generated in 2050 considering the regular loss scenario and 30 years span lifetime of solar module [40]. However, a recent Harvard study review suggests that this amount can be 50 times more [42]. Presently, most of the countries do not recycle this waste except EU because of high cost involved ~15\$ and bury it in landfills that $\cot -1-2$ for one solar panel [42]. However, considering future scenario processes needs to be developed to recycle this waste and extract useful materials out of it because of large amount of waste and corresponding land requirement.

Like solar energy, wind energy also generates a huge amount of waste. Tazi et. al. [43] have carried out a study on the waste generated from wind industry in France Champagne-Ardenne (CA) region. This region has a total installed capacity of 181 GW. They have estimated that ~1 million ton of waste will be generated between 2002 to 2020 from this region majority of which includes ferrous and nonferrous metals, polymers, glass and concrete. This is a huge waste amount to handle. Most of this waste is non-recyclable and goes into landfills and India needs to think about this waste disposal because of limited land availability.

Both solar and wind energy industries also generate waste from the storage battery. Over a period of time much work has been done with storage battery waste and reuse, refabricate and refurbish practice is prioritized. The battery material from electric vehicle is used in storage batteries and then after treatment and extraction of valuable components it is released as a waste. China is pioneer in this work and by 2019 it was reported that 58% of Li ion batteries have been recycled [37].

Let us compare this waste amount to the waste generated from well established nuclear industry. By an estimation there is ~ 0.265 million tonnes of heavy metal of spent fuel in storage worldwide in 2016 out of which 127 000 tons has already been reprocessed [44]. This number represents the contribution from ~95% of nuclear power installation worldwide with an overall capacity of 384 GW [44]. Taking into account the capacity factor for nuclear (~80%) this value comes around 2691.072 TWh/Y. If we compare this to predicted electricity generated by solar taking 20% capacity factor into account, the value is 1051.2 TWh/Y. Therefore, the electricity produced by the nuclear in the world today is almost 2.5 times the value predicted for India by solar in 2050 however the waste generated from solar alone in India is 20 times more as compared from all nuclear installation. This shows that solar industry will generate a huge waste and actions needs to be taken to handle this waste. Here we would also like to mention that India follows close fuel cycle operation where reprocessing of fuel is done to recover the useful materials with application in other industries and make 'wealth from waste' [44]. Also the average operating life of nuclear reactors is ~60 years. As of 2020, ~66% of the

global nuclear power plants have operated for >31 years and $\sim 20\%$ have operated for >41years [44]. It is already recognized as one of the most reliable and clean technology for base load power generation. This can be seen by looking at the mortality rate from various energy producing industries and compare it with nuclear technology. In 2012, the global mortality rate (deaths/ billion kWh) was only 0.04% for nuclear while for solar and wind it was 0.44 and 0.15% respectively. This is against the global electricity production of ~17% from the former as compared to ~1% each from the later industries. In spite of many advantages its expansion is not at par the rate needed. One of the major problems with nuclear energy expansion is public acceptability and radiation fear because of the Linear no threshold model (LNT). Although many researchers have carried out studies to oppose this model [45-47] still the policies are not being reframed to make nuclear energy as the fuel of the future. However, the Indian government is now planning to install Small Modular Reactors (SMRs) along with rapid solar and wind energy expansion to meet the India's target for clean energy and achieving net zero emission by 2070.

4. Conclusions: Greenhouse gas emissions, resource availability, waste generation and space requirement are major factors that decide the merits of an energy source. India particularly has enormous potential for solar and wind energy, but has poor reserves of materials needed because of which it is heavily dependent on the imports from other countries. This problem needs to be solved by design and production of new innovative material and favourable technologies so that the possibility of self reliant technology can be realized. Moreover these energy sources are intermittent in nature and generate huge amount of waste for which no measures has been taken yet. In our opinion researchers have over predicted the growth of solar and wind energy in India without taking into consideration other important factors and to sustain the energy need and meet the 2070 criteria of net zero emission nuclear energy expansion at a larger scale is needed along with other renewable energy sources.

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SUPPLIMETARY INFORMATION

Figure SF1A and SF1B and Supplementary Sheets 1-4.

Notes

The authors declare no competing financial interest.

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Supplementary Information



Figure SF1A: Annual CO₂ emission and SF1B: Per Capita CO₂ emission by fossil fuel for various countries at different time period.

Supplementary Sheets

Sheet 1						
Energy generation using			Wind Energy Generation	Solar Energy Generation		
solar and wind as per Liu	Increase Rate	Year	considering 6.5% annual	considering 6.5% annual growth		
prediction (TWh)			growth (TWh)	(TWh)		
1078.42871	0.065	2020				
1148.526576	0.065	2021	62			
1223.180803	0.065	2022	66.03	89.814		
1302.687556	0.065	2023	70.32195	95.65191		
1387.362247	0.065	2024	74.89287675	101.8692842		
1477.540793	0.065	2025	79.76091374	108.4907876		
1573.580944	0.065	2026	84.94537313	115.5426888		
1675.863706	0.065	2027	90.46682239	123.0529636		
1784.794847	0.065	2028	96.34716584	131.0514062		
1900.806512	0.065	2029	102.6097316	139.5697476		
2024.358935	0.065	2030	109.2793642	148.6417812		
2155.942266	0.065	2031	116.3825228	158.303497		
2296.078513	0.065	2032	123.9473868	168.5932243		
2445.323616	0.065	2033	132.003967	179.5517839		
2604.269651	0.065	2034	140.5842248	191.2226498		
2773.547179	0.065	2035	149.7221994	203.6521221		
2953.827745	0.065	2036	159.4541424	216.88951		
3145.826549	0.065	2037	169.8186617	230.9873282		
3350.305275	0.065	2038	180.8568747	246.0015045		
3568.075117	0.065	2039	192.6125715	261.9916023		
3800	0.065	2040	205.1323887	279.0210564		
			Total in 2040 = 484.15 TWh			

Sheet 2

Year	Wind Power (MW)	% Increase	Solar Power (MW)	% Increase	Total Power (MW)	% of Solar Power in Total Output	% of Wind Power in Total Output	Total energy generated by Solar in electricity sector (GWh/Y)	Total energy generated by Wind in electricicty sector (GWh/Y)	Total energy consumption in electricicty sector (GWh/Y)	% of Solar energy generated in total enegy consumption in electricity sector	% of wind energy generated in total enegy consumption in electricity sector
2012	18,421									10,56,838		
2013	20,150	9.4	2,319							11,08,498		
2014	22,465	11.5	2,632	13				3,350		11,77,810	0.284426181	
2015	23,447	4.4	3,744	42				4,600	28,214	12,71,872	0.361671615	2.218304987
2016	26,777	14.2	6,763	81				7,450	28,604	13,51,970	0.55104773	2.11572742
2017	32,280	20.6	12,289	82	3,26,841	3.759932199	9.876361901	12,086	46,011	14,33,392	0.843174791	3.209938384
2018	34,046	5.5	21,651	76	3,44,002	6.293858757	9.897035482	25,871	52,666	14,86,493	1.740405101	3.54296993
2019	35,626	4.6	28,181	30	3,56,100	7.913788262	10.00449312	39,268	62,036	15,46,517	2.539125014	4.011336442
2020	37,669	5.7	34,627	23	3,70,106	9.35596829	10.17789498	50,103	64,639	16,22,983	3.087093334	3.9827281
2021	38,785	3.0	40,085	16	3,82,151	10.4893092	10.14912953	60,402	60,150	15,73,187	3.839467272	3.823448833
2022	40,355	4.0	56,951	42	3,99,497	14.25567651	10.10145258					

Year	Installed Capacity Solar Energy (MW)	Energy generated from Solar (GWh/Y)	Solar Capacity Factor	Installed Capacity Wind Energy (MW)	Energy generated from Wind (GWh/Y)	Wind Capacity Factor
2013	2,319					
2014	2,632	3,350	14.53			
2015	3,744	4,600	14.00	23,447	28,214	13.73
2016	6,763	7,450	12.57	26,777	28,604	12.19
2017	12,289	12,086	11.22	32,280	46,011	16.27
2018	21,651	25,871	13.64	34,046	52,666	17.66
2019	28,181	39,268	15.90	35,626	62,036	19.87
2020	34,627	50,103	16.51	37,669	64,639	19.59
2021	40,085	60,402	17.20	38,785	60,150	17.70

Sheet 3

Sheet 4

Energy consupmtion (QUAD) INDIA	Energy consumption (kWh)	Material weight needed for Li ion battery (kg)	Amount of Li ion needed (kg)	Uranium needed (kg)
12.12	3.55E+12	1.18E+13	1.60E+11	4.28E+05
17.48	5.12E+12	1.71E+13	2.31E+11	6.17E+05
22	6.45E+12	2.15E+13	2.91E+11	7.77E+05
36.48	1.07E+13	3.56E+13	4.83E+11	1.29E+06
58	1.70E+13	5.67E+13	7.67E+11	2.05E+06
82	2.40E+13	8.01E+13	1.08E+12	2.90E+06
120	3.52E+13	1.17E+14	1.59E+12	4.24E+06

Significant Role of Fe³⁺ Sites on the Activation Energy Barrier at Electrode Interface in SnO₂-Fe₂O₃ Composite Based Hydroelectric Cell

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Abstract: Hydroelectric cell (HEC) is a green energy device known for its potential to replace solar cell and fuel cell in coming decades. Among number of materials explored, tin oxide-based cells have shown a huge potential to deliver high current densities with high activation losses. In this study, to overcome the activation loss, tin oxide-hematite composite based HEC power characteristics has been analysed. The composite cell delivered a short circuit current density of $I_{sc} \sim 7.0 \text{ mA/cm}^2$ and peak power of $P_{den} \sim 26.9 \text{ mW}$. More structural defects were found to nucleate in the composite compared to pure tin oxide confirmed by X-ray diffraction (XRD) and Raman spectroscopy. Scanning electron microscopy (SEM) revealed the high surface area and porous microstructure of the composite. Fourier transform infrared spectroscopy (FTIR) confirmed the presence of chemi-dissociated and physisorbed water molecules on the composite surface. The composite based hydroelectric cell displayed low activation losses compared to the bare SnO₂ HEC observed by the V-I characteristics. A significant role of Fe³⁺ cations has been found crucial for the reduction in activation energy barrier in the composite based HEC.

Keywords: Tin Oxide, Hematite, HEC, Water splitting, Activation energy

1. Introduction: Energy generation in a sustainable way is the foremost requirement in today's scenario. As the global concern has risen towards the environmental crisis, it has become more important to generate energy in the greener way. Hydroelectric cell (HEC) is one of such energy sources known to generate electricity and hydrogen without polluting the environment [1,2]. Till date, a number of materials have been successfully synthesized to fabricate hydroelectric cell and among all tin oxide-based cells have shown promising results [3-7]. The primary requirement for the cell material is its oxygen deficient, nanoporous structure. The reaction in hydroelectric cell is initiated by the interaction of water molecules with the defective material surface followed by its chemisorption and then physi-dissociation. Defects mediated catalytic reactions on semiconducting oxide's surface has attracted the world-wide attention due to fast rate of reaction. Catalysts initiate a wide variety of energy extensive reactions at low energy potentials by providing an alternative

route with low energy barrier [8-10]. Water splitting is also an energy intensive process, on high energy defective material surface. Water splits by forming bond with the two neighboring defect sites (under coordinated cation and oxygen vacancy) and restructuring the material surface to low energy, the process known as the chemi-dissociation of water [11]. Splitting of physisorbed water in hydroelectric cell takes place via high electric potential created by the accumulation of charges (hydronium ions) inside nanopores [1]. The transfer/migration of these ions from the material surface to respective electrode is a crucial process. The supply and accumulation of ions determines the rate of reaction at the electrode and consequently the power output of the HEC. In tin oxide, water dissociation takes place in abundance due to inherent defects and the material exhibits high activation losses due to changes in its chemistry on interaction with water. Consequently, it affects the reactions at electrode and hence the polarization losses.

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Although the internal resistance of tin oxide is low in comparison to other materials like silica, alumina, magnesium oxide etc. which shows high charge transfer resistance due to resistive grain boundaries [3]. This charge transfer resistance was found to decrease by multiple orders in antimony doped tin oxide (Sb-SnO₂) which resulted into high currents and low activation and ohmic polarizations [7]. However, in Sb-SnO₂ the transformation of material take place which limits its durability for long. On the other hand, iron oxides are abundant, low cost and eco-friendly materials. Various iron oxides have been used for hydroelectric cell application. From the iron oxides based hydroelectric cells it was conclusively found that magnetite (Fe_3O_4) showed highest current density with low open circuit potential (OCP) and high activation losses due to the oxidation of Fe^{2+} ions as the case in SnO₂ [6]. Maghemite (γ -Fe₂O₃) showed low current owing to the cation vacancies in the material which led to the associative adsorption of water at material surface [12]. Amongst all hematite (α -Fe₂O₃) showed the maximum OCP of 0.92 V and short circuit current of 30 mA with the least activation losses owing to low energy barrier in the fabricated cell [13]. Therefore, in this study, hematite was used to synthesize a composite with tin oxide. The engineering of tin oxide to alter H₂O-SnO₂ interaction chemistry for the tuning of polarization losses can make it a better alternative amongst all materials.

2. Material and methods: SnO₂-Fe₂O₃ composite was synthesized by solid state reaction. Analytical grade precursors- SnO₂ (Thomas Baker, 99% pure) and Fe₂O₃ (Alfa-Aesar 99.9 % pure) were used without further purification. SnO₂ and Fe₂O₃ taken in stoichiometric molar ratio 0.8:0.2 were wet grinded using acetone in pestle mortal for 1 hour. Sample was pre-sintered at 750 °C for 2 hours. Mixture was further hand grinded and pelletized using a manual hydraulic press into a 2 \times 2 \times 0.1 cm³ pellet followed by sintering at 950 °C for 3 hours. The pure SnO₂ sample was also processed in the similar way. Hydroelectric cell was fabricated with both the pellets by pasting zinc anodic sheet on one face and silver paste on the other face. Electrical contact wires were taken from individual electrodes to test the performance of SnO₂-Fe₂O₃ composite hydroelectric cell. X-ray diffraction (XRD) analysis of the pure and composite samples was performed with Bruker AXS D8 advance XRD, Cu-K α radiation of wavelength λ = 1.542 Å to investigate the phase of the samples. Scanning electron microscopy (Bruker AXS Microanalysis GmbH, Germany) and energy dispersive X-ray spectra (EDX) of the sample was obtained to analyze the surface morphology and elemental composition of the sample respectively.

Raman spectroscopy using the laser excitation wavelength of 514.5 nm was performed by Renishaw in-Via Raman spectrometer to examine the micro structural disorders in the samples before and after making the composite. Photoluminescence spectroscopy was performed with Perkin Elmer LS55 luminescence spectrometer to detect the formation of defect levels within the band gap of pure and composite samples. Characteristic V-I polarization curve was plotted by varying external loads using a Keithley power source meter to investigate the performance of the composite based HEC cell with respect to pure tin oxide based HEC. Sn-O, Fe-O and hydroxyl on the sample surface groups were characterized by PerkinElmer 1750 FTIR spectrophotometer. Electrochemical impedance spectroscopy of the pure and composite based wet HEC was performed using Wayne-Kerr Impedance Analyzer 6500B (UK) at an applied AC voltage of 10 mV in the frequency range 20-200MHz.

3. Results and Discussion: Composite samples have been analyzed by its X-ray diffraction pattern shown in Figure 1. Distinct polycrystalline XRD peaks attributing to SnO_2 and Fe₂O₃ were observed matching well with standard JCPDS card no- 721147 of cassiterite SnO_2 and 79-1741 of corundum hematite. The same peaks were also identified in the composite sample for both the compounds. Absence of any other impurity or phase in the composite indicated no other phase is formed in composite material. Low concentration of Fe₂O₃ in composite material might be



Figure 1: XRD spectra of a) Tin Oxide b) Hematite c) Tin Oxide-Hematite Composite

responsible for its reduced intensity compared to tin oxide. The average crystallite size of SnO₂ for pure and composite samples was calculated with XRD peak (101) using Debye-Scherr's equation $D = k\lambda/\beta_{hkl}Cos\theta$. The average crystallite size for pure tin oxide was calculated to be 42.94 nm while for composite it reduced to 20.56 nm. Pure tin oxide showed the crystal growth along (101) plane which indicated its reduced state due to the presence of some inherent defects [14]. However, in composite the preferred growth plane reoriented along (211) plane. XRD peaks of SnO₂ in composite got relatively broadened compared to individual pure phase SnO₂ and Fe₂O₃. This might be due to the inhibition of crystallite growth in composite sample induced from diffusion of some Fe atoms in SnO₂ lattice sites. The similar observations have been already reported in literature for Sb doped SnO₂ and Fe doped SnO₂ (7,15,16). This might be due to limit the exposure of high energy surface of (211) plane in the composite [17]. Dominant exposed high energy surface (211) plane interacts strongly with polar water molecule [7]. Lower crystallinity of SnO₂-Fe₂O₃ nano-composite is also supposed to enhance the effective surface area hence the water sensitivity.

To get deep insight of the micro-structural disorders in the SnO₂-Fe₂O₃ composite Raman spectroscopy of the sample was performed (Figure 2a). Characteristic Raman bands of SnO₂ were observed at around 481, 629 and 770 cm⁻¹ confirming the tetragonal rutile structure of tin oxide. A strong mode near 571 is assigned to the in- plane oxygen cm⁻¹ vacancies in the composite [18]. The two peaks observed for tin oxide at 546 and near 693 cm⁻ ¹ are closely related to the crystal vacant sites and micro-structural disorders [19]. The appearance of IR active mode A_{2u} near 695 cm⁻ can be assigned to the decreased crystallite growth and hence increased grain boundary defects. The band near 546 cm⁻¹ is known to arise due to the imperfections or distorted symmetry of the particle surface. The signature



Figure 2: (a) Raman spectrum and (b) SEM image of the synthesized composite

bands for hematite at 226, 243, 293 and 411 cm⁻¹ correspond to the corundum crystal structure. The band between 200-300 cm⁻¹ are assigned to the vibration modes related to iron atoms while at higher frequency region (400-650 cm⁻¹) modes are ascribed to vibration of oxygen atoms [13]. The Raman forbidden mode at wave number 660 cm⁻¹ is assigned to the presence of structural disorder in hematite (20). Raman results are in agreement with the XRD that the composite synthesized from SnO₂ and Fe₂O₃ have reduced crystallite size and more structural defects than the parent compounds.

Figure 2(b) represents the SEM image of the synthesized composite. The inset represents the high resolution SEM image of the composite. Two distinct morphologies of the particles can be clearly seen. The EDAX spectra revealed the rod and oval shaped particles are SnO₂ and Fe₂O₃ respectively (figure 3 a & b). The oval shaped hematite particles were seen in close contact with tin oxide nano rods as evident from SEM. Both type of oxide particles showed a broad range of size distribution. The average grain size for Fe₂O₃ particles was estimated to be 350 nm. Nano rods with a thickness of 200 nm and length up to 1.2µ could be resolved by high resolution SEM image. Tin oxide particles were found accumulated with each other, may be due to reduce the exposure of high energy surface (211) and minimize the surface energy as inferred from the XRD data. The oval shaped hematite particles are attached to the tin oxide rods in close contact. Wide spread distribution of varying size pores can be seen throughout the composite. The rod shaped morphology of the tin oxide particles increased the effective surface area of the composite, making it more reactive towards the adsorption and dissociation of large number of water molecules.

To investigate the energy levels created in the forbidden energy region due to the defects like anion, cation vacancies or interstitials, room temperature photoluminescence spectroscopy of the pure and composite samples was performed (Figure 4). To ensure the emission from the trap states like self trapped excitons, vacancies and interstitials the excitation was done using a 375 nm laser source. Two major emissive regions were observed in PL spectra near 500 and 560 nm. Both the spectra showed a peak near 430 nm which can be ascribed to metal interstitials or dangling bonds [21, 16]. However, in case of composite this peak has become broad which indicates the presence of other defects also which are obvious. When the size of the crystallite reduces it introduces many other structural defects. The peak at 500 nm is originated from the deep trap emission is assigned recombination and from conduction band to the sub bridging oxygen or in-plane vacancies. This peak has become quenched in the SnO₂-Fe₂O₃ composite due to the presence of Fe₂O₃. As Fe₂O₃ is present in



Figure 3: (a) Spot EDAX rod shaped particles (b) Spot EDAX oval shaped particles

large concentrations a process known as cross relaxation can lead to non-radiative energy Vibrational modes observed at 1245, 1121, 1055 and 995 cm⁻¹ are ascribed to the Sn-OH



Figure 4: Photoluminescence spectra of Pure SnO2 and SnO2-Fe2O3 Composite

exchange between two neighbouring Fe³⁺ centers that quenches the radiative process [22,23]. The other major peak at 560 nm is assigned to the bridging oxygen vacancy. In the composite the peak was found slightly broadened. To get more insight into the origin of peak, it was deconvoluted by multi peak Gaussian fitting into three peaks centered at 555, 559.68 and 568 nm. The emission in this green region is assigned to the recombination of electron from neutral oxygen vacancy center with the singly or doubly ionized oxygen vacancy centers located deep in the energy gap Furthermore, a valence band edge [24]. transition (band gap ~ 2.0 eV) is supposed to contribute to the peak centered at 568 nm [8]. FTIR spectroscopy of the composite sample was performed in the range 4000-400 cm⁻¹ to investigate the interaction of water molecules on its surface. Figure 5 represents the FTIR spectra of composite sample treated with water and finally dried at 50 °C. Vibrational modes observed at 477 and 539 cm⁻¹ are characteristic of the lattice vibrations of hematite related to Fe-O stretching [25] Vibrational mode at 619 cm⁻¹ is assigned to the Sn-O stretching in SnO₂ crystal lattice. Vibrational modes at 1622 and around 3150 are attributed to H-O-H bond bending and stretching respectively due to physisorbed water molecules on sample surface [26].

bond stretching vibrations generated due to the chemi-dissociation of water molecules on the under coordinated composite surface at terminal sites. A sharp band at 1400 cm⁻¹ is assigned to the Sn-O-Sn bridge vibration harmonics on the sample surface formed after



Figure 5: FT-IR Spectra of water treated SnO₂-Fe₂O₃ composite

the heating of wet sample [27]. A weak band near 3020 cm⁻¹ is due to the Sn-OH stretching of bridging hydroxyl groups while the broad band centered at 3140 cm⁻¹ contains several modes which may be assigned to the different stretching modes of –OH group existing in different forms and environment like Sn-OH (Bridging), H₂O- hydrogen bonded to surface hydroxyl etc. indicating highly active composite surface. The weak bands between 2050 to 2800 cm⁻¹ are assigned to various symmetric and coupled vibrations of water molecules [28]. give rise to ionic conduction within the cell. Dry composite based cell also showed a diffusion tail which may be due to the presence of some dissociated water molecules already present at the electrode interface owing to composite's strong affinity towards water,



Figure 6: EIS Spectra of (a) dry and (b) wet composite based hydroelectric cell

Dissociation of water molecules and the ionic conduction within the composite based cell was further confirmed by electrochemical impedance spectroscopy. The EIS spectra of dry and wet composite based hydroelectric cell is presented in figure 6(a) and 6(b)respectively. In both the spectra a semicircle is followed by a diffusion tail at low frequency. Plot indicating the cell spectra in dry state (Figure 6a) exhibited a high resistance of the order of mega ohm. After the cell was partially dipped in the de-ionized water, the drop in cell resistance was observed of the order of 10^5 (Figure 6b). This is due to the reason that as the water falls on to the cell it dissociatively adsorbed on the pellet surface and forms a chemisorbed layer of -OH groups which is also verified by FTIR results. The physisorption of water molecules take place on the chemisorbed hydroxyl layer due the electrostatic field created by this layer on the material surface. Proton hopping starts on physisorbed water layer by Grotthus mechanism. The hopping protons get trapped inside the nanopores, creates electric field of the order of 10^4 V/cm that is high enough to dissociate physisorbed water molecules [1]. The dissociated ions migrate towards the respective electrodes and

In order to investigate the effect of hematite on the polarization losses in SnO_2 -Fe₂O₃ composite based hydroelectric cell the V-I curves were plotted shown in Fig 7 (a, b). In the figure 7 (a) and (b), region AB represents the activation losses at low current density

adsorbed from the humid environment.

the activation losses at low current density region where point A indicates the open circuit potential of the cell. BC represents the ohmic loss region where the potential falls due to the resistance of the material faced by the migrating ions. Region CD represents the mass transport loss in the cell at high current density. The composite based cell delivered short circuit current of Isc ~28.3 mA and OCP ~0.95 V while bare SnO₂ based cell delivered Isc \sim 22.2 mA and OCP \sim 0.797 V. The maximum power output for composite based HEC increased to 6.1 mW/cm² from 4.0 mW/cm² for bare SnO₂ based HEC. A high OCP was observed in composite base cell in comparison to the SnO₂ based HEC.

It may be due the internal conversion of Sn^{2+} to Sn^{4+} in pure SnO₂, which onsets a negative redox at cathode and lowers the overall cell potential. The same effect was also observed in magnetite based HEC (6). A high activation loss of 0.34 V was observed for bare SnO₂



Figure 7: V-I polarisation curves of HEC (a) Bare SnO₂ (b) SnO₂-Fe₂O₃ composite

based HEC, however in the composite based cell the activation loss reduced to 0.15 V. In general SnO₂ based hydroelectric cell shows high activation loss in spite of inherent defects. One of the causes of this activation loss is the high bonding energy of hydrogen to SnO₂ surface at high pH which limits the hydrogen evolution from cathode surface [2]. In contrast to bare SnO_2 the OCP and I_{sc} were found to be increased in composite based cell along with reduced activation loss. It may be possible that Fe³⁺ cations substituted Sn²⁺ in the composite and therefore eliminated the Sn²⁺/Sn⁴⁺ redox reaction within the material, which is verified by the observed high OCP in composite based HEC. Further, as long as the tin oxide surface has Sn^{2+} sites, it facilitate the evolution of hydrogen gas however, oxidation of Sn^{2+} to Sn⁴⁺ surface causes the surface rearrangement and makes it sluggish for hydrogen evolution reaction which may contribute to high activation barrier in pure SnO₂ based cell [29]. It may be possible that the substitution of Sn²⁺ by Fe^{3+} formed Fe^{3+} -V⁰ defect pairs reduced the conversion of Sn^{2+} to Sn^{4+} , releases hydrogen easily, which ultimately reduced the activation barrier in composite based hydroelectric cell. The ohmic region represents the resistance faced by the charge flow due to the internal resistance of the cell. This region also represents the useful window where the cell operates. A linear ohmic region was observed in composite based cell due low internal resistance of the cell. It improved easy charge migration within the material. Region

CD represents the mass transport losses. This loss was almost negligible in tin oxide based cell however a prominent mass transfer loss was observed in composite based cell compared to tin oxide. It may be due the increased crowding of ions at electrode due to more number of dissociated ions and their effective transfer to the electrode interface [7]. 4. Conclusions: A tin oxide-hematite composite was synthesized for green energy generation by hydroelectric cell. The composite based cell delivered short circuit current of Isc ~28.3 mA and OCP ~0.95 V while bare SnO2 based cell delivered Isc~22.2 mA and OCP ~ 0.797 V. Tin oxide based cells shows high activation losses due to the inherent defects and therefore presence of Sn²⁺ sites on the surface. The oxidation of Sn^{2+} to Sn⁴⁺ increased the internal losses in the cell and found responsible for sluggish EMF cathode kinetics. Composite of tin oxide with hematite increased the effective surface area with water interaction thus increased current output in composite based cell. It also reduced the internal losses by replacing Sn²⁺ by Fe³⁺ cations in the lattice. Incorporation of Fe³⁺ cation in SnO₂ lattice improved the cathode kinetics for hydrogen evolution and hence reduced the activation energy barrier at the electrode material interface. Hence SnO2-Fe₂O₃ composite based cell is a promising solution to deliver high power density with reduced cost compared to tin oxide based hydroelectric cell. Further engineering of the

composite can enhance the power generation which can be explored in future.

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Mechanical Activation of CaSO₄ Enriched Petroleum Coke Fly Ash for Development of Green Pellets Varsha Parmar^{1,2*}, Prabha Padmakaran^{1,2}, Mohd. Akram Khan^{1,2}

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Abstract: Mechanical Activation of calcium sulphate enriched petroleum coke fly ash (PCFA) generated from circulation fluidized bed combustion (CFBC) boiler was investigated to improve the surface reactivity of PCFA. The physico- chemical, mineralogical (XRD), morphological (SEM) characteristics of PCFA, activated PCFA and developed green pellets were studied in detail. It was found that the milling time of 45 minutes is efficient for the activation of PCFA and results in fragmentation of coarse particle into fine porous particles. Mechanical activation results in enhancing physical properties and reactivity of PCFA without any further chemical treatment. The mean particle size of activated PCFA with 45 min milling time was 12.51-12.60 μ m and the porous morphology were seen through SEM. The hydration phases like ettringite, portlandite and calcium silicate hydrate mainly contribute to the development of mechanical strength in activated PCFA pellets which were also confirmed through morphology of needle-shaped crystallites. The study recommends that mechanically activated PCFA could be used as an adsorbent material for heavy metals removal from waste waters.

Keywords: Petroleum Coke Fly Ash; Grinding; Pellets; CFBC; Heavy Metals

1. Introduction: The rapid development of economics and industries have led to an upsurge in the release of toxic heavy metals such as Zinc, Nickel, Lead and Copper discharged into the environment resulting in significant environmental contamination and health issues to the human body for their nonbiodegradable and persistent nature [1]. Removing these heavy metals from contaminated water has become critical. Various reported techniques were used to remove heavy metal ions from different types of wastewaters. Treatments based on adsorption, membranes, chemicals, electricity, and photo-catalysis can be made using these techniques. Adsorption is one of the more efficient and common techniques used for removal of heavy metal [2]. Many research has been done for the adsorption of toxic heavy metals from contaminated water using inexpensive adsorbents [3]. Fly ash is one of the most extensively researched materials for adsorption with solid wastes due to its affordability and easy availability [4]. Nevertheless, fly ash has a limited capacity to adsorb substances. Fly ash's capacity to

remove heavy metal ions from the environment can be improved by increasing its specific surface area [5,6].

Petroleum coke (Petcoke) is a by-product of the petroleum refining process, which is mainly used as primary fuel instead of coal due to its higher calorific value for power generation [7]. Petcoke fly ash (PCFA) is produced when sulfur-containing petcoke fuel is burned at 900°C in circulating fluidized bed combustion (CFBC) boilers utilizing limestone as a desulfurizing agent [8]. The chemical composition of ash, which significantly influences its activity, is reliant on the raw fuel mixture and the temperature at which combustion occurs. Desulphurization additives in CFBC boilers have an impact on the mineral and chemical content of the ash [9]. Although CFBC technology is efficient for combustion of low-grade fuel rich in calcium and sulphur [10,11] but due to the variation in their chemical compositions and having substantial amount of lime and SO₃ the use of CFBC ash in cement concrete system is limited [13-15]. The objective of this study is to investigate the use of PCFA for making green pellets. The

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PCFA was mechanically activated using high energy planetary ball mill for enhancing the surface reactivity of PCFA for making economically and environment friendly green pellets which can be used for heavy metal adsorption in future studies. The raw PCFA, activated PCFA and pellets were analysed through X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Particle Size Distribution (PSD) to assess its suitability for its further application.

2. Material and Methods

2.1. Petroleum Coke Fly Ash: Fresh PCFA was collected from Electrostatic silos of Captive Power Plant of an Oil Refinery located in Madhya Pradesh which used petroleum coke as primary fuel. The industry used CFBC boiler for combustion of high calorific value sulphur rich petroleum coke and produced large quantities of ash around 5 million tons annually. The petroleum coke fly ash is produced at combustion temperature (800-900°C) and is calcium rich solid waste with value range between 40-50 wt%.

2.2. Mechanical Activation of PCFA: The activation of PCFA was done by grinding it in a high energy planetary ball mill (INSMART MRM-07) using 5 mm and 10 mm in a grinding jar of 500 mL capacity. PCFA was grinded for different milling time of 15, 30, 45 and 60 min at a bowl rotation speed (rpm) of 400 in 250 gram batches. The various parameters like sample to ball ratio and rotation speed were fixed and time was varied as per need. The efficiency of the grinding process in the ball mill reduced after 45 minutes of milling due to the material

agglomerating and adhering to the walls of the grinding jars and balls. Particle size analysis was performed with raw and milled ash samples using a Laser Scattering Particle Size Distribution Analyzer make Particle LA– 950, HORIBA Scientific Northampton, UK.

2.3 Pelletization: The disc pelletizer used in the pelletization procedure has a diameter of 100 cm and a collar height of 15 cm. The disc is set at a fixed angle of 45° and rotates at a speed of 35 revolutions per minute. To begin with, the raw and milled ash were manually combined with a precisely measured quantity of water (water-to-solid ratio of 0.3) in order to achieve a uniformly mixed substance. The material is introduced into a disc, and additional water is applied via a spraying bottle as needed during the pelletization process. The disc continues till the appropriate size granules are achieved (Figure 1). The duration of one cycle is around 15 minutes. The prepared pellets were collected and allowed to undergo the curing process in an ambient condition for a duration of 7 days.

2.4. X-Ray Fluorescence Spectrometry Analysis of Pellet

The chemical composition of the raw ash was analysed using Wavelength- Dispersive X-Ray Fluorescence (WDX-XRF), S8 TIGER BRUKER, Germany.

2.5. X-Ray Diffraction Analysis of Pellet

The mineral composition of raw ash and milled ash pastes were determined by means of X-ray diffraction (XRD) analysis by Rigaku, Mini Flex II Desktop with Cuka (λ =1.5419 Å)



Figure 1. Schematic representation for preparation of green pellets through activated PCFA

radiation over the $10-70^{\circ} 2\theta$ region with step size of 0.02° and for approximately 30 min total scan time. The obtained peak was identified using JCPDS file.

2.6. Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy Analysis

The Fourier Transform Infrared Spectroscopy (ATR-FTIR) patterns of raw ash and milled ash were measured by using Thermo Scientific, iS50 FT-IR. The IR spectra were obtained by measuring the transmittance of light in the range of 400–4000 cm⁻¹, with a resolution of 4 cm⁻¹ and 64 scans per sample.

2.7 Scanning Electron Microscopy Analysis

The microstructure was investigated using Scanning Electron Microscope JEOL JCM 6000 plus. In SEM, samples were investigated by making its surface conductive in high vacuum mode with deep gold coating. Samples were sprayed on carbon tape and then gold coated. Backscattered electron (BSE) images were obtained at $2000 \times$ magnification, 10μ m resolutions and 5 kV.

3. Results & Discussion

3.1. Particle Size Distribution of Raw and Activated PCFA: The particle size distribution pattern of raw PCFA and mechanically activated PCFA as a function of milling time are as shown in Figure 2. The particle size distribution was determined by Laser Scattering Particle Size Distribution Analyzer make ParticalLA- 950, HORIBA Scientific Northampton, UK. The raw PCFA is characterized by a particle size distribution with mean particle size of 16.79-19.23 um (D10-7.64 µm, D50-13.56 µm, D90-28.08 μm). In scanning electron microscope (SEM), the raw PCFA mainly comprise of coarse, angular and irregular particles with a broad particle size typically $< 50 \ \mu m$ as shown in Figure 3(a). The material is dominated by irregular coarse particles of 5-20 µm. Few agglomerated particles are occasionally found typically ranging from 10-40 µm. The agglomeration of PCFA particles may be due to condensation and deposition of volatile

species [12,16] on the surfaces of PCFA. The grinding of PCFA in high energy planetary ball mill causes breaking up of larger particles of PCFA into sub-micron fine particles (Figure 3). The effective milling causes reduction in particle size with increase in milling time but after 45 mins of milling time larger particles start appearing due to agglomeration of particles as depicted in Table 1.



Figure 2. Particle Size Distribution Curve of the Raw PCFA and Activated PCFA



Figure 3. Scanning Electron Microscopy Images (a) Raw PCFA (b) Activated PCFA

The prolonged milling results in sticking of sample to the ball and to the surface of the container which further results in larger particle size than their primary particle due to agglomeration [17] which results in reduction of particle size decreases. The particles are so

Sample: Ball	Time (in min)	RPM (Plate/Bowl)	Mean Size	D ₁₀	D ₉₀	
1:2	15	200/400	20.3-23.12	7.24-7.36	28.4-29.2	
1:2	30	200/400	12.12-13.06	5.5-6.29	19.9-21.2	
1:2	45	200/400	12.51-12.60	5.57-6.01	19.9-20.9	
1:2	60	200/400	12.51-12.78	5.6-6.1	20.0-21.13	

Table 1: Grinding details of PCFA and its Particle Size Distribution

fine that the electrostatic forces induce them to clump together [18]. These results are in accordance with the study reported by Fernández-Carrasco L [19] in which maximum size reduction fall in second stage grinding with milling time (30- 50 min). The mean particle size of activated ash for 30 min milling time is found to be 12.12-13.06 μ m (D10-5.895 μ m and D90- 20.55 μ m) which results in internal porosity of the particle which may also be confirmed through SEM morphology (Figure 3(b)).

3.2. Chemical Composition of the Raw and Activated PCFA: The primary chemical components of raw PCFA and activated PCFA are predominantly CaO and SO₃, with an average value of 45.95 and 28.1 weight%, respectively (**Table 2**). The average content of SiO₂, MgO Al₂O₃, Fe₂O₃ and V₂O₅ in raw ash is 10.5, 4.0, 2.65, 0.7 and 0.08 wt% respectively. Like other CFBC ashes, PCFA exhibits a significant concentration of sulphur, specifically in the form of SO₃, which is a result of the desulphurization process in the CFBC boiler.

3.3. Phase composition and microstructure of Pellets: The raw and activated PCFA based pellets were crushed and finely powdered manually using mortar and pestle & passed through sieve number 200 (75µm). The prepared powder sample was tested for analysis using X-ray hydration phase diffraction. The resultant intensity peaks were confirmed through JCPDS files. The mineral phases of the pellet derived from raw and activated PCFA (Figure 4) exhibit notable distinctions from the mineral phases of the raw ash PCFA. The differences arise from a sequence of hydration reactions. The main hydration peak found in both the samples were portlandite and calcium silicate hydrate and ettringite. The main peaks of ettringite were found at (20-17.0°, 17.8°, 11.4° and 35.8°) (JCPDS- 9-414) and peaks of calcium silicate hydrate were found at (20- 32.0°, 39.2° and 27.3°) (JCPDS- 29-368). The presence of the gypsum phase indicates the dissolution of anhydrite in hydrated pastes at (20-30.9°, 20.5°

Metal Oxide (in wgt %)	CaO	SO₃	SiO2	MgO	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	TiO ₂	V ₂ O ₅	LOI
PCFA	46.1	28.2	10.8	4.07	2.62	0.78	0.54	0.12	0.086	8.99
Activated PCFA	45.8	28.0	10.3	4.06	2.60	0.75	0.54	0.13	0.085	9.06

Table 2: Chemical Composition of Raw and Activated PCFA, * LOI - Loss on ignition at 900 °C.



Figure 4. XRD Patterns (a) PCFA based Pellets; (b) Activated PCFA based Pellets (P: Portlandite; A: Anorthite; Et: Ettringite; F: Iron Vanadium Oxide; G: Gypsum; C: Calcium Silicate Hydrate; Q: Quartz

33.2°) (JCPDS-21-816). ATR-FTIR and spectra of pellet from raw PCFA and activated PCFA are shown in Figure 5. The molecular bonds produce narrow peaks in highly crystalline structures; wider peaks show an amorphous structure. The prominent and welldefined peaks observed at approximately 1096 and 1112 cm⁻¹ in PCFA and activated ash, respectively, as well as the moderately intense but distinguishable peaks at 594, 611, and 676 cm^{-1} in PCFA and at 594, 611, and 677 cm^{-1} in activated PCFA can be attributed to the bending and stretching vibrations of the S-O bonds in the SO_4^{2-} ions present in the Calcium Sulphate Anhydride mineral. Such effects indicate the presence of anhydrite [20]. The characteristics band at 2933 cm⁻¹ in PCFA and BA corresponds to the vibration mode of C-H. Sharp visible band at 3642 cm⁻¹ in activated PCFA is due to the vibration of O-H in portlandite (Ca(OH)₂) compound. A moderate intense band at an extreme value of 1411 cm⁻¹, 1457 cm⁻¹ represents C-O stretching, band at 873 cm⁻¹ and 874 cm⁻¹ corresponding C-O out of plane band. The observed effects suggest the presence of calcite (CaCO₃) in PCFA and activated PCFA, as indicated by the respective changes. Additionally, the band at around 1620 cm⁻¹ corresponds to the stretching vibrations of O-H bonds of water molecules. The presence of an additional distinct peak at 797 cm⁻¹ in the activated sample matches to the vibrational frequency of the Si-O bond in Quartz [21]. The above FTIR results confirmed the hydration of lime to portlandite (Ca(OH)₂) in pellet sample with activated ash with the presence of band at 1620 cm⁻¹ & 3642 cm⁻¹ which may also be confirmed through the XRD pattern.



Figure 5. Fourier Transformation Infrared Spectra of PCFA and activated PCFA based Pellets

The SEM analysis of pellet from raw PCFA and activated PCFA shows a porous structure with substantial pore space partially filled with hexagonal shaped portlandite crystals (Figure 6(A)(B)).



Figure 6. SEM Image (A) PCFA based Pellet (B) Activated PCFA based Pellets

The microstructure of pellets containing mechanically activated PCFA slightly differ from those containing PCFA alone. exhibits distinct It а morphology characterized by needle-shaped crystallites of ettringite, which are submicron in size (Figure 6B). The SEM image of activated ash pellets also confirms the hydration reaction between the water and PCFA the clear spiky and elongated microstructure of calcium silicate hydrate. The production of ettringite and calcium silicate

filled the pores and increased specimen compaction [22]. It was confirmed that the lime (CaO) in PCFA and activated PCFA get converted into portlandite (Ca(OH)₂) by mean of hydration reaction and used for the formation of C-S-H and Ettringite [23].

4. Conclusions:

- The mean particle of size of raw PCFA is 16.79-19.23 μm (D10-7.64 μm, D90-28.08 μm) and the mean particle size of activated PCFA (45 min) is 12.51-12.60 μm (D10-5.57 μm D90-19.9 μm).
- The mechanical activation of 45 minutes is efficient for the activation of PCFA which enables the fragmentation of coarse particles and results in improving the surface reactivity and physical properties which is confirmed through particle size distribution.
- The XRD & FTIR analysis confirms the hydration reaction of CaO and CaSO₄ which get converted into portlandite, calcium silicate hydrate and ettringite phases which are mainly contributing in mechanical strength development in PCFA pellets.
- The microstructure of mechanical activated PCFA based pellet confirmed the formation of needle shaped ettringite that occupied the pore space between unreacted particles and hence improve the mechanical strength.
- The findings of the study suggest that mechanically activated PCFA could be used as an adsorbent material for adsorption of heavy metal and also as an alternative binder.

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Iron oxide (Fe₃O₄) and Ciprofloxacin Loaded Magnetic Nanoparticles for Magnetic Drug Targeting

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Abstract: Iron oxide (Fe₃O₄) pristine and ciprofloxacin loaded nanoparticles are synthesized successfully using co-precipitation method. X-ray diffraction analysis confirms the pure phase formation of the synthesized Fe₃O₄ particles. The grain size of the Fe₃O₄ calculated from the SEM images comes out to be 50 nm. UV-VIS spectrophotometric analysis indicates the accuracy of the results in which an absorption maximum of blank and ciprofloxacin containing iron oxide (Fe₃O₄) particle was observed at 260 and 265 nm respectively. The spectrum band shows the maximum absorption band shift of around 4-5 nm which may be explained by the drug conjugation to the Fe₃O₄ nanoparticles. The spectrum indicates the formation of Fe₃O₄ magnetic nanoparticles having black color and obtained material is found with energy band gap (E) of 2.12 eV and 2.19 eV. On the basis of the findings from dynamic light scattering (DLS) results, it can be concluded that overall particle size of magnetic iron oxide nanoparticles is observed as 765 nm. In the present study the polydispersity index (P.I.) of bare Fe₃O₄ magnetic nanoparticles is 0.221, which indicate the hydrodynamic property of the synthesized particles.

Keywords: Magnetic nanoparticles; UV-VIS spectrophotometer, Magnetic drug targeting.

1. Introduction: Magnetic nanoparticles and micron sized spheres are widely used in biomedical applications as their unique properties are granted by their high surface area and behavior in the presence of a magnetic field. Recently, magnetite Fe₃O₄ as magnetic material is being widely used in human treatment because of its stable quality, high magnetic responses and easy achievement [1-5]. Due to the biocompatibility, the most common material is iron oxide (magnetite, Fe₃O₄) these days. Looking to the importance of these magnetic particles present study has been under taken to explore the possibility of such biocompatible material [6-10]. Present study reveals the preparation of magnetic iron oxide Fe₃O₄ nanoparticles, optimization of the synthesis parameters, and characterization of the synthesized product. In accordance of the objective, a general synthesis of magnetic Fe₃O₄ nanocrystals via a simple co precipitation method applied herein provides a promising preparative approach to such

magnetic particles. The structure, morphology and magnetic properties of as-prepared were characterized by X Ray Diffraction (XRD), Scanning Electron Microscope-Energy Dispersive X Ray Spectrometry (SEM-EDS) and Vibrating Sample Magnetometer (VSM). The result of XRD characterization indicated Fe₃O₄ as the product. SEM and TEM image showed that Fe₃O₄ nanoparticles have the mean diameter 5-20 nm. The EDS spectra showed strong peaks of Fe and O. Magnetic characteristics of Fe₃O₄ nanoparticles indicated super paramagnetic properties. Magnetite nanoparticles were synthesized through co-precipitation of aqueous solutions of ferric and ferrous chloride ions in the presence of 9.26 kDa dextran. The CaCo-2 cell model was employed as the biological system. X-Ray diffraction was used to characterize the structure of the synthesized nanoparticles, showing a crystallite size of 9.0 nm. FTIR spectroscopy indicated the presence of dextran in the magnetite samples. SQUID

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magnetometry was employed to measure the DC magnetization response of the samples, demonstrating superparamagnetic behavior at room temperature. with а saturation magnetization of about 50 A/m, and a magnetic core diameter of about 7.0 nm. TEM measurements confirmed the average size of approximately 9.0 nm. Viability and apoptosis experiments in CaCo-2 cells in contact with 0.15 mg/ml of nanoparticles were determined at different contact times. No cytotoxic effects were observed. In other study, Drug carrying amino silane coated magnetic nanoparticles were synthesized and used as a flexible magnetic targeted delivery of antibiotics. Magnetic nanoparticles were prepared by chemical co-precipitation method and the surfaces were coated bv 3aminopropyletriethoxy The silane. characteristics of the Effects of pH and temperature on the release of the drugs were studied. The drug loading efficiency was found 93.4 and 91.1 % for ofloxacin and ciprofloxacin, respectively.

2. Materials and Methods: Ciprofloxacin (CPF) attached Iron oxide (Fe₃O₄) nanoparticles (NPs) were synthesized surface adsorption using method. Ciprofloxacin was the drug to be used and polyethylene glycol (PEG) was used as a surface coating polymer to bind the drug to the surface of the iron oxide nanoparticles. Polyethylene glycol was added to 20 ml of magnetite fluid (140 mg/ml) and stirred for 10 min. Two tablets of 500 mg ciprofloxacin were then dissolved in 10 ml of de-ionized water and added to the 20 ml of solution. The solution was then sonicated for 2 hours at 500 °C. The microspheres were then collected from the emulsified solution by centrifugation at 4500 rpm. The microspheres were then decanted, diluted with distilled water and centrifuged again at 4500 rpm for 3 to 4 times. Particles collected were dried in oven at 80 °C for 24 hours leading to formation of PEG-CPF-Fe₃O₄ NPs microspheres. The conditions for the preparation of Fe₃O₄ magnetic nanoparticles Ciprofloxacin drug loaded Fe₃O₄ and nanoparticles were optimized, and developed

Fe₃O₄ magnetic nanoparticles. Further, X-Ray Diffraction (XRD), elemental analysis, and Fourier Transform Infrared Drug delivery behavior of the amino silane coated MNPs was studied by selecting ofloxacin and ciprofloxacin as model drugs.

3. Results and discussion:

3.1. X-ray diffraction: The X-ray diffraction patterns of both Iron oxide (Fe_3O_4) nanoparticles and PEG-CPF-Fe₃O₄ NPs microspheres synthesized at 80 °C are recorded from 20° to 80° with X-ray diffractometer using Cu-Ka (λ =1.549 Å) having an accelerating voltage of 30 kV. Data are collected with a counting rate of 4°/min. The X-ray diffraction powder patterns of ciprofloxacin attached iron oxide (Fe₃O₄) nanoparticles is shown in Figure 1 and the relative comparison with the pure iron oxide (Fe₃O₄) nanoparticles is shown in Figure 2. Most of the characteristic lines in the diffraction patterns were generally prominent and sharp. Proper sample preparation helps to attain accurate peak positions for qualitative analysis. If the sample surface is irregular or if it is displaced from the focusing circle, peak locations and intensities may be varied. Identification of a structure from developed powdered Fe₃O₄ diffraction pattern is based upon the position of peaks and their relative intensities.



Figure 1. XRD pattern of CPF loaded Fe₃O₄ nanoparticles.

A series of characteristics peaks observed in the XRD pattern of **PEG-CPF-NPs** microspheres corresponds to (220), (311), (400), (422), (511), (440) and (533) Braggs reflection and indicate that the iron oxide magnetic nanoparticles is well crystalline Fe₃O₄¬(JCPDS card No. 03-0863) [11]. These peaks are characteristic of the cubic magnetite structure as corroborated with the standard data of JCPDS. Using the Scherrer equation the average crystallite sizes of the magnetic Fe₃O₄ containing ciprofloxacin are found to be as~ 8 nm. The results of X-ray diffraction (XRD) of iron oxide and ciprofloxacin attached iron oxide nanoparticles revealed crystallinity of the developed product and accordingly the diffraction pattern and profiles of prepared particle are expressed in the Figure 1 and 2. From the peaks of both samples (Figure 2) it is evident that there are no major differences between the two patterns. However, ciprofloxacin containing iron oxide particles indicate that the intensity of major characteristic peaks specifically at 34.70° and 56.22° decreases and peaks become broad, which indicate the decrement in crystallinity of iron oxide nanoparticles by attaching the CPF particle.



3.2. Scanning Electron Microscopy: The surface morphology of the developed Ciprofloxacin attached Fe₃O₄ nanoparticles was characterized by scanning electron microscopy (SEM) and shown in the Figure 3. As per the SEM images, the iron oxide

magnetic Fe₃O₄ nanoparticles- containing Ciprofloxacin (CPF) confirms that the samples taken into consideration during the study period are spherical in shape and are highly dense in nature. The nanoparticles are showing large degree of accumulation. It is also noticed through SEM images that the whitish material of CPF is attached with blackish iron oxide nanoparticles. It is further observed through SEM image that grain size of drug loaded iron oxide NPs decreases ~ 40 nm as compared to 50 nm of pristine Fe₃O₄ due to coating of PEG over the iron oxide NPs, which reduce the agglomeration of Fe₃O₄ NPs.



Figure 3. SEM micrograph of Ciprofloxacin attached Fe₃O₄ magnetic nanoparticles.

3.3. **UV-Visible Spectroscopy:** The absorption spectrum obtained through UV-Visible spectroscopy of Fe₃O₄ and ciprofloxacin loaded iron oxide (Fe₃O₄) nanoparticles is presented in Figure 4. The absorption intensity start to take off or where the absorbance value is minimum at 566.3 nm in visible range between 370 nm to 800 nm wavelengths (Figure 4). However, the presence of absorption maxima of iron oxide (Fe₃O₄) and ciprofloxacin containing iron oxide (Fe₃O₄) particle was observed at 260.8 nm and 265 nm respectively. The spectrum band shows the maximum absorption band shift of around 4-5 nm which may be explained by the drug conjugation to the Fe₃O₄ nanoparticles [12]. The spectrum indicates the formation of Fe₃O₄ magnetic nanoparticles having black color and obtained material is found with energy band gap (E) of 2.12 eV and 2.19 eV according to equation as $E(eV) = \frac{1240}{(wavelength in nm)}$.





3.0

2.5

2.0

1.5

Absorbtion (%)

Figure 4. UV spectra of Fe₃O₄ and ciprofloxacin attached Fe₃O₄ particles.

The findings of the present study regarding UV-VIS spectrophotometric analysis are in the support of the observations of the researchers who found the band gap energy of the iron oxide nanoparticles was 2.3 eV of iron oxide nanoparticles developed by co-precipitation method [13].

3.4. Particle Size Distribution Using Dynamic Light Scattering (DLS): DLS measures the light scattered from a laser that passes through a colloidal solution and by analyzing the modulation of the scattered light intensity as a function of time, the hydrodynamic size of particles and particle agglomerates can be determined. Larger particles diffuse slower than smaller particles and the DLS instrument measures the time dependence of the scattered light to generate a correlation function that can be mathematically linked to a particle size. The analytical results as shown in figure 5, revealed that the diameter (d) of the particles containing drug Ciprofloxacin was 619 nm having polydispersity index (P.I.) 0.263 whereas, the intensity distribution (D) was higher (90%) as 1172 nm followed by D (50%) as 591nm and D (10%) as 293 nm. Overlay normalized Intensity distribution of magnetic iron oxide nanoparticles attached with drug Ciprofloxacin and Intensity distribution of drug Ciprofloxacin attached iron oxide (Fe₃O₄) nanoparticles is shown in Figure 6 and Table 1. On the basis of the findings of the present analysis it can be concluded that overall magnetic iron oxide nanoparticles were observed in 765 nm (Pure) and 619 nm (with drug Ciprofloxacin), therefore, further efforts are needed not only for highly crystalline particles formation but also mono disperse size distribution.

Polydisperse nanoparticles solutions or stable solutions of aggregated nanoparticles have no visible particulates and no particle settling. This class of materials includes dried nanoparticles dispersed with sonication. Polydispersity index is a measure of the width of the particle size distribution. Polydispersity indices less than 0.1 are typically referred to as "monodisperse". Typically, the DLS measures diameters of the particles with a polydispersity index of 0.3 or below. In the present study the polydispersity index (P.I.) of Fe₃O₄ nanoparticles and drug Ciprofloxacin attached Fe₃O₄ magnetic nanoparticles were as 0.221 and 0.263 respectively Therefore efforts should be made for further analysis to develop monodisperse magnetic nanoparticles of Fe₃O₄ used for targeted drug delivery system.



Figure 5. Intensity distribution of ciprofloxacin attached iron oxide (Fe₃O₄) NPs.

3.5. Bulk Density and Tapped Density: The bulking properties of a powder are dependent upon the preparation, treatment and storage of the sample, i.e. how it was handled. The particles can be packed to have a range of bulk densities and, moreover, the slightest disturbance of the powder bed may result in a changed bulk density. Thus, the bulk density of a powder is often very difficult to measure with good reproducibility and, in reporting the

results, it is essential to specify how the determination was made. Density was measured to predict the flow properties and its compressibility which requires that loose powders be compacted into a durable solid form with the correct mechanical strength, porosity and other characteristics. It is observed that loose bulk density (LBD) and tapped density of ciprofloxacin attached Fe₃O₄ nanoparticles was 0.453 g/cm^3 and 0.548g/cm³. Compressibility index (CI) was also found from the results of loose bulk density and tapped bulk density, and it was reported as 15.41 for Fe₃O₄ and 17.33 for ciprofloxacin attached Fe₃O₄ nanoparticles, which indicate good flow property of the magnetic particles [14].

magnetic response of Fe₃O₄ magnetic powder. In the present study magnetic response of the magnetic CPF attached Fe₃O₄ sample powder in the magnetic field was analyzed and evaluated not only to assess the importance of this selected targeted drug in clinical application but also to give more direct data for further research of targeted drug Ciprofloxacin. Present data revealed that the maximum intensity of the ferromagnet itself was 206.5 mT tested at 0 cm position from ferromagnet. However, the number of the ferromagnets which were changed to investigate the higher magnetic response and it was found that all the ferromagnets had the same magnetic performance, therefore, the distance between ferromagnets and CPF



Fig.6: Normalized Intensity distribution of ciprofloxacin attached iron oxide NPs.

3.6. Magnetic Field Intensity and Magnetic **Response:** The magnetic density of ferromagnet was measured by using Gaussmeter whereas the relative magnetic response of ciprofloxacin attached Fe₃O₄ nanoparticles magnetic nanoparticles were measured using an electronic balance. To this context magnetic Fe_3O_4 powder (0.05 g) was placed in the balance 2 cm below a magnet of known strength and the reading on the balance in the unit of g was used as an index of the attached Fe₃O₄ magnetic powder was fixed at 2 cm. Present study showed that the intensity of magnetic field and the magnetic response of CPF attached Fe₃O₄ magnetic nanoparticles weaken as the distance increases, moreover, the magnetic response depends on the magnetic intensity. The magnetic response increases nearly 60 times when the distance is changed from 3 cm to 1 cm. Thus, in the clinical application, the distance between ferromagnet and drug Ciprofloxacin has been

No.	Data	Repeat No	Ave Diameter (nm)	Polydispersity index	D(10%) (nm)	D(50%) (nm)	D(90%) (nm)
1	S ₁	1	670.4	0.262	305	522	965
2	S ₂	2	669.9	0.257	299	541	1002
3	S ₃	3	619.9	0.263	293	591	1172

Table 1: Intensity distribution table of magnetite iron oxide (Fe₃O₄)drug Ciprofloxacin containing nanoparticles

highlighted especially in the present study (Table 2).

The data revealed that, a 32.6 mT magnetic field intensity produced by four ferromagnets was sufficient to excite the dipole moments of the 0.05 g CPF attached Fe₃O₄ magnetic powder which was 2 cm away from the ferromagnets. From the data as obtained during the study period indicated and concluded that the obtained ciprofloxacin attached Fe₃O₄ magnetic nanoparticles were accomplished and qualified as the magnetic carriers for further tests in targeted-drug therapy. From the results obtained during the study

nanoparticles) defined here as a small object that behaves as a whole unit in terms of its transport and properties and that's why their magnetic response may be slightly higher than that of Fe_3O_4 (pure) sample.

LBD: Loose Bulk Density, TBD: Tapped Density, Magnetic Response*/g is out of 0.05 g magnetic Iron Oxide powder with the ferromagnets 2 cm away.

4. Conclusion: In summary, magnetic Iron oxide (Fe₃O₄) nanoparticles were synthesized successfully using co-precipitation of a Fe (II) and Fe (III) precursor mixture in basic aqueous

Magnetite Iron Oxide Fe ₃ O ₄ NPs	LBD (g/cm ³)	TBD (g/cm ³)	Magnetic field intensity of ferromagnet (mT)	Magnetic Response*/g	Compressibility index
Fe ₃ O ₄	0.461	0.545	206.5	0.0487	15.41
Fe ₃ O ₄ - containing Ciprofloxacin	0.453	0.548	206.5	0.0501	17.33

Table 2: Magnetic density and Magnetic Response of ciprofloxacin attached Fe₃O₄ nanoparticles

period support the fact that the nano powder are agglomerates of nanoparticles, or nanoclusters. Nanoparticles may or may not exhibit size-related properties that differ significantly from those observed in fine particles or bulk materials. Synthesized grown iron oxide nanoparticles in the term of nano powder (Black colour) and their aggregates (ciprofloxacin attached to magnetic iron oxide solution and then the synthesized Fe₃O₄ nanoparticles attached with the ciprofloxacin drug stabilized with a polymer poly ethylene glycol (PEG). XRD analysis confirms the pure phase formation of the synthesized product. XRD analysis of the present study reveals that the peaks of both samples do not have major differences between the two patterns. which indicate the decrement in crystallinity of iron oxide nanoparticles by the attachment of the CPF particle. As per the SEM images, the iron oxide magnetic nanoparticles of Fe₃O₄ pure and Fe₃O₄ - containing Ciprofloxacin, confirms the shape of the powdered material as spherical. The grain size of the Fe₃O₄ pure and Fe₃O₄ - containing Ciprofloxacin calculated from the SEM images comes out to be 50 nm and respectively. **UV-VIS** 40 nm spectrophotometric analysis indicate the accuracy of the results in which an absorption maxima of blank and ciprofloxacin containing iron oxide (Fe₃O₄) particle was observed at 260.8 and 265 nm respectively. The spectrum indicates the formation of Fe₃O₄ magnetic nanoparticles having black color and obtained material is found with energy band gap (E) of 2.12 eV and 2.19 eV. On the basis of the findings from dynamic light scattering (DLS) results, it can be concluded that overall particle size of magnetic iron oxide nanoparticles is observed as 765 nm (Pure) and 620 nm (with drug Ciprofloxacin). In the present study, the polydispersity index (P.I.) of bare and drug Ciprofloxacin containing Fe₃O₄ magnetic nanoparticles is 0.221 and 0.263 respectively, which indicate the hydrodynamic property of the synthesised particles. Present findings indicate good flow property of the magnetic particles because of the compressibility index (CI) 15.41% and 17.33% for Fe₃O₄ and Fe₃O₄ containing Ciprofloxacin magnetic nanoparticles, respectively. The CI was worked out from the loose bulk density and tapped bulk density. Present data reveals that, a 32.6 mT magnetic field produced by four ferromagnets was sufficient to excite the dipole moments of the 0.05 g Fe₃O₄ magnetic powder 2 cm away from the ferromagnets.

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A Brief Overview of Carotenoids and Their Applications

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Abstract: Carotenoids are naturally occurring pigments found abundantly across various fruits, vegetables, and other foods that are plant-based. They impart variety of colors to the microorganism, fruits, vegetables with their striking red, orange, and yellow colors. Beyond contributing to the aesthetic appeal of these foods, carotenoids make a significant impact on human health. They are known for their antioxidant properties, offering protection against oxidative stress and damage caused by potentially harmful free radicals. Antioxidant property of carotenoids is due to presence of conjugated double bonds (CDB) that are present in their chemical structure. By reducing oxidative stress, carotenoids help protect the body against various chronic diseases, including cardiovascular diseases, and cancers. They are also well known for their pro-vitamin A activity, immune system modulation, and ability to scavenge free radicals while protecting against UV radiation. Because humans are not able to synthesize carotenoids, they must be obtained through diet or supplementation. Carotenoids' anti-cancerous/cancer preventative action is the main factor contributing to their pharmacological significances. Carotenoids also known for bacterial pathogenicity by acting as virulence factors. Carotenoids are also known to impart color hence beneficial for the food and beverage industries, textile industries etc. They are being used more frequently as substitutes for artificial colorants and additives as growing consumer interest in sustainable and natural products. Thus, the primary focus of this review is on the fundamental knowledge of carotenoids and its numerous applications in industries and human health.

Keywords: Carotenoids, human health, antioxidant, functions, industrial applications

1. Introduction: Carotenoids are a class of isoprenoid compounds, mainly composed of eight isoprene units (Fig.1.1) (C₅) forming a C40 carbon compound [1,2]. They have a characteristic polyene chain of conjugated double bonds (CDB) (Fig.1.2) is responsible for giving carotenoids distinguished absorption patterns and also impart a variety of colors to the microorganisms. CDB in carotenoids play a crucial role in their functional properties and energy transfer capabilities. The term "carotene" came into existence when Wilhelm Ferdinand Wackenroder in 1831 initiated the identification of carotenoid in the carrot. Within 50 years, Hartsen was able to isolate lycopene from *Tamus communis L. berries*[3]. Carotenoids are found in all organisms including phototrophic as well as in a variety of non-phototrophic organisms. It occurs

widely in all three domains: Prokaryotes, Archaea and Eukaryotes [4]. Up until 2018, 1178 naturally occurring carotenoids with a wide range of structural variations and physicochemical characteristics have been documented and described in the literature[5]. It is synthesized by plants and microorganisms, while animals depend upon dietary sources since they are incapable of de novo synthesis^[4]. Carotenoids are responsible for imparting various colours like yellow, red, orange to micro-organisms, algae, fungi, fruits, vegetables and plants. However, chlorophyll masks the colour of carotenoids in plants. This phenomenon can be observed in the autumn leaves as well as at the time of ripening of fruits [6]. Carotenoids are primarily located in hydrophobic regions of the cell since they are hydrophobic and cannot dissolve in water.

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Figure 1.1: Isoprene (C5)



Figure 1.2: Lycopene

They can access the aqueous environment only when associated with proteins [7]. The polarity of carotenoids is altered by either polar functional groups or by the interaction of carotenoids with other molecules. Usually, a carotenoid molecule consists of 9-13 alternate single double bonds in a conjugated system which can exist in *cis* or *trans* isomeric forms. *Cis* forms do not aggregate or crystallize easily as compared to trans form. Trans form of carotenoids is more rigid. Carotenoids can be linear with no cyclic structures at the end of the molecule (acyclic carotenoids) or cyclic carotenoids with cyclic structures at the end [2,8]. Detailed explanations of the carotenoid's reactions i.e. oxidation, reduction, hydrogen abstraction, and addition properties have been reviewed [2,8]. Carotenoids have a variety of functions including the variation of colors in plants and animals, anti-oxidant molecules, protecting the reaction center from oxidative free radical species and also light-harvesting molecules. Animals use the carotenoid derivative in their retina as visual pigment, and it also functions as a chromophore in bacteriorhodopsin photosynthesis. Plants and animals use abscisic acid and retinoic acid respectively as antioxidant molecules to harvest light, shield the reaction center from oxidative free radical species, and shield egg protein from protease in some invertebrates[9]. It also acts as a vitamin A precursor and also plays a role in the prevention of human diseases such as cancer. Another important property of carotenoids is photochemical properties which is explained by their lowlying excited energy (both singlet and triplet)[10]. Carotenoid's ability to protect the reaction center from photo damage or reactive radical species as well as its function of light harvesting is all due to its long polyene chain structure [11].

2. Structure of carotenoids: Carotenoids are colored fat-soluble pigments sensitive to oxygen, heat and light[12,13]. Carotenoids are polyisoprenoid substances from a chemical perspective, and they can be generally divided into two classes (Fig.2) a) Carotenes, which are mostly composed of hydrocarbon molecules like lycopene, β -carotene, and b) xanthophylls, also contain oxygen atoms in the form of hydroxyl, methoxy, carboxyl, keto, or epoxy groups in their hydrocarbon chains[14]. Carotenoids are potentially strong antioxidant molecules due to the presence of an alternate single double bond conjugated system and thereby can quench the peroxy radicals[15]. Carotenoids are often identified using their chromophore and light absorption properties[16]. Carotenoid is a long C40 polyene structure with alternate single double bonds hence constitutes a conjugated system. More than nine alternate double single bonds in a conjugated system are responsible for the pigment properties of carotenoids. This conjugation property was demonstrated by Richard Kühn in 1935 and was awarded the Nobel Prize in chemistry[17]. Since they absorb wavelength between 400-600 nm, therefore, are pigmented molecules ranging from red, yellow, orange color [8]. The intensity and the depth of colors of these molecules depend upon the number of alternate single double bonds as well as the functional group present. C40 parent molecule is formed by the tail-to-tail linkage of two C-20 geranylgeranyl diphosphate molecules which further undergo several reactions to get a variety of different carotenoids. The primary changes in the parent C40 molecule include cyclization at one or both ends, which produces seven different end groups, a change in hydrogenation level, and the addition of functional groups containing oxygen, which results in a family of more than 750 compounds[8].

Initially, trivial names were assigned to carotenoids. These names were derived from their biological source, however, since such names do not give any information regarding their structure, therefore, IUPAC- semi systematic scheme was designed. All names are derived from the stem name "carotene" preceded by the Greek letter prefixes (Ψ , Φ , β , γ , ε , κ , χ) that designate the two end groups[2]. The IUPAC-IUB rules are given in detail in volume 1A of the series carotenoids. Those carotenoids which have lost CH₃, CH₂, or CH group from ends of the carotenoid molecules are known as nor-carotenoids while oxidative cleavage of carotenoids is known as apocarotenoids (less than 40 carbon atoms) e.g. Vitamin A, abscisic acid[18].

2.1. Ultrastructural Organization of Carotenoids: Carotenoids being large and bulky form aggregates easily due to their hydrophobic nature mainly located at the integral part of the membrane. They also influence membrane fluidity, increase rigidity and mechanical strength hence play a vital role media. In higher organisms, carotenoids are mainly found in chromoplast in the form of microcrystalline aggregates[20].

3. Pigments from Microbes: A diversity of pigments is available in the form of natural and synthetic pigments in the market. Due to the carcinogenic and teratogenic toxicity, properties of the synthetic pigments, attention has been drawn towards natural pigments derived from microbial sources. Carotenoids, anthocyanins, flavonoids, and tetrapyrroles (chlorophylls and phycobiliproteins) are known derived natural pigments from various species of fungi, algae and bacteria [21,22]. The favorable characteristics that should be present in the ideal pigment-producing microbes are mainly able to dissimilate a wide range of C and N sources, tolerant to pH, temperature, and minerals, produce adequate amounts of color, be non-pathogenic, non-toxic, and easy to separate pigments from cell biomass[23]. The fermentation process is faster and more productive as compared to the chemical process. Utilizing microbial sources has



Fig 2. Classification of Carotenoids

in the structural properties of membrane[19]. Interaction with polar molecules is only possible when carotenoids either form a complex with protein or with its side functional polar groups. They also crystallize in aqueous several benefits, including the capacity to manipulate genes, growth independent of weather conditions, and ease of development on low-cost substrates. Additionally, microbial pigments have the key benefit of being significantly less hazardous than synthetic inorganic colors. As the public's awareness of "synthetic food additives" increased, industries are now focusing on extracting microbial pigments using genetic engineering and fermentation. If in-depth research is done on safe microbial pigments, the economics of natural food additives may be significantly improved[24]

4. Functions of carotenoids: Due to their antioxidant (anti-radical) properties, carotenoids are extensively used in the pharmaceutical industry for the manufacturing of medicines and supplements to boost immunity (Fig 3). According to experimental evidence, oxygen radicals are already thought to be a major development of many factor in the diseases[25,26]. It has been already established that carotenoids can significantly reduce infection by quenching radicals only if taken at threshold level[27] which is the case for lung cancer, arteriosclerosis, cataracts, age-related problems like macular degeneration, Parkinson's disease. multiple sclerosis. disease, cardiovascular and skin-related problems and eye diseases. In addition to their antioxidant properties, studies have revealed that carotenoids may also exert their effects by influencing enzymes that break down drugs in Phase I and II of their metabolism. These mechanisms include junction gap communication, cell growth regulation, gene expression regulation, immunological response, and cell growth regulation[28,29]. Dietary antioxidants are another name for carotenoids, which include lutein, lycopene, α carotene, β -carotene, β -cryptoxanthin, and zeaxanthin.

4.1. Carotenoids as a precursor of vitamin A: Vitamin A is essential for humans since it is important for immune system health, eyesight, reproduction, and cellular communication. Since humans cannot synthesize vitamins on their own, they must get them from diet or supplementation. Carotenoids and Vitamin A share a lot of structural similarities[30]. Hence, some carotenoids like α -carotene, β -carotene, and β -cryptoxanthin can act as a precursor of vitamin A while others like lycopene, and zeaxanthin can't. Retinol, retinal, and finally retinoic acid are produced through the oxidation of provitamin A carotenoids. The



Figure 3: Functions of carotenoids

retina must function as the precursor of 11-cisretinal-dehyde, or as a crucial part of rhodopsin, which supports the appropriate differentiation and functioning of the cornea and conjunctival membranes. Deficiency may lead to xerophthalmia (dry eye) and ultimately to night blindness or total blindness [31]. Vitamin A and its active compound retinol, is widely known to influence the innate immune system and regulate the antibody response hence resist infections. In addition to supporting cell growth, vitamin A is essential for the regular development and functioning of the heart, lungs, and kidneys. It is known to maintain healthy skin, teeth, skeletal and soft tissue, and mucous membranes. It plays a vital role in the differentiation and proliferation of epithelial tissues[32,33]. Vitamin A also plays a crucial role in the male by maintaining genital tract and spermatogenesis while in the case of females, vitamin A is required throughout the lifetime as it plays a signal role for the initiation of meiosis in female gonads and helps in pregnancy i.e., fertilization, implantation, development of the embryo as well as placenta [33-35].

β-carotene is known to quench efficiently singlet molecular oxygen, peroxides, and peroxide radicals especially during lipid metabolism, due to the presence of conjugated alternate carbon-carbon single double bonds. β-carotene is known for its 100% conversion from pro-vitamin A to vitamin A which is later converted into retinoid compounds in the intestine and liver by the enzyme 15-15'- βcarotenoid dioxygenase and by alcohol dehydrogenases respectively. Conversion may be enhanced by α-tocopherol & zinc [34,36].

4.2. Carotenoids and nutraceuticals (nutrition + pharmaceutical): The term nutraceutical was defined as "any substance that is a food or part of a food that provides medical or health benefits, including the prevention and treatment of disease" by Stephen DeFelice[37]. Due to their many advantageous properties like antioxidant activity, ability to modulate the immune

system, scavenging free radicals, and Provitamin A activity, carotenoids could be exploited for pharmaceutical purposes against many diseases as well as for health epidemiological maintenance. Additional research has demonstrated that carotenoids protect people from a variety of illnesses, including cardiovascular diseases[38,39]. The antioxidant properties of carotenoids like lycopene, β -carotene, canthaxanthin, zeaxanthin, and astaxanthin, which are widely used in a variety of foods, cosmetics, vitamin supplements, health products, and feed additives for fish, crustaceans, poultry, and other livestock, could be utilized and exploited by the nutraceutical industries to make enormous profits. According to Globe Newswire, Feb 2023, it is expected that feed carotenoids will surpass the revenue of USD 2.75 billion by growing at a CAGR of 2.2%. For human health, β -carotene along with supplementation of canthaxanthin was used for patients suffering from erythropoietic protoporphyria to reduce some of the deleterious effects of light[40,41]. B-carotene is known to inhibit progressive carcinogenic pathways. Certain cancers like oral, mammary tumors, and skin cancers were reduced[42]. Lycopene quenches the reactive oxygen species which is the causative agent for sperm damage and hence can be used to treat infertility in men. The best approach to lower the risk of prostate cancer is to consume lycopene, which can be found in processed tomatoes [43,44]. Carotenoids further protect the cell membrane lipids, proteins, lipoproteins and DNA from oxidative damage [45]. It is given as a supplement to patients with liver diseases for lowering LDL cholesterol and is thought to help prevent atherosclerosis[46,47]. Another significant carotenoid to be utilized as a supplement for a variety of ailments is lycopene, which has been shown in vitro and in vivo research that slow the growth of breast, lung, cervical, ovarian, prostate and pancreatic cancers[48-52]. Lycopene also suppressed insulin-like growth factor-I-stimulated growth. This growth factor is a key hormonal regulator

that controls the proliferation of endometrial and breast cancer cells[52]. It is advised to include carotenoids, particularly lutein and zeaxanthin, in a balanced diet or take pure supplements to lower the risk of developing acquired illnesses such retinal degeneration, neurological diseases, cataracts, and coronary heart disease.[53,54]. It also helps in improving eyesight as they absorb blue light thereby often recommended to eye patients by ophthalmologists[55]. Carotenoids can also be taken as supplements to reduce inflammation especially astaxanthin as it is known as an antiinflammatory and work against inflammatory cytokine interleukin-6, tumor necrosis factoralpha (TNF-a), interleukin 1B (IL-1b), nitric oxide (NO), Cox-2 enzyme, prostaglandin E-2 (PGE-2), and nuclear factor kappa-B. Hence, there is no argument that carotenoids as a part of whole foods or taken as supplements can benefit human health by protecting from UV radiation, cell health, eye health and cancers.

4.3. Role of carotenoids in Immunity: The free radicals created during metabolic and immunological processes are quenched by carotenoids' scavenging action [56,57]. Acquired immunity consist of lymphocytes that invariably generate reactive oxidative products (ROS) to oxidize contaminants and kill infections by damaging their cell membranes, proteins, and nucleic acids. But reactive species do not differentiate between self and non-self hence as a defense mechanism, the body utilizes antioxidant molecules to quench them effectively and safeguard the "self" cells. The dietary antioxidants that are most frequently used are zinc, selenium, carotenoids, flavonoids, vitamin E, and vitamin C. Furthermore, it is well recognized that carotenoids are important for signal transduction, gene regulation, apoptosis, and the disease etiology [58,59]. By promoting effector T-cell activity, boosting macrophage and cytotoxic T-cell capacity, and promoting T- and B-lymphocyte proliferation, carotenoids strengthen vertebrates' immunity. Additionally, it has been discovered to have immunomodulatory benefits in mammals

[60,61]. Carotenoids are known to modulate and influence the functioning of the immune system by reducing the reactive species that immune-suppressive peroxides and immuneactive cells can produce[4,62]. They are also known to protect membrane receptors; control the release of lipid compounds that have immunomodulatory properties like prostaglandins and leukotrienes; also known to improved gap junction communication and immunological function in vitro; decreased or stopped cell transformations and mutagenesis[7,62,63].

4.4. Role of carotenoids in prevention and protection from cancers: Numerous studies have established a plausible link between carotenoids and their effect on therapy and prevention of cancer. Several meta-analysis studies have further verified the role played by carotenoids in cancer pathogenesis. The carotenoids having anti-cancerous activity include α and β carotenes, lycopene, lutein, zeaxanthin, fucoxanthin, canthaxanthin, astaxanthin etc. The anti-cancerous activity is primarily attributed to their anti-oxidant activity, however, a few of them modulate signaling pathways involved in apoptosis, cell autophagy[64-66]. proliferation, and Numerous carotenoids e.g. α and β -carotenes are known for their anti-cancerous activity[67]. However, α -carotenes are believed to possess higher antioxidant activity while β -carotenes are known for their anti-tumor activity [68]. Lycopene has been described to protect and prevent a variety of cancers including colon cancer, prostate cancer[69], lung cancer[70], mammary tumors [71], cancers of urinary bladders [72], ovarian cancers [73] and hepatocarcinoma [74]. Lutein has been associated with the chemoprevention of cancer [75] however its role in specific cancers remains to be established. Fucoxanthin, canthaxanthin and astaxanthin have been demonstrated to possess anti-cancerous activity in several cell lines and animal models [76-78]. Astaxanthin is known to inhibit cell proliferation and induce apoptosis and both

could be used for potent anti-cancerous activities [79].

4.5. Carotenoids as virulence factor in bacteria: By virtue of their antioxidant properties carotenoids could impart survival advantage for intracellular pathogens that are exposed to toxic levels of reactive oxygen species and reactive nitrogen species. The role of the carotenoids as virulence factors was first described in Staphylococcus aureus [80]. This pigment was demonstrated to function as an anti-oxidant inside neutrophils and protect the bacterium from ROS [80]. The role of carotenoids in the virulence of the bacterial pathogen is further exemplified in Group B Streptococcus which has hemolytic and cytolytic toxins. Interestingly, it was observed that the cylE gene enables bacteria for both the toxin and the pigment production [81,82]. Interestingly, several mycobacterial species also produce small amounts of carotenoids. exact While their function in the pathophysiology of tuberculosis remains unknown, carotenoids are crucial for the intracellular survival of Mycobacterium marinum [83]. Even in phytopathogens, the carotenoids are key players. For instance, carotenoids are crucial for both neutralizing ROS and protecting from UV light in Pantoea stewartii. Interestingly the pigmentation in this phytopathogen is regulated by virulence and quorum sensing regulator EsaI/EsaR. Du et al proved that carotenoids accumulated during the formation of biofilm in Rhodococcus sp. **SD-74** Cronobacter sakazakii [84]. Carotenoids play an important role in the virulence of parasites affecting humans. which causes Toxoplasma gondii fatal toxoplasmosis immuno-compromised in individuals is known to produce abscisic acid. Abscisic acid plays a major role in pathogenesis and transmission [85]. Similar to T. gondii, Plasmodium falciparum, which causes malaria in humans also possesses machinery to synthesize carotenoids[86].

5. Industrial applications of Carotenoids: Carotenoids are highly pigmented chemicals

that impart bright hues to fruits, vegetables, and other natural sources. Owing to their distinct qualities as colouring agents and possessing antioxidant properties, they are employed in a variety of industry sectors (Fig 4). It is reported that the market for carotenoids is expected to expand from its 2021 valuation of \$1.8 billion to \$2.7 billion by 2031, with a compound annual growth rate (CAGR) of 3.9% from 2022 to 2031[87]. Carotenoids are a natural food colouring ingredient that the food industry uses extensively because they can produce a wide range of vivid tones. Additionally, as dietarv supplements, carotenoids offer significant health advantages by serving as antioxidants that shield the body from oxidative stress[63]. Carotenoids act as natural antioxidants in food preservation, extending the shelf life of items. They are also excellent flavour enhancers, enhancing the visual appeal of a variety of foods[63]. Carotenoids are used by the pharmaceutical industry for medical purposes in addition to food. Their anticancer qualities have been found by research, which makes them useful in cancer therapies[88]. the creation of Carotenoids also exhibit anti-inflammatory properties, which may be advantageous in the treatment of inflammatory diseases[89]. Finally, carotenoids are now present in the cosmetics sector. Because of their antioxidant qualities, they are utilized in skincare products; in hair care products because they strengthen hair; and in makeup and beauty boosters because of their vivid pigmentation[90]. All things considered, carotenoids are essential to many different businesses because they offer several benefits and uses. Carotenoids are useful in a wide range of industrial applications, from food and cosmetics to pharmaceuticals and biotechnology. Carotenoids are also being used more substitutes frequently as for artificial colourants and additives due to the growing consumer interest in natural and sustainable products[87].

6. Conclusions: Owing to carotenoids' numerous applications due to the presence of



long hydrocarbon chains with conjugated

carotenoids from the bacterium is therefore of

Figure 4: Applications of carotenoids in various industries

systems led to the exploitation and search of novel carotenoids for the benefit of human society. Carotenoids are not only anticancerous molecules but also utilized as natural food colorants, in cosmetics as they protect the skin from UV light, quenching excessive reactive species formed by immuneactive cells, protecting the cells from peroxides and maintaining membrane fluidity, acting in the release of immunomodulatory lipid molecules such as prostaglandins and leukotrienes [91] and so forth. Owing to its application and despite industrial the natural availability of and synthetic carotenoids, there is currently a resurgence of interest in microbial sources. As a response to а variety of environmental challenges, microorganisms tend to collect a variety of carotenoids. By doing this, they defend themselves from free radicals and play a significant role in photoprotection. Microbes like algae, fungi, and bacteria generate carotenoids, but only a few of them are used economically [92-96]. It's intriguing to learn that different microorganisms produce variety of carotenoids, which can neutralize the effects of toxic dietary additives. The discovery of unique, stable, and highly anti-oxidant active interest to the researchers.

Conflict of Interests: The authors declare that there is no conflict of interest regarding the publication of this paper.

7. References

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Influence of Physico-chemical Conditions on Mobility of Uranium from Wastes

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Abstract: Dynamic leaching tests were carried out on solid wastes generated from the uranium mining and milling industry under different physico-chemical conditions to assess the mobility of uranium from these matrices. The mobile/ soluble fraction of uranium leached out very slowly; being faster in the initial stages and then attaining a near steady state condition in most cases. Uranium leaching was observed to increase with decreasing initial pH, reducing particle size and increasing temperatures. A maximum of 2.4% uranium was leached out under highly acidic conditions in the experimental time period. Leachability index values indicated weak leaching of uranium from the wastes under all conditions. Leaching kinetics was examined with the help of a heterogeneous reaction model. Model results and apparent activation energy values indicated the leaching process to be initially reaction controlled and subsequently diffusion controlled. The apparent rate constants displayed dependence on the particle sizes of the tailings. All results obtained from this study imply that the extent of uranium leaching from these solid mining wastes is extremely low. This indicates low mobility and negligible transfer to other environmental compartments.

Keywords: Uranium; Mining wastes; Mobility; Batch leaching; Leachability index; Kinetics

1. Introduction: Uranium is the basic fuel of the present global nuclear power programme. This radiologically and chemically toxic element has been prevalent in the atmosphere, hydrosphere, lithosphere and biosphere with wide variation in concentration since the inception of the Earth [1]. It is present in ppm levels in soils to a few percentages in minerals/ rocks used in the mining industry and also in the waste forms generated. The presence of uranium in surface water, groundwater and seawater arises due to its mobility from soil/sediment/rock into the water medium depending on several factors like, the initial U concentration in the solid matrix, pH of the system, redox potential, concentration of complexing anions, concentration of competing ions, porosity of the medium, ambient temperature, presence of organic compounds, amount of water available for leaching, flow rate of water and microbial activity [2].

The potentially harmful constituents from any mineral/rock/waste used in the mining industry may contaminate the groundwater by geological processes like leaching and erosion, as runoff and waters percolating through these materials carry the constituents eventually into the aquifers or surface streams. Many leaching procedures have been developed with the aim of assessing the risk associated with such solid matrices [3]. These leaching procedures are useful tools to assess the impact of changing conditions on long-term release of pollutants from a matrix to evaluate their potential environmental impact. Apart from mathematical modeling, leaching tests also estimate the elemental release under field management scenarios [4]. Because the leaching process is inherently extremely complex, no single leaching test or a set of leaching conditions is appropriate for a wide variety of objectives and

applications [5]. Equilibrium leaching tests offer more realistic simulation of long-term leaching processes that occur in environmental conditions [6]. In such tests the material is in contact with the leaching solution and the variables generally include: contact time, agitation rate, pH of the leachate solution and L/S ratio [5]. Equilibrium batch leaching tests offer the advantage of simple design, high reproducibility and shorter experimental period, ranging from a few hours to a few days. For the above advantages, and in order to provide a better tool for decisionmaking, the equilibrium batch tests have been used routinely to study the environmental fate and transport of pollutants. Dynamic leaching tests include multiple or serial batch test, and percolation and flow through (i.e., column) tests [7].

The mining of uranium bearing minerals is essential for the extraction of uranium to meet the power requirements of India [8]. Mining and milling activities produce large quantities of low active tailings that are contained in engineered Tailings Ponds. The nature of tailings depends on the mineralogy of ore and host rock and their quantity depends on the configuration of the ore body and mining methods [9]. Mine tailings are generally characterized by low pH, low organic carbon content and high levels of heavy metals. These tailings are amenable for interaction with the geochemical forces of leaching and infiltration and hence can act as a potential source of contamination [10]. This necessitates the physical and chemical characterization of the tailings as well as studying the mobility of contaminants therefrom under different environmental simulated conditions. The mobility of the contaminants may lead to their presence in the groundwater, leading to their eventual uptake by plants which ultimately culminate in the human food chain.

Mining and processing of low-grade uranium ore commenced in the mid-sixties and has since been carried out at different locations in the Singhbhum Thrust Belt (STB) of Eastern India [11]. The low grade ore from these mines is processed at the ore processing plant at Jaduguda. A hydrocyclone separates the finer fraction of the solid tailings (<74 μ m) from the coarser fraction. A final alkaline pH is maintained in the solid tailings, which are then pumped to engineered tailings ponds for permanent containment [12]. The solid mass settles down and the clear liquid is decanted and sent to the Effluent Treatment Plant. At Jaduguda, around 1.5 x 10⁵ tonnes per annum of tailings are disposed in the Tailings Ponds [13,14].

In the present study, equilibrium batch leaching has been employed to represent the mobility of uranium from mill tailings generated from the uranium mining industry and its release has been studied over widely varying physicochemical conditions (e.g., contact time, particle size of sample, pH of leachate solution, temperature etc.). LED fluorimetry has been used as the analytical tool to quantify the amount of uranium extracted into the leachate solution. The amounts of uranium leached out under different conditions, cumulative leach fraction (CLF) and leaching intensities have been calculated. The kinetics of uranium leaching has also been modeled using a heterogeneous reaction model. Hence this study gives an insight into the of different physicochemical influence conditions on uranium leaching from mining wastes and the governing kinetic processes.

2. Physiography of the region: Samples were collected from the STB, which is a uranium mineralized region located in Jharkhand State of Eastern India. This hilly and undulating terrain, falling within the Singhbhum Shear Zone, is known for hosting vein/disseminated type of deposits uranium [15]. The uranium mineralisation has occurred primarily within the narrow cracks in Arachean metamorphic rocks, filled with pitchblende as the primary mineral, and are hence named vein type deposits [16]. This region receives an annual rainfall of around 1200 mm and experiences true tropical climate.

Maximum temperature of 39-42°C is observed during the summer months (March to May) and average temperature in the winter months (November to February) comes down to 9-15 °C. Relative humidity ranges from nearly 50% in the summer to 85% in the monsoons (June to September) [17].

3. Materials and Methods

3.1. Sample collection and processing: Uranium bearing tailings were collected from the tailings ponds located in the study area. Tailings samples were collected from the surface of the tailings ponds using random sampling method. Multiple samples were collected from a location and homogenized to make one representative sample by coning and quartering technique [18]. The samples were dried at 80°C till constant weight and then sieved below 2 mm mesh size for use in subsequent experiments. All stored preconditioned samples were in polyethylene containers for further experiments.

3.2. Physicochemical characterization: The physicochemical characteristics of samples help us in understanding the association, transport and biological activity of elements present therein. The physicochemical characteristics of the mine tailings were measured following standard methods [19]. In the present study, the pH of the samples was determined by a digital pH meter (Mettler Toledo) at 1:2.5 w/v of soil: ultrapure water. Organic matter content was determined by loss-on-ignition method [20] involving weight loss after calcination of the samples in a muffle furnace at a temperature of 550°C until constant weight was achieved. The samples were separated into different particle size classes by dry sieving using an electromagnetic sieve shaker and by sedimentation method using Stoke's law for the settling velocity of spherical particles. All the measurements were carried out at room temperature (25 °C), wherever applicable [21].

The mean bulk density, pH, porosity and organic matter content of the uranium tailings were 1.7 \pm

0.4 g/cm³, 6.5 ± 0.1 , 41 ± 4.3 % and 0.9 ± 0.2 % LOI (Loss on ignition), respectively. The texture of the uranium tailings was observed to be sandy loam, with the sand %, silt % and clay % ranging from 70-80 %, 13-24 % and 2-7 %, respectively. The tailings samples were segregated in different particle size classes and the particle size distribution of a typical tailings sample is given in Figure S1 of supplementary information. The maximum mass fraction for uranium tailings was present in the 63-125 µm particle size class.

3.3. Elemental analysis: Major elements and uranium were measured in the samples by CHNS Elemental Analyser (Vario EL Cube), Instrumental Neutron Activation Analysis (INAA) technique and Gamma spectrometric technique.

The CHNS Elemental Analyser works on the principle of combustion of the samples (conversion to gaseous products), subsequent separation of gases in Gas Chromatographic columns and determination of C, H, N and S by a Thermal Conductivity Detector [22].

To perform analysis by relative method of INAA, samples were sealed with Certified Reference Materials and blanks for irradiation. Irradiation was carried out at a neutron flux of 10^{12} neutrons/cm²/s and subsequent counting was carried out on a 50 % relative efficiency HPGe detector coupled to a PC based MCA. Details of the procedure are given elsewhere [23]. Prior to gamma spectrometry counting, the samples were dried, homogenized and sealed in standard geometry for 1 month. An n-type vertical germanium detector (DSG, Germany) having 100 % relative efficiency (with respect to 7.6 cm* 7.6 cm NaI(Tl) detector at 1332 keV of ⁶⁰Co gamma energy measured at 25 cm) and associated electronics coupled with 8 K MCA were used for counting. PHAST software (Electronics Division, BARC) was used for spectrum analysis. The detector was surrounded by 7.5 cm thick lead shield. Energy and efficiency calibration of the detector was done

using IAEA Certified Reference Materials (CRMs), RGU-I and RGTh-I. Details of the procedure are given elsewhere [23]. The total concentrations of major elements and uranium in the samples, obtained by the above-mentioned techniques, are given in Table 1.

Element	Unit	Concentration
Na	%	0.6 ± 0.2
K	%	0.8 ± 0.3
Fe	%	7.2 ± 1.3
С	%	1.0 ± 0.8
Н	%	0.7 ± 0.3
Ν	%	0.1 ± 0.03
S	%	0.2 ± 0.1
U	ppm	91.2± 5.8

 Table 1. Major element and uranium concentrations in uranium tailings samples

3.4. Dynamic Leaching experiments: Physicochemical conditions of leaching: The goal of equilibrium batch testing was to represent constituent solubility and release of uranium over a range of conditions by varying a physical parameter/condition of leaching (e.g., pH, particle size etc.). The dynamic leaching method involved shaking a known mass of soil (a few grams) with an extractant (ultrapure water) for a predefined period of time on a horizontal shaker at a speed of 80-100 rpm. All experiments were conducted at ambient temperature (22-25 °C), except where the temperature was the variable parameter to study the effect on leaching. A solid: liquid ratio of 1: 25 has been proposed for nutrient leaching; 1:10 for radionuclides and 1:8 for heavy metals [24,25]. If the solid: liquid ratio is kept very low, for example 1:5, there is a possibility of heavy metal re-adsorption onto the solid phase and in such cases the equilibrium condition may not be attained [26]. However, a solid: liquid ratio of 1: 20 was maintained throughout the experiments in this study to minimize any change in leachate

composition and also to ensure adequate concentration of leached uranium for subsequent analysis by LED Fluorimetry. Water was used for these experiments as the leachate, to allow the waste matrix be a dominant factor in determining the pH of the leachate; a scenario similar to the ambient environmental conditions. This is similar to the ASTM test, DIN 38414 S4 batch test of Germany and the AFNOR X 31-210 batch test of France employed for testing elemental leachability from waste matrices [27]. Also, the use of relatively non-specific extractants leads to a kinetic approach towards elemental leachability since measurements of trace elements extracted at equilibrium cannot be related to their speciation. Leachate was separated from the solid matrix by vacuum filtration through 0.22µm membrane filter and analysed for total U concentration by LED Fluorimetry. A portion of leachate was sampled out at regular time intervals and replaced with fresh solvent. All experiments were carried out in duplicate.

The variables during the equilibrium batch tests included: contact time, pH of the leachate solution, temperature during leaching experiment and particle size of the material. Contact time was varied from 2-95 h for the leaching tests. The samples were subjected to dynamic batch leaching with water as solvent under acidic (pH 4), neutral (pH 7) and basic (pH 9) conditions. Particle sizes of the tailings subjected to dynamic leaching were <36 µm, 36-63 µm, 63-125 µm, 125-212 µm and 212-500 µm. The dynamic leaching tests were carried out under ambient temperature (25 °C) and at an elevated temperature of 40 °C and 60 °C.

3.5. Analytical technique: The total uranium content in leachate samples was analysed using a LED based Fluorimeter system fabricated by LED Instruments Section, Raja Ramanna Centre for Advanced Technology, Department of Atomic Energy, India. It is a compact analytical instrument based on fluorimetric technique and micro-optics. The instrument contains a nitrogen

LED (radiation source), sample compartment (sample in quartz cuvette, 9 ml) and a PhotoMultiplier Tube (PMT) placed in rightangle optical configuration. The uranium complex formed in the sample, by the addition of fluorescence enhancing agent, is excited by the LED light, which upon de-excitation emits fluorescence, measured by the PMT. The fluorescence interference originating from organic matters in the samples, is corrected by optical filter, fixed electronic delay and gating. The optical filter at 450 nm and measurement of delayed fluorescence signal helps in nullifying the interference due to organic matter. The working range and Minimum Detection Level (MDL) of the instrument are $0.2-20 \,\mu\text{g/L}$ and 0.2μg/L, respectively.

The leachates generated from the equilibrium dynamic batch tests were analysed by standard addition technique. A working solution (500 μ g/L mass concentration) of uranium was used as the standard, for analysis. It was prepared from an Atomic Absorption Standard solution of uranium (973 μ g/ml mass concentration, Sigma Aldrich). A typical standard addition curve used for sample analysis is shown in given in Figure S2 of supplementary information.

The concentrations of uranium (ppb) in samples were calculated by using the equation,

$$U\left(\frac{\mu g}{ml}\right) = \frac{D_1 * V_1 * C}{(D_2 - D_1) * V_2}$$
(1)

Where D_1 is the fluorescence due to sample alone, D_2 is the fluorescence due to sample and U-standard, V_1 is the volume of U-standard added (ml), V_2 is the volume of sample used for analysis (ml) and C is the concentration of U in U-standard (µg/ml)

3.6. Quality control: Appropriate qualityassurance protocols were adopted and precautions were taken to ensure reliability of results. All reagents used in the entire study were of analytical reagent (AR) grade. Ultrapure water (Type-1, ~18.2 M Ω , Barnstead T11, Barnstead Nanopure, Thermo Scientific) was used throughout the study. The laboratory

glassware used for sample processing and storage were soaked in 10% nitric acid for 15d and then rinsed thoroughly with ultrapure water before use. Multiple samples and instrumental/analytical blanks were used throughout the study for quality control purposes. Reagent blank was taken along with each batch of sample during sample processing and the concentrations observed were subtracted from the same batch of samples. Certified reference standards and blanks were analysed for quality control of the measurements. Various precautions were taken in order to achieve a dust-free laboratory environment and steady temperature. Careful handling of the samples was ensured to avoid cross contamination. Statistical quality of the instrumental output was controlled by constructing quality control charts by monitoring the output of the instrument over a long period of time. The various procedures undertaken for quality-control purposes are elaborately mentioned elsewhere [28].

4. Theoretical basis of calculation

4.1. Cumulative leach fraction: Uranium leaching was quantified by the cumulative leach fraction (CLF). CLF is a measure of the elemental mobility in terms of the leaching rate, from a sample. It is calculated by the following equation [29]:

$$CLF(cm) = (\sum A_n / A_0) / \frac{V}{S}$$
(2)

where, $\sum A_n$ is the cumulative content of element leached during the cumulative time t_n , A_0 is the initial element content present in the sample, V is the volume of sample (cm³), and S is the exposed surface area of sample (cm²).

4.2. Leaching intensity: Leaching intensity (I) is another parameter to quantify elemental leaching. I for a solid-liquid system can be determined by the following equation [30]:

$$I(h^{-1}) = \frac{[U] \text{ in leachate}\left(\frac{\mu g}{ml}\right) * \text{Volume of Leachate(ml)} * 1000}{[U] \text{ in sample}\left(\frac{\mu g}{g}\right) * \text{Weight of sample (g)} * \text{Time (h)}}$$
(3)

The larger the value of I, the greater is the rate of leaching. Wang et al. [30] have classified the elemental leaching from wastes as strong: $I \ge 5$; medium: $1 \le I \le 5$; weak: $0.5 \le I \le 1$; very weak: $I \le 0.5$.

4.3. Governing kinetic processes: It can be considered that chemical reaction in a solidliquid system is controlled by one or more of the following steps: a) diffusion through the liquid film; b) diffusion through the product layer formed on the surface of the particle; and c) chemical reaction at the surface of unreacted particles which then diffuse across the solidliquid interface or through the porous solid layer [31]. Considering the dissolution of uranium from mill tailings, if the particles are considered to be spherical, the elemental leaching can be described by the shrinking core model (SCM), a heterogeneous kinetic model. This model considers the dissolution of spherical solid particles in a solid-liquid system [32,33].

For a chemical reaction, the step with the highest resistance is the rate controlling step. According to SCM, if the reaction is controlled by the surface reaction step, the kinetic equation is [34]:

$$1 - (1 - x)^{1/3} = k_r t \tag{4}$$

But, if the reaction rate is controlled by the diffusion step, the kinetic equation is [34]:

$$1 - \frac{2}{3}x - (1 - x)^{2/3} = k_{d}t$$
 (5)

where, x refers to the fraction of element reacted/leached, t is the time period of reaction, k_r and k_d are the rate constants of chemical reaction step and diffusion step, respectively. These two equations indicate that if the chemical reaction step or the diffusion step is the rate controlling step in the leaching process, then a plot of the left hand side of the equations with respect to time t will yield a straight line with slopes of k_r and k_d , respectively.

The apparent rate constants k_r and k_d have been used to study the temperature dependence according to the Arrhenius' equation [34], in Fig. 5:

$$\mathbf{k} = \mathbf{A} * \mathbf{e}^{-\mathbf{E}_{\mathbf{a}}} \mathbf{R} \mathbf{T}$$
 (6)

where, A is the frequency factor, E_a is the activation energy of a chemical reaction, R is the universal gas constant and T is the temperature in K.

5. Results and Discussion: Considering the physico-chemical characteristics of the samples, it was observed that porosity and organic matter showed positive correlation with the clay content of these samples, as evident in Table ST1 of supplementary information.

Different physicochemical factors like pH, particle size, time, temperature, concentration of complexing agents, concentration of competing ions, etc. influence the leaching of uranium from a matrix. We have made an effort to investigate the variation of U leaching with the variables like contact time, leachate pH, particle size and temperature from the U tailings, in this study. We have also made an attempt to study the kinetics of uranium leaching from these tailings.

5.1. Effect of leaching duration: The leached U concentrations have been observed to increase with time; contact time varying from 2 h to nearly 95 h, considering all experimental conditions. In all the cases, viz. varying pH, temperature and particle size, an initial faster rate of leaching was followed by a slower rate of leaching, which finally reached a near steady state condition in most of the cases. The faster rate of leaching continued nearly for the first 10 h. This trend of leaching can be attributed to biphasic kinetics i.e., a rapid reaction rate

followed by a much slower reaction rate, explained by two first order reactions taking place in the biphasic system [35,36].

5.2. Effect of leachate pH: The uranium tailings were subjected to acidic (pH 4), basic (pH 9) and neutral (pH 7) conditions of leaching, with water as the leachate, modified by acid and base, as required. The pH was maintained initially, using small amounts of an acid (dilute nitric acid) and a base (dilute sodium hydroxide). The maximum uranium concentrations were observed in the leachates in the acidic conditions of leaching. The extreme conditions of acidic and alkaline environments do not exist in the natural environment. However, leaching experiments were carried out to assess the extent of increased leaching under these conditions and to ascertain the applicability of the shrinking core model.

In Figure 1(a) it can be seen that the U leached concentrations increased with time under all pH conditions. The uranium leached (%) from the tailings reached a maximum of 19% under acidic pH during the entire leaching time period, as evident from Figure 1(a). The maximum U% leached from the tailings was 0.4% in basic and 0.7% in neutral conditions, respectively. A much

higher rate of U leaching in the acidic conditions may be because of the oxidative dissolution of the pyritic tailings in acidic media [9,37]. Figure 1(b) shows the variation of pH in the leachates with time. It can be observed that the pH in neutral conditions of leaching varies around the neutral pH of 7; leachate pH in this condition is totally dependent on the pH of the sample (uranium tailings). In the basic condition, initially the leachate pH had a dominant role to play, but towards the end the pH of the leachate was dominated by the pH of the sample. For the acidic condition, the pH showed least variation and the leachate pH was dominant throughout the experimental period.

5.3. Effect of particle size: The uranium tailings were subjected to dynamic leaching with water for the different particle sizes viz. $<36 \mu m$, 36-63 μm , 63-125 μm , 125-212 μm and 212-500 μm . Decrease in the particle size of tailings leads to enhanced U leaching, with the maximum U % leached varying from 0.5 % (212-500 μm) to 2.4 % (< 36 μm). It is evident from Figure 2 that the rate of leaching is higher for smaller particle sizes, which may be due to the increase in surface area with reducing particle size



Figure 1. (a) Trend of uranium leaching at different pH; inset showing the zoomed image for neutral and basic pH and (b) variation of pH with time
5.4. Effect of temperature: The uranium tailings were subjected to dynamic leaching at 25°C, 40°C and 60°C with water. An increase in uranium% leached was observed with the increase in temperature, reaching a maximum of 0.6% at 25°C and 1% at 60°C, as evident from Figure 3. Again, the rate of uranium leaching was observed to increase at elevated temperatures. The movement of ions increase with an increase in temperature, thus increasing their migration and diffusion, finally resulting in an increase in the rate of chemical reaction.



Figure 2. Trend of uranium leaching with different particle sizes

5.5. Leachability indices: The U CLF values ranged from 0.001-0.04 cm under the different pH of leaching, as evident from Table 2. The Leaching intensity from the matrices varied from 0.05-2.56 h^{-1} in the acidic, basic and neutral conditions of leaching.

The leaching indices were higher for the smaller particle sizes compared to the larger ones, as evident from Table 3. The CLF values ranged from 0.001-0.005 cm. The Leaching intensity from the different particle sizes varied from $0.09-0.46 \text{ h}^{-1}$.

An increase in the leaching indices was observed with the increase in temperature as evident from Table 4. The CLF values ranged from 0.001-0.002 cm. The Leaching intensity varied from 0.07-0.1 h^{-1} from 25- 60°C.



temperatures

Condition	I (h ⁻¹)	CLF (cm)
Neutral	0.098	0.001
Acidic	2.557	0.039
Basic	0.053	0.001

Table 3. Leaching indices for different particle sizes

Particle size	I (h ⁻¹)	CLF (cm)
<36	0.456	0.005
36-63	0.221	0.002
63-125	0.214	0.002
125-212	0.167	0.002
212-500	0.09	0.001

Table 4. Leaching indices at differenttemperatures

Temperature	I (h ⁻¹)	CLF (cm)
25⁰C	0.065	0.001
40⁰C	0.081	0.002
60°C	0.107	0.002

Highest I value was obtained for acidic condition of leaching. Comparing the I values in this study

with literature [30] it can be concluded that the uranium leaching from these wastes ranged from

5.6. Kinetics of uranium leaching: The kinetic analysis of uranium leaching from mine tailings was conducted on experimental data obtained leaching experiments at different from temperatures for different time periods. We have made an attempt to divide the uranium leaching process from the tailings into two regions, the initial process being faster and the later process being slower. Considering SCM, we have attempted to fit the experimental data with chemical reaction step in the initial stages of leaching and diffusion step in the later stages, as the rate determining steps. The initial stage has been considered to be up to 13 h from the inception of the leaching time period. The leaching of uranium from the mill tailings at different temperatures for different time periods with respect to the kinetic equations of the SCM are presented in Figure 4. It can be seen from the figure that the experimental data fit the SCM with chemical reaction in the initial stages (<13 h) and diffusion in the late stages.

Usually, high values of E_a indicate strong influence of temperature on a process as is the case of chemical reaction, whereas low E_a values indicate weak influence of temperature as in diffusion processes [32]. From Fig. 5 the apparent activation energy of U leaching from tailings in the temperature range of 25-60 °C was calculated to be 25.66 kJ/mol and 14.4 kJ/mol for the chemical reaction and the diffusion step very weak to weak under all the experimental conditions, except under the acidic condition.

of SCM, respectively. Several authors have used the SCM to calculate the apparent activation energies in elemental leaching from solid wastes [38,39].

Since the activation energy for diffusion process is nearly 20 kJ/mol [40,41], we can conclude from figures 4 and 5 that initially uranium leaching was controlled by surface reaction step being followed by the diffusion step. Also, the apparent activation energy for the chemical reaction control step obtained from this study was considerably low compared to those for typical activation controlled reactions [42].

According to SCM, the constants k_r and k_d are related to the particle sizes of the solid in the solid-liquid system. The apparent rate constants from the reaction control step and diffusion step, k_r and k_d , vary with the inverse of the particle radius and inverse square of particle radius, respectively [32]. To investigate this relationship we plotted the apparent rate constants with the particle size terms in Figure S3 of supplementary information. It is evident from the figure that k_r and k_d have a positive correlation with the particle radii. This further supports the assumption that the uranium leaching in this study follows an initial chemical reaction step followed by a diffusion step, according to the SCM.



Figure 4. Fits of SCM to experimental data considering, (a) chemical reaction and (b) diffusion through product layer steps (1:20 S/L; Neutral pH; water leachate; 80-100 rpm; composite sample)



Figure 5. Arrhenius plots of kr and kd for the experimental data

6. Conclusions: The release of uranium from mining wastes was evaluated in this study using a dynamic leaching test using water. The mobile/ soluble fraction of uranium leached out under the leaching conditions. Leaching was very slow from all the samples; being faster in the initial stages and then attaining a near steady state condition in most cases.

Leachate pH was observed to be a primary factor for uranium leaching from mining wastes, with the leached uranium content decreasing with increasing pH. Particle size of the tailings was also observed to have an effect on the overall uranium leachability, with smaller particle sizes displaying higher leaching. Uranium leaching also increased with increasing temperatures. Under all experimental conditions the uranium leaching from the tailings were observed to be low, reaching a maximum of 2.4% under acidic pH conditions of leaching. From the values of leaching intensity it can be concluded that uranium leaching from these wastes mostly ranged from very weak to weak. All the results obtained from this study imply that the extent of uranium leaching from these tailings is extremely low.

The shrinking core model with reaction control and diffusion control fitted the experimental data in the initial stages and final stages of leaching, respectively. The apparent activation energy calculated during the initial stages of leaching was higher than in the final stages; reiterating that the process is chemically controlled during the initial stages and diffusion controlled in the later stages. Also the apparent rate constants displayed dependence on the particle sizes of the tailings, according to the shell core model.

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Supplementary Information





Fig S2. Typical standard addition curve for U analysis by Laser Uranium Analyser



Figure S3. Plot of (a) k_r vs. 1/r, and (b) k_d vs. 1/r²

	BD	pH	Porosity%	OM%	Sand%	Silt%	Clay%
BD	1.00						
pH	-0.07	1.00					
Porosity%	-0.95	0.29	1.00				
OM%	-0.29	0.48	0.44	1.00			
Sand%	0.12	0.89	0.05	0.39	1.00		
Silt%	0.19	-0.91	-0.36	-0.64	-0.93	1.00	
Clay%	-0.81	0.25	0.86	0.78	0.04	-0.41	1.00

Table ST1. Correlation between different physicochemical characteristics

Analysis of Range and Speed Detection Using A Commercial RADAR module at 24GHz

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Abstract: In this work, the performance of OmniPreSense Module OPS243-C has been studied for range and speed detection, at 24 GHz, whose results are obtained using Fast Fourier Transform (FFT) commands using a MATLAB script and verified with the physical range of objects used. Four custom-made scenarios have been created, two using stationary objects namely a stand and a tripod for their range at two different distances, and two using moving objects, a person and a ceiling fan for their respective speed. A total of 10 observations for range detection are taken inside an anechoic chamber and reported with a range of percentage errors, which varies for objects and their range. The mean values of the tripod and stand range are detected at 4.06 m and 0.42 m, respectively, in scenario 1 whereas in scenario 2, the mean values of the tripod and stand range are found to be 2.56 m and 1.53 m, respectively. The standard deviations in these observations are found from 0.09 to 0.12 m for range detection. In scenario 3, the speed of a moving person is found to be varied from 2.0 m/s to -2.1 m/s for Inbound and Outbound directions from the module at a distance of 4.62 m. For scenario 4, a variation in the speed of the rotating fan is observed at the knob positions (0 to 4) from the OFF to ON condition of the fan and is found to be varied from 0.1 m/s to 4.9 m/s at different knob positions. In both scenarios 3 and 4, the speed data is found with a standard deviation less than 0.5 m/s from 10 observations. In this analysis, results confirm that the OPS243-C can detect stationary and moving objects successfully.

Keywords: Range, speed, TeraTerm, FFT, MATLAB, RADAR.

1. Introduction: RADAR (Radio Detection and Ranging) is an electromagnetic sensing technique that uses wireless technology to work on the principle of emitting and receiving radio waves reflected by an object or target. Based on this, the radar system is used to detect motion, speed, direction, shape, and angle estimation of distant objects. It can detect stationary (range) and moving targets (speed and motion). There are various RADAR systems available that operate in the frequency range between 2.4 GHz and 77 GHz. In a Probabilistic Data Association Filter (PDAF) method to monitor traffic on the road using a 24.1 GHz radar system [1], the radar uses Frequency Modulated Continuous Wave (FMCW) mode to estimate the distance, speed, and angle of the vehicle and reported a maximum detectable range of 300 m and a range resolution of 0.80 m, to detect vehicles in multiple lanes. Also, a detectable velocity is from -250 km/hr to 250 km/hr and the Field of View (FoV) is from -15° to 15°. A 24 GHz

radar system is proposed using an envelope detection method and Constant False Alarm Rate (CFAR) threshold calculation algorithm to calculate target detection and angular measurements for automotive applications [2]. Authors reported a maximum target range of up to 20 m, object map update rates of 20 ms, and an angular range of approximately 5° to 40°. A radar network is developed that operates in Continuous Wave (CW) Mode with a bandwidth of 200 MHz at 24 GHz to detect range speed and angle (azimuthal and elevation) [3]. In this report, a maximum target range of up to 20 m, obstacle detections moving at the speed of more than 1 km/h, and the FoV of 12° azimuthal angle and 70° elevation angles are reported. A radar based on the FMCW mode System on Chip (SoC) is proposed for air writing characters or words in free space [4]. It uses Single Input Multiple Output (SIMO) antennas covering up to 4 GHz bandwidth from 23.5 GHz to 27.5 GHz. It shows the capability of a maximum measured

velocity of 2.94 m/s, a range resolution of 4.63 cm, and a maximum detection range of 3 m.

Using a double negative index metamaterial structure for the transmitter and receiver antenna, a 5.8 GHz Doppler radar is made [5]. In this work, the maximum velocity of the ball (indoor experiment) is calculated as 4.15 m/s and the maximum velocity of the car (outdoor experiment) is approximately 44 km/hr when the car is 72.5 m away from the radar. A mmwave radar remote monitoring system is developed for the elderly living in a home which monitors their breathing and heartbeat signals [6]. It consists of a 60 GHz FMCW system, a TIC3220 WiFi communication module, an IWR6843 mm-wave transceiver sensor and a cloud service software architecture for real-time data monitoring and database storage. The heartbeat is calculated by the radar system is 63 from a distance of 2.5 m.

A novel vital sign application is developed using a 24 GHz flexible antenna for Doppler radar, which uses a Vector Network Analyzer (VNA) for measuring S21 parameters and implements these parameters in MATLAB program for filtering, FFT, and peak detection [7]. The average chest displacement from the heartbeat and breathing is found to be 0.2-0.5 mm and 4-12 mm. A pulse coherent radar at 60 GHz is proposed for online monitoring of the withering of leaves [8]. In this work, the authors used the XM112-XB112 module evaluation kit (EVK) and reported that a decrease in water content in the leaf causes a gradual decrease in signal strength. Nowadays, different models of commercial radars are available for the above applications. A complete characterization is required for optimum application of these radars at their respective operating frequency. At the same time, these radars should report the range and speed detection with proper accuracy.

In this paper, the results of range and speed detection of various stationary and moving targets are reported which are obtained using a commercial radar model OPS243-C from Omnipresence firm at 24 GHz. The outputs of these results are extracted using custom-made MATLAB coding for two scenarios of range detection and two scenarios of speed detection. The values of range detection are verified from the physical range of the objects used. The percentage error is found from -250% to 27.77% in range detection for stationary targets. The standard deviation is evaluated from 10 observations for each scenario.

2. OmniPresense OPS243-C Radar module: The OmniPreSense module OPS243-C is a short-range radar that provides motion detection. speed detection. direction (Inbound/Outbound), and range reporting at 24 GHz [9]. It has two types of sensors, an FMCW RADAR sensor for reporting range and a Doppler radar sensor for reporting motion, speed, and direction. Two basic principles used by this module are the Doppler frequency shift to detect speed and direction and the FMCW time of flight (TOF) to detect range. It has a capability of range and speed detection up to 100 m and up to 348 mph, respectively, at 24 GHz [9]. It can be operated using two interfaces: Tera Term and Putty. Using the command instructions of the interface, the object range, speed, motion, and direction from the radar module of stationary and moving objects are detected [10].

The range and speed detection results of the OmniPreSense module can be verified and analyzed physically with a meter scale and speedometer, respectively. The data extracted using the Tera Term/Putty are the range FFT and speed FFT command output of the module and then plotted using MATLAB script [10]. A flowchart representing the complete process is shown in Figure 1.

3. Experimental procedure: The experimental data of the OmniPreSense radar module is obtained using the interface, i.e. Tera Term, with its command instructions. For this, the OmniPreSence module OPS243-C is placed over a rotating motor to scan the surrounding environment in a 360° field of view.



Figure 1. Flowchart of extracting data of OmniPreSense module OPS243-C.

Different scenarios created for the experimental purposes are:

a) Scenario 1: One tripod and one stand are kept as objects at a distance of 3.76 m and 0.2 m in an anechoic chamber, respectively, from the module.

b) Scenario 2: The same tripod and stand are kept as objects at different distances i.e. 2.39 m and 1.8 m in an anechoic chamber, respectively, from the module.

c) Scenario 3: For speed detection, a person's movement is experimentally done in the lab.

d) Scenario 4: For speed detection, the rotational movement of the ceiling fan from the OFF state to the ON state at different control knob positions (1 to 4) is considered a moving object.

These scenarios are shown in Figure 2 and Figure 3. The range and speed FFT data outputs detected by the module are obtained for four scenarios i.e. range resolution multiplied by the bin value or speed resolution multiplied by the bin value. Such experiments are being performed for the first time in four scenarios, which involved data recording with Tera Term and MATLAB commands, so 10 observations in range detection are considered for standard deviation estimation.



Figure 2. Experimental setup of OPS243-C radar module with rotating motor, (a) Tripod (Object 1) and stand (Object 2) placed at 3.76 m and 0.2m distance from the radar, respectively, (b) Tripod and stand (as seen from the tripod end) at 3.76 m and 0.2m distance from the radar module (c) Tripod and stand at 2.39 m and 1.8m distance from the radar, respectively, and (d) Tripod and stand (as seen from the tripod end) at the distance of 2.39m and 1.8m away from the radar, respectively.



Figure 3. Experimental setup of OPS243-C radar module, (a) Person's inbound movement from 4.5m distance from the radar, (b) Person's outbound movement from 4.5m distance from the radar, and (c) Rotating fan speed at different knob (state) position at a distance of 2.94 m from the floor.

4. Results & Discussion:

A. Range Detection: As discussed above, 10 observations are taken for scenario 1 where the tripod and stand are placed at 3.76 m and 0.2 m distance from the radar module. The results of these 10 observations are given in Figure 4.

As can be seen from Figure 4(a-j), the detection range is obtained in a range of 0.3-0.7 m and 3.8-4.1 m for the stand and the tripod, respectively, using the OPS243-C radar in scenario 1, when these objects are kept at 0.2 m and 3.76 m from the radar module inside the anechoic chamber as illustrated in Figure 2(a) and Figure 2(b).

The obtained ranges are a little higher than the actual ones in all 10 observations for both objects. For scenario 2, when the tripod and stand are at a distance of 2.39 m and 1.8 m from the radar, respectively, the results of 10 observations are shown in Figure 5(a-j).

The range values are found from 1.3 to 1.6 m for the stand and from 2.5 to 2.8 m for the tripod inside an anechoic chamber as shown in Figure 5. So, the radar module detects the objects and shows a little higher range than the actual one for Tripod, a little lower for the stand. As the difference between the actual and

measured ranges is almost the same in all 10 observations, the additional coding in MATLAB programming can be helpful to get the correct detection of targeted objects with the removal of systemic error.

To analyse these differences in 10 observations, the results from MATLAB coding are compared with the actual physical distance of these objects. The percentage error in the detection range can be calculated using the formula (1):

$$\frac{\text{Actual distance-Measured distance}}{\text{Actual distance}} \times 100\% \quad \text{---(1)}$$

The percentage errors in 10 observations for range detection in two scenarios 1 and 2 are shown in Table 1.

Further, the standard deviation in 10 observations for range detection is shown in Table 2.

So, for objects near the radar module, as in the example in scenario 1, the standard deviation is higher than for the object away from the module, which indicates the radar module gives better values for objects kept a little far (>1.8 m) from the module.



Figure 4. Experimental results of 10 observations (a)- (j) for Scenario 1 when the tripod and stand kept at a distance of 3.76 m and 0.2 m from the radar, respectively.



Figure 5. Experimental results of 10 observations (a)- (j) for Scenario 2 when the tripod and stand were kept at a distance of 2.39 m and 1.8 m from the radar, respectively.

Observations	Scenario 1		Scenario 2	
	Tripod	Stand	Tripod	Stand
1 st	-1.06 %	-50 %	-4.60 %	11.11 %
2 nd	-9.04 %	-100 %	-4.60%	11.11 %
3 rd	-9.04 %	-250 %	-17.15 %	11.11 %
4 th	-9.04 %	-100 %	-4.60%	11.11%
5 th	-9.04 %	-100 %	-17.15%	11.11%
6 th	-9.04 %	-100 %	-4.60%	11.11%
7 th	-9.04 %	-100%	-4.60%	11.11%
8 th	-9.04 %	-50%	-4.60%	11.11%
9 th	-9.04 %	-100%	-4.60%	27.77%
10 th	-6.38%	-150%	-4.60%	11.11%

Table 1. Percentage errors in 10 observations for range detection in Scenario 1 and Scenario 2.

 Table 2. Standard deviation for range detection in Scenario 1 and Scenario 2.

Standard deviation	Scenario 1	Scenario 2
Tripod	0.09 m	0.12 m
Stand	0.10 m	0.09 m



Fig.6(a) Speed (m/s) vs Time (s) graph of person's movement at 4.5 m towards (Inbound) and away (Outbound) from the radar (b) Speed (m/s) vs Time (s) graph of the ceiling fan at different knob positions (states) from OFF to ON at a distance of 2.94 m from the floor.

4.2. Speed Detection: For speed detection using the OPS243-C module, two scenarios 3 and 4 are considered where a person's movement (inbound and outbound) and the speed of the ceiling fan are observed as shown in Figure 3 (a-c), respectively. The results of scenarios 3 and 4 are given in Figure 6.

Figure 6(a) shows the speed range of a person moving towards (inbound) and away (outbound) from the radar module, which is observed in the range of 2.0 m/s to -2.1 m/s. On taking 10 observations of the same person's movements, the average values are found to be 1.10 m/s (Inbound) with a standard deviation of 0.37 m/s and -1.25 m/s with standard deviation of 0.31 m/s.

Figure 6(b) shows the variation in the speed of the rotating fan from OFF state to ON state with various knob positions (0 to 4). The speed of rotational movement is detected at 0 m/s in the 0th state and its speed increases from 0.1 m/s to 1.3 m/s in the 1st state. When the fan is kept at the 2nd state of the knob positions its speed is recorded from 0.1 m/s to 1.7 m/s. Further, at the 3rd and 4th states of the knob positions, the speed of the rotational movement is observed from 0.6 m/s to 3.0 m/s and from 1.1 m/s to 4.9 m/s. respectively. So, with the increasing state of knob positions, the fan rotates faster and hence the frequency of receiving signals from the fan becomes larger. However, the speed is growing slightly as the ceiling fan is at one position only i.e. stationary. To verify this, 10 observations are recorded in the scenario 4. The average speed data are evaluated as 0.71 m/s with standard deviation of 0.26 m/s, 0.95 m/s with standard deviation of 0.18 m/s, 1.48 m/s with standard deviation of 0.31 m/s and 2.44 m/s with a standard deviation of 0.50 m/s for state 1, 2, 3 and 4 of the knob positions for the rotating fan. Thus, the OPS243-C radar module can detect a person's movement and the speed of the ceiling fan with a small deviation of less than 0.5 m/s. To obtain the percentage error in the speed, the results of this radar module can be compared with the data obtained from a calibrated speedometer.

5. Conclusions: In this paper, range and speed detection is performed bv OmniPreSense firm OPS243-C Module which works both on FMCW and Doppler mode at 24 GHz. The TeraTerm is used to extract data from the module and MATLAB coding is performed to plot the results. Four different scenarios of detection are considered for two stationary and two moving objects. From the experimental results, it can be concluded that the module is detecting the range of the stationary objects quite efficiently with percentage errors of -250% to 27.77% (in case of close range) in range detection. The standard deviation in the range detection is obtained from 0.09 m to 0.12 m, while for speed detection, it is less than 0.5 m/s. The measurement results verified that the system is capable of detecting the object's range and speed at far distances better. In future work, MATLAB coding is required to reduce the error for precise detection of objects with more numbers of scenarios.

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Synthesis and Promising Applications of Graphene and Related Materials

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Abstract: In recent years, there has been extensive research on graphene and its derivatives, driven by their remarkable physicochemical and functional properties. Various forms of graphene, such as multi-layer graphene, graphene oxide, and graphene quantum dots, have shown immense potential to revolutionize multiple technologies. This review critically examines the synthesis and applications of graphene and related materials. In the synthesis section, we explore methods ranging from top-down techniques, which involve breaking down larger structures into graphene layers, to bottom-up approaches, where graphene is built up from smaller constituents. In the application segment, we comprehensively discuss the diverse uses of graphene and its derivatives. This includes their roles in electronic applications, energy storage systems, tribological applications, healthcare technologies, water desalination processes, and mechanical applications. By exploring various applications, we aim to highlight the wide-spread applications of graphenebased materials and their composites in shaping the future of multiple technologies.

Keywords: Graphene, Electronics, Energy storage, Tribology, Healthcare

1. Introduction: Graphene, a promising multifunctional material, has vast applications from pencil lead[1] to neural computing [2]. Graphene can be rolled, bundled, and stacked into 0D (fullerene, graphene quantum dots) [3, 4], 1D (nanotube, nanoribbon), and 3D (graphite) materials. The chemical model of graphene is depicted in Figure 1. Graphene exhibits exceptional properties such as high electron mobility which is 200 times higher than that of silicon under ambient conditions, ballistic electrical conductivity of $\sim 10^3$ S/m, thermal conductivity of ~5300 W/mK, excellent mechanical properties like ultimate tensile strength (UTS) of 130 GPa and elastic modulus of ~1 TPa, very high specific surface area of 2630 m²/g, excellent optical transparency (~97.7%), and less break-over voltage of ~0.3 V [5-11].

Due to these astonishing properties graphene and graphene-related materials (GRMs) are extensively used in different applications. Researchers have used various methods to synthesize graphene to obtain desirable properties and potential applications. To expand their usage, the chemical modifications of GRMs have also been executed. Despite the fact that graphene will probably enter the market as a composite, several teams are attempting to realize the full potential of the isolated sheets.

In this review, we critically discuss the synthesis and properties of graphene and GRMs. We compiled recent literature on graphene and GRMs and discussed their potential applications in the fields of high strength systems, electronics, healthcare, sensors, tribology, water desalination, and composites.

2. Synthesis of graphene: The synthesis of single-layer graphene was tried in 1975. The researchers showed that single and multilayer graphene could be produced by thermal decomposition of carbon on Pt crystal as a substrate.



Figure 1. Chemical model of graphene-related material.



Figure 2: Graphene synthesis method

However, due to the lack of understanding about such sheets and the failure to find the potential applications of these sheets, a detailed study was not conducted at that time. Later on, in 1999, scattered efforts were reported for the synthesis of graphene. However, in 2004, Geim and Novoselov were credited for the discovery of graphene [12]. For the first time, they showed the repeatable synthesis of graphene through exfoliation. After that, several methods have been reported and some of the most important synthesis (Figure 2) methods are discussed below.

2.1 Exfoliation: In graphite, the graphene sheets are bonded together by weak van der Waals bonds. These bonds can be broken to produce graphene from graphite. In exfoliation processes, mechanical or chemical energy is used to break these weak bonds and separate individual graphene sheets.

2.1.1 Chemical exfoliation: This method uses a liquid suspension that converts graphite to graphene through the formation of an intermediate compound known as a grapheneintercalated compound. Alkali metals are used to increase the interlayer spacing between the graphite layer by reducing the van der Waals forces, as these large alkali ions are placed in between the graphitic layer of graphite dispersed solution, owing to the potential ionization difference between the graphite and alkali metal. Chemical exfoliation has the benefits of a high yield and low operating temperature, but the graphene it produces tends to reassemble into graphite, hence surfactants or immiscible liquids are required [13].

2.1.2 **Mechanical exfoliation:** One of the most effective methods for obtaining singlelayer graphene flakes on desired substrates is mechanical exfoliation. In this method the peeling of the graphitic layer is happened with the help of scotch tape, ultrasonication, electric field, or even the transfer printing technique. Geim and Novoselov used mechanical exfoliation for the development of graphene [12]. They used highly oriented pyrolytic graphite (HOPG) to create 4-5 µm deep mesas. The flakes of graphene were peeled from mesas using scotch tape. These flakes were washed with acetone several times and put onto the silicon substrate.

2.2 Thermal Chemical Vapor Deposition Techniques

(i) Thermal Decomposition of SiC

The graphene can be synthesized using the thermal decomposition of silicon carbide. In this technique, SiC is heat-treated up to temperatures ranging from 1200-1500°C in an ultra-high vacuum. This leads to the removal of Si, thus leaving behind a layer of carbon [14]. Transmission electron microscopy studies were used to confirm the graphitic nature of the carbon layer or graphene. The ultrathin epitaxial films of graphite were grown by this technique on the 6H-Sic surface. The films typically contain mono and bilayer graphene sheets [15]. The primary benefit of the thermal breakdown of SiC over other traditional methods is the direct production of graphene layers on a semiconducting or semi-insulating substrate that is readily accessible for purchase, negating the need for transfer before processing electrical devices.

(ii) Molecular Beam Deposition

This technique is successfully used for the graphene growth on a variety of substrates. For example, ethylene gas is used as a carbon source and Ni substrate is exposed to a higher temperature (200°C) in an ethylene gas environment. High-quality graphene layers can be produced by this method and are capable of forming a layer on top of another [16]. The main advantage of this method is that the graphene layers are not dependent on the cooling rate which indicates that carbon was not absorbed into the Cu and Ni substrate as in CVD processes.

iii) Chemical Vapor Deposition.

In the chemical vapor deposition (CVD) technique, one can produce graphene on the transition metal (e.g. Fe, Co, Ni, Cu) at high temperature (>1000°C) with the carbon source supplied in gas form and metals like Cu and Ni is preferred as a substrate to grow the graphene layer [17-19]. Methane and acetylene gas are generally used as a source of carbon. Along with methane, hydrogen and argon are also utilized as reaction stabilizers and to improve the homogeneity of the film [20]. Furthermore, the CVD approach can be



Figure 3. Synthesis of high-quality single-layer graphene and its characterization at CSIR-AMPRI, Bhopal.

modified enhanced, including and atmospheric pressure CVD (AP-CVD), radiofrequency PE-CVD (RFP-CVD), microwave plasma CVD (MP-CVD), ultra-high vacuum CVD (UHV-CVD), plasma-enhanced CVD (PE-CVD), low-pressure CVD (LP-CVD), inductively coupled PE-CVD (ICP-CVD), and surface-wave plasma CVD (SWPCVD). A good quality graphene layer growth was demonstrated using rapid thermal process (RTP) CVD (Figure 2). For graphene deposition, firstly, Cu foils are placed in a quartz tube and heated up to 1000°C in an H₂ atmosphere for 30 min to remove residual oxide. After annealing, the sample is cooled down to room temperature. Following the preconditioning step, the Cu foil is again heated up to 1000°C and subsequently CH4 and H2 gases are introduced for 20-30 min leading to growth of graphene. After growth the sample is cooled down to room temperature.

2.3 Chemical Methods

i) Chemical oxidation and reduction

A large amount of graphene can be produced through the oxidation of graphite by treating it with strong acidic and basic oxidants. It was first introduced by Brodie in 1859 when graphite was treated with potassium chlorate (KClO₄) and fuming nitric (HNO₃) and Later in 1898, Staudenmaier NO₂.[21] modified Brodie's method and used nitric and sulphuric acid in 1:4 in an ice bath, which is considered a safer method [22] but toxic gases are still an issue. After several modifications, Hummer developed a new method that is more common for the preparation of graphene oxide using NaNO₃, KMnO₄, and H₂SO₄. Moreover, graphene oxide (GO) is prepared from high-purity graphite powder [23]. In this

method, 3g graphite powder and 1g NaNO₃ are mixed with 100 ml sulphuric acid and stirred for several minutes. After that 12g KMnO₄ is added slowly into this solution at 20°C. Then this mixture is stirred for 4-5 hours until the solution becomes dark green. After that, 140 ml of deionized water is added to this solution and stirred for 30 minutes at 98°C. Hydrogen peroxide (40 ml) is added drop by drop for removal of KMnO4 and cooled down using an ice bath. After cooling, 10 ml of hydrochloric acid and 250 ml of deionized water are added and stirred for 1 h. The residual is washed 3-4 times with 1M hydrochloric acid and deionized water. The washed GO solution is dried using an oven at 90-100°C for 24 h to produce GO powder. The prepared GO powder is sonicated and reduced to obtain graphene. Later on, the Hummers method was modified by Tour et. al. in 2010 to eliminate the toxic gases NO_2 and N₂O₄. They replaced NaNO₃ with potassium permanganate and a mixture of reactions consisting of (9:1) H₂SO₄: H₃PO₄ for oxidation reaction [24].

Graphene can also be obtained through the reduction of the conjugate structure of GO, referred to as reduced GO (rGO). Also, the electrically insulated GO is converted to the conductive by the removal of the oxygen atom to develop a partial sp² character. Reduction of GO is done by thermally, chemically, electrochemically, or green synthesis route [25].

ii) Unzipping Carbon Nanotubes

In this technique, sulphuric acid and KMnO₄ are used for cutting multi-walled carbon nanotubes (MWCNTs) in a longitudinal direction, followed by the chemical reduction of the oxidized graphene produced through hydroxide and hydrazine ammonium monohydrate. The graphene nanoribbons are developed using this method, and the developed nanoribbons are reduced by different chemicals. These nanoribbons are conducting in nature, however, due to the presence of oxygen defects, these graphene nanoribbons display electrical properties slightly inferior to graphene [11]. The were unzipped by various MWCNTs

experimental methods such as a mixture of acid, a catalytic cutting method, electrical zipping, and H-based zipping, etc.

2.4 Other Methods.

There are several other methods to produce graphene such as arc discharge of graphite, electron beam irradiation of PMMA nanofibers, thermal fusions of polyaromatic hydrocarbons, and conversion of nanodiamonds.

In addition, different types of graphene-based materials such as graphene nanoribbons, graphene quantum dots, and graphene foam or aerogel can be fabricated. Particularly, graphene foam is a 3-dimensional honeycomb structure that possesses many interesting properties such as low density, high open porosity and high surface area, good mechanical strength, excellent electrical and thermal conductivity, and good chemical and corrosion-resistant. These extraordinary properties make graphene foam a promising candidate for many engineering applications.

3. Applications of Graphene

Graphene is a wonderful material that holds promising properties such as high electron mobility which is ~100 times or even higher than silicon that is commonly used in electronics, electrical conductivity higher than copper, high transmission (about 97.7%), high thermal conductivity even higher than 3dimensional diamond, high impermeability, and many more. These properties make graphene and graphene-related materials promising candidates for numerous applications.

High Strength: The mechanical strength of graphene can reach ~130 Giga Pascal (130 Giga Pascal = 13256310768.713 Kg/m²) which is about a few hundred times higher than steel. The hexagon lattice developed by sp^2 carbon atoms restricts in-plane deformation depicting impressive mechanical strength. So, graphene can be used as fillers in polymers and metals to exceptionally enhance their mechanical strength. Numerous studies have been performed on the mechanical properties of graphene reinforced composites and their mechanical strength is generally

analyzed through stress-strain curves obtained by tensile tests. The mechanical strength of the graphene and GRMs reinforced composites depends on filler geometry, dispersion, number of graphene layers and size, the interaction between matrix and filler, and the fabrication process. Gong et.al studied the effect of how the number of graphene layers influences the mechanical properties of polymer matrix [34].

Kim et al designed nanolayered composites with alternate layers of single-layer graphene and a layer of metal (copper or nickel) and found high mechanical strength of 1.5 GPa and 4 GPa in graphene-copper and graphenenickel structures, respectively [35]. Jeon et. al



Figure 4: Schematic representation of graphene in different applications (a) miniature ballistic tests by firing tiny silica spheres at sheets of graphene [26] (b) metal-graphene-metal (MGM) photodetectors with asymmetric metal contacts [27](c) Schematic illustration for the preparation process of epirubicin/ NGO-HA complex and the target specific delivery of the complex to cancer cell via HA receptor mediated endocytosis [28] (d) illustration of the relationship between graphitization degree and lubrication performance [29] (e) sweat sensor [30] (f) schematic depiction of the synthesis and electrochemical performance of PdPGO for supercapacitor [31] (g) Side view of an individual simulation system, composed of a piston, a membrane with a nanopore and two water boxes. The left water box is saline while the right one is fresh water[32] (h)polymer-graphene nanocomposite in aerospace [33].

investigated the effect of the size of graphene nanosheets (1 µm, 750 nm, 250 nm, and 20 nm) on the mechanical properties of polymer nanocomposites and found that effective interfacial adhesion is greater for large size graphene nanosheets due to large contact area that influences the mechanical properties [36]. However, the concentration percentage of the graphene and GRMs for both polymer and metal matrix goes through the threshold value up to which the mechanical strength increases, and after that distortion of properties occurs. In civil structures, the application of 0.05 wt. % of graphene resulted in 8%, 79%, and 9% enhancement of compressive strength, tensile strength, and Young's modulus of ordinary Portland cement, respectively [37]. The graphene reinforced shape memory polymers [38], shape memory metallic alloys [39], automobile components, and engineering components are some examples where graphene has been exploited to enhance the mechanical strength and other mechanical properties of the systems. For example, Krishnamoorthy et. al designed a siloxenegraphene heterostructure electrode-based symmetric supercapacitors that delivers a maximum power density of 15 000 W kg⁻¹ and high energy density $(55.79 \text{ Wh kg}^{-1})$ [40]. Le et al. designed alligned graphene/carbon nanotube fibers that possess high mechanical strength and excellent electrical properties [41].

Electronic Applications: Graphene displays extremely high carrier mobility that can be reached to about 10^5-10^6 cm²V⁻¹s⁻¹, which is about 2 to 3 orders of magnitude higher than commonly used semiconductors such as silicon. Thus, graphene has a bright future for electronic applications such as in the development of micro- and nano-electronics devices. It is the potential alternative to silicon technology [42] and its distinct optoelectronic characteristics make it a perfect medium for rapid photodetectors [43], optical modulators [44], plasmonic devices [45], ultrafast lasers [46] etc. A graphene-based transistor can develop faster electronic devices. GRMs,

especially nanoribbons, are appealing structures for logic microprocessors due to high current-carrying capacity, high carrier mobility, and, saturation velocity, thereby enabling high performance at a lower power supply. Moreover, semiconducting GNRs are appealing not just for logic applications but also for low power radio frequency (RF) technologies and a variety of novel devices in quantum informatics, thin-film electronics, and spintronic (such as flexible devices and sensors)[47, 48]. Importantly, in silicon-based CMOS technology, the number of transistors per processor is increased by reducing the gate However, conventional length. CMOS technology is reaching the fundamental limit. Thus, not only the graphene's extremely high carrier mobility important, but also atomic thinness can play a vital role, and together both these properties can enable the development of futuristic high-speed fieldeffect transistor (FET) technology. Indeed, graphene-based FET has shown exceptional electrical behavior [49-51]. Owing to their high mobility and conductivity, high optical transparency, and sharp edges the graphene, GRMs and their composite have also broad applications in electromagnetic shielding and electronic packaging [52]. Graphene-based touchscreen panels have also been designed [53]. Graphene and GRMs have also been explored for solar power generation owing to their optical transparency and high carrier mobility. In solar cells, graphene has been utilized as a buffer layer, electrode, and electron/hole transport medium material [54]. Sim et. al developed a graphene based CIGS solar cell in which graphene film was coated on the flexible copper foil through the CVD technique and used as a hole transport layer that yielded a power conversion efficiency of 9.91±0.89% [55].

Healthcare Applications: Microbial contamination is a big problem across the world that affects human health and in severe cases, it leads to the death of humans. The world has just witnessed one such infectious disease viz. COVID-19. Owing to their appealing properties, graphene and graphene-

related materials (GRMs) have shown potential to contribute to the fight against COVID-19 [56, 57]. Graphene and GRMs show antimicrobial and antiviral properties. Thus, graphene and GRMs can be used as fillers in polymeric materials or other biomaterials to boost their antimicrobial properties or can be applied as coatings on surfaces to prevent infection spread. Furthermore, graphene and GRMs display excellent electrical and surface properties. Moreover, their surfaces can be functionalized by various functional groups. These properties of graphene and GRMs make them promising candidates for high-performance biosensors too [58, 59]. The graphene-based biosensors have the potential for fast, precise, and highly sensitive diagnosis of viruses, various biomolecules, etc. A lot of work is underway on this subject across the world. Graphene stimuli responsive materials also snatch the attention of polymeric implants for on demand drug delivery [60]. According to reports, electroactive scaffolds retain their structural integrity while exhibiting regulated drug release in a pulsatile manner when modest electrical voltages are applied at low graphene concentrations (0.2 mg mL⁻¹) [61]. The most fascinating research GRMs on for regenerative medicine applications includes bone, nerve, cartilage, muscle, heart, skeletal, skin, and adipose tissue regeneration [62]. For example, the 3D graphene foams were developed and employed in bone regeneration. Crowder et al. fabricated 3D porous graphene foams by growing graphene on a 3D nickel scaffold and employed the 3D graphene foams as culture substrates for hMSCs [63]. Chen et al. developed graphene enhanced electronic skin (E-skin) for biomedical applications [64].

Tribological Applications: Tribology deals with friction, wear, and lubrication. t of contact sliding systems immensely suffer from high friction and wear. High friction, a force that renders the motion of the object, contributes to a huge amount of energy wastage [65]. A significant amount of energy in automobiles is used to combat friction. On

the other hand. wear is the damage/degradation the of components/systems. Manv commercial systems such as automobile components, turbines, MEMS/NEMS devices, nanoscale contact sliding devices, magnetic storage devices, engineering systems, etc., are hugely suffer from high friction and wear. Controlling/reducing friction and wear is essential for increasing the operational lifetime of the components, minimizing energy wastage, reducing economic loss, and saving the environment. Graphene has shown excellent tribological properties despite being just a single-atom-thick material [66]. It exceptionally reduces the friction of a wide variety of surfaces such as silicon, glass, ceramic, gold, mica, steel, etc., and considerably increases the wear resistance. Bilayer and few-layer graphene also show extraordinary tribological properties [66]. Thus, the application of graphene-based overcoats or graphene-reinforced composites can help to increase the operational lifetime of contact sliding components in various commercial systems [67].

Functional and soft robotic systems use graphene-based materials to increase the movement and response of sensors, actuators, and biomedical transplants [68-70]. In graphene composites, graphene addition also increases the thermal conductivity, which helps to increase the heat dissipation at the contact interfaces and reduces wear and deformation [68].

Sensors Applications: Graphene and GRMs are potential candidates for sensing applications. Graphene can attain a large strain without a considerable change in its electrical conductivity.

Thus, graphene-based high-performance strain sensors (in combination with other flexible polymers) can be designed and developed. The prototypes of graphene, GRMs, and graphene/GRMs-polymer composites-based flexible pressure sensors have already been demonstrated. The graphene, GRMs, and their composites-based sensors are crucial for healthcare applications such as in the development of blood pressure sensors. Kireev et. al developed a wearable, atomically thin, self-adhesive graphene electronic tattoo as a human bioelectronics interface for monitoring blood pressure based on electrical bio impedance [71]. Gao et.al developed a completely integrated sensor array for multiplexed in-situ perspiration analysis [72]. Kang et al. designed a graphene-based wearable thermal patch device that is used for thermotherapy and continuous skin temperature monitoring for self-care [73]. Graphene-based electrochemical sensors have also been developed to detect small biomolecules like uric acid, ascorbic acid, and dopamine in the human body [74, 75]. GRMs have also shown remarkable gas-sensing capability [76]. Graphene-based devices have been developed to detect toxic gases like SO_x, CO_x, and NO_x [77]. Moreover, Hu et.al used graphene-based plasmon devices for the detection of gas molecules such as SO₂, NO₂, N₂O₂, and NO [78].

Energy Storage: In contemporary society, there is a pressing demand to enhance the energy and power densities of electrochemical energy storage devices. Graphene has recently brought about significant advancements in portable electronics and electric vehicles by offering superior methods for electricity storage [79]. Battery and capacitors are important ways of storing energy; they follow the electrochemistry mechanism(s) to store the energy. However, there are always challenges that need to be solved for advanced technologies. The lithium-ion battery is commonly used as an energy storage device that uses a LiCoO₂ cathode and a graphite anode. The performance of the battery considerably depends on the properties of electrode materials. Since graphite anode has a low specific capacity (372 mAh g^{-1}), there is always a search for efficient anode material for Li-ion batteries. Graphene, rGO, and their composites with metal and metal oxides have been employed as anode material for Li-ion batteries. For example, Cu-supported graphene can reach specific capacities of 1500

mAh g⁻¹. Graphene and its hybrid with metal oxide are also proposed to be used as a current collector at the cathode. replacing conventional Al current collectors. There are many other components of Li-ion batteries where graphene and its composites with other materials can show promising properties and replace conventional materials. Furthermore, the combination of an aluminum anode with a cathode featuring high energy and power densities shapes the trajectory of aluminiumion battery technology [80]. The outlook for the Al-graphene pairing appears promising, provided immediate and focused efforts are directed toward overcoming the inherent technological challenges. While the concept of Aluminium-Ion Batteries (AIB) was initially conceived in the early 1970s, it gained significant attention in 2011 when the secondary nature of an Al-V2O5 cell at ambient temperature was demonstrated [81, 82]. The Al-graphene cell demonstrates the potential to provide an unexpectedly high power density (approximately 175 kW kg⁻¹), comparable to supercapacitors, while simultaneously maintaining an energy density (around 66 Wh kg⁻¹) higher than that of a leadacid battery [83]. Instances exist where combinations of energy and power densities reach 200 Wh kg⁻¹–200 W kg⁻¹ and 160 Wh kg⁻¹-50 kW kg⁻¹ [84]. Remarkably, the Algraphene cell achieves an exceptionally long lifespan, enduring up to a quarter-million cycles with minimal loss in specific capacity (approximately 111 mAh g⁻¹) when subjected to an immensely high current rate of 100 A g⁻¹ [85].

The supercapacitor is another important device for the giant storage of energy. A supercapacitor contains two electrodes and an electrolyte [86]. Unlike batteries, they function as energy storage devices that exhibit high power performance, featuring rapid charge and discharge times, minimal degradation over extended cycling periods, and environmental sustainability [87]. Nevertheless, these devices are unable to attain the elevated energy density achievable with batteries. Supercapacitors can be categorized into two types based on their

charge storage mechanisms: electric doublelayer capacitors (EDLCs) and well hvbrid pseudocapacitors, as as combinations thereof [88]. For the development of a good quality supercapacitor, the surface area of the materials must be as high as possible and the separation between the charges must be minimum. In particular, for electrodes, the materials should have high electrical conductivity and many other physicochemical excellent properties. Graphene, GRMs, and their composites have been explored for supercapacitor applications. Graphene has garnered considerable attention in the field of supercapacitors due to its exceptionally high surface area, reaching up to 2,630 m² g⁻¹ [89]. In the realm of energy storage, graphene emerges as a promising candidate for the next generation of supercapacitor electrodes owing to three primary factors. Firstly, its unrivaled surface area of 2630 m² g⁻¹ and remarkably low theoretical density of 2.28 g cm⁻³ grant the material a dual advantage of high packing density capability and an expansive specific surface area, facilitating efficient interaction with electrons and ions. Secondly, graphene exhibits exceptional electrical conductivity, featuring high motilities of up to 200,000 cm² V^{-1} S^{-1} at room temperature. This characteristic enables rapid electron and ion transfer across various device interfaces, such electrode/electrolyte as and electrode/collector. Additionally, the high electrical conductivity allows graphene to serve as both an active material and a current collector, eliminating the need for additional materials like binders and additives. Lastly, graphene demonstrates notable mechanical strength, boasting Young's modulus of 1 TPa and showcasing reversible strain up to 25%. This strength makes graphene suitable for applications flexible and printable in electronics while maintaining high capacitance retention [10. 89]. These graphene-based materials considerably change the electrode and electrolyte properties and suitably tailor the performance of supercapacitor. Graphene and GRMs have the high surface area and they are ultrathin both these properties make them potential candidates for electrode development. Owing to its large surface area and excellent conductivity, graphene was employed as an electrode for supercapacitors for the first time by Ruoff's research group [10]. Subsequently, efforts have been consistently directed towards strategies aimed at minimizing the agglomeration of graphene sheets to optimize both the accessible surface area and the development of extensive supercapacitors. Among the successful methodologies employed thus far is the utilization of graphene foam (GF) synthesized through chemical vapor deposition (CVD) [90-92]. Graphene exhibits a capacitance significantly lower than the theoretical capacitance values of 550 F g⁻¹ for supercapacitors and 744 mA h g^{-1} for lithium-ion batteries [93]. The charge storage mechanism observed in pristine graphene supercapacitor materials falls under electrical double-layer capacitance (EDLC), wherein the charge is physically stored through the adsorption of electrolyte ions onto the graphene surface [94]. When the entire specific surface area (SSA) of 2630 m² g⁻¹ is fully utilized, graphene electrode materials exhibit an electrical double-layer can capacitance (EDLC) of 550 F g⁻¹. further to this capacitance doped enhance and functionalized graphene, and graphene have been engineered composites to incorporate extra pseudocapacitance [95, 96]. Achieving the theoretical charge storage limit electrode materials of graphene for application in electrochemical energy storage devices demands extensive efforts in the systematic design of the structure and chemistry of graphene materials.

Water desalination: Graphene demonstrates high impermeability against contaminants and allows the water to pass through it. This property of graphene and GRMs enables them to be promising candidates for water purification applications [97]. Graphene and GRMs are used not only for drinking water desalination but also effective in the purification of the sea and industrial waste water[98, 99]. Water desalination requires effective ion sieving as well as ultra-fast water flow for continuous supply, in which graphene and GRMs possess an extensive advantage through nanofiltration membranes with sub-nano to atomic-scale capillaries (6 Å)[100, 101]. Graphene and graphene possess antimicrobial properties that improve water purification quality [102]. Moreover, various molecules and methods are utilized to control and modify the graphene and GRM pour size for selective ion sieving. For example, Chung et al modified GRMs (GO)with ethylenediamine, which was used for the separation of Pb²⁺, Ni²⁺, Cd²⁺, and Zn²⁺ with obtained maximum rejection up to 95.7, 96.0, 90.5, and 97.4%, respectively and attained the water permeability of ~5.0 L m⁻² h⁻¹ bar⁻¹ [103], Gong et.al confined the GRMs (GO) interlamination to 0.71nm with 99.9% restriction of organic ion NaCl. [104] Likewise, Chen et. al demonstrated a scalable production of subnanometer porous ultrathin graphene membrane by subsequent reduction and carbonization of the GO nanosheets and polymer on the ceramic porous substrate; they achieved a water evaporation flux of $49.8 \pm 1.5 {-}472.3 \pm 14.2 \ L \ m^{-2} \ h^{-1}$ and

99.99% NaCl rejection at 20-70 °C [105]. Salt dve separation from water is also a big concern, Padmavathy et. al exploited a GRMs-based system for various dve separation and divalent ion rejection [106]. Although, the graphene and GRMs-related framework performs better in water desalination their commercialization and scalability are the most critical aspect, along with the large quantity and high quality production of graphene.

Graphene-composites: Composites of graphene with metals and polymers display enhanced properties due to the application of graphene. The introduction of graphene and GRMs improves various properties of metals and polymers such as electrical properties (increase the electrical conductivity) [107], thermal properties (increase the thermal conductivity) [108], mechanical properties (increase the mechanical strength) [109], tribological properties (reduce the friction and wear) [110], corrosion property (reduce the

corrosion) [111], shielding properties (enhance the electromagnetic shielding) [112], and so on. Thus, graphene-metal and graphene-polymer composites are promising candidates for many commercial applications. GRMs are majorly investigated in most graphene-polymer composites considering their low cost and high yield production. GO enhances the mechanical and thermal properties of hydrophilic polymers like POP [113] and PVA[114]. Considerable work has been carried out on amination[115]. esterification [116], isocyanate modification[117], and polymer grafting [118] for the functionalization of GO by forming chemical bonds with the carboxyl and hydroxyl groups to enhance the applications of GO [119]. As polymers are mostly electrically insulating, reduced GO can significantly increase its electrical conductivity [120], but agglomeration or restacking causes difficulty in composite fabrication. CVD graphene as a filler offers various π interactions (C- π , π – π , π –H, etc.) because of plenty of π electrons on the CVD graphene that results in the ample amount of interfacial interaction with polymer matrix [121]. Yan et.al successfully synthesized aligned graphene nanowalls vertically (GNWs) which were covalently bonded by high-quality CVD graphene nanosheets; this filler yielded high thermal conductivity (12.8 \pm 0.77 W m⁻¹ K⁻¹) of polyvinylidene fluoride (PVDF) at a low filler content of 4.0 wt.% [122].

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